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DETERMINATION OF
ANIONS IN NATURAL
AND TREATED WATERS

T.R. CROMPTON

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Determination of Anions in Natural and Treated Waters

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T.R.Crompton



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Preface

The presence of inorganic and organic substances in environmental and other waters is a matter of increasing concern to the water industry, environmentalists and the general public alike from the point of view of possible health hazards presented to both human and animal life, represented by domesticated and wild animals and bird, fish and insect life.

This awareness hinges on three facts: the increasing interest by the scientist and the public alike in matters environmental, an increased usage of organic and inorganic materials in commerce coupled with the much wider variety of these substances used nowadays, and finally, the availability of analytical methods sensitive enough to determine very low concentrations of these substances, the presence of which we formerly were unaware.

While several books have been published, including several by the author, on the determination of metals, organic compounds and organometallic compounds in environmental waters no comprehensive works have been published on the determination of inorganic and organic anions in waters of various types. The aim of the present book is to rectify this situation. As well as anions occurring in water either naturally or as a direct result of industrial activity there are those which occur more indirectly from other causes such as the use of crop sprays and agricides and the breakdown of organic pollutants in soils which are leached by rain and enter watercourses and eventually the oceans.

The purpose of this book is to draw together and systemise the body of information available throughout the world up to the end of the millennium on the occurrence and determination of anions of all types in non saline and saline natural and treated water. In this way reference to a very scattered literature can be avoided. Naturally the content and balance of the book is dictated by what is reported in the available literature.

This is not a recipe book, ie methods are not presented in detail, space considerations alone would not permit this; instead the chemist is presented with details of methods available for the determination of all types of anions in a variety of types of water samples. Methods are described in broad outline giving enough information for the chemist to decide whether he or she wishes to refer to the original paper. To this end, information is provided on applicability of methods, advantages and disadvantages of one method compared to another, interferences, sensitivity and detection limits. Examples of results obtained by various methods are given.

Microbiological methods are not included as this subject would justify a separate book. Some enzymic assay methods are included.

Special emphasis is given to the application of relatively new analytical techniques for the determination of anions such as ion chromatography, and high performance liquid chromatography (Chapters 12–14). These techniques have the advantages of the ability to perform multianion analysis rapidly, specificity, sensitivity and the ability to perform automated analysis.

Where available, preconcentration techniques are discussed, enabling the sensitivity of methods to be improved by several orders of magnitude, a refinement often needed in environmental water analysis.

Chapter 1, which forms an introduction, discusses the principles of the various techniques now being employed in water analysis, and the types of determinations to which these techniques can be applied. This chapter also contains a useful key system so that the reader can quickly locate in the book sections in which are discussed the determination by various techniques particular anions in particular types of water sample.

The contents are presented in as logical a sequence as possible, starting in Chapter 2 with a discussion of the determination of 109 anions in non saline waters such as river and stream waters. Chapters 3 and 4 similarly deal with sea, estuary and coastal waters. It is pointed out here that coastal and estuary water is seawater that (a) may or may not have become diluted with river water or coastal discharges in localised areas where there are such outfalls, and (b) because of this these discharges may or may not contain higher or lower concentrations of anions than are present in open seawater (ie seawater well away from coasts).

When a method has been reported in the literature for the determination of a particular anion in, for example, seawater but not for other high saline waters such as estuary or coastal waters, then in the latter cases it is always worth trying out the method discussed for carrying out the analysis of seawater, or vice versa.

Chapter 5 deals with the analysis of aqueous precipitation such as rain and snow. Potable waters are discussed in Chapter 7, while waste waters, sewage and trade waters are discussed in Chapters 8–10 respectively. Finally, Chapter 11 deals with high purity waters such as boiler feed and cooling waters.

Several specialist chapters follow including preconcentration techniques to improve sensitivity (Chapter 15); equipment for on site analysis for anions (Chapter 16), and automated equipment for the online analysis of anions (Chapter 17).

Sampling and sample preservation techniques are very important in the analysis for anions (Chapter 18).

Examination for anions combines all the exciting features of analytical chemistry. First, the analysis must be successfully completed and in many cases, such as spillages, must be completed quickly. Often the nature of the substances to be analysed for is unknown, the substances might occur at exceedingly low concentrations and might, indeed, be a complex mixture. To be successful in such an area requires analytical skills of a high order and the availability of sophisticated instrumentation.

The work has been written with the interest of the following groups of people in mind: management and scientists in all aspects of the water industry, river management, fishery industries, sewage effluent treatment and disposal, land drainage and water supply; also management and scientists in all branches of industry which produce aqueous effluents. It will also be of interest to agricultural chemists, agriculturists concerned with the ways in which chemicals used in crop or soil treatment permeate through the ecosystem, the biologists and scientists involved in fish, plant, insect and plant life, and also to the medical profession, toxicologists and public health workers and public analysts. Other groups of workers to whom the work will be of interest include oceanographers, environmentalists and, not least, members of the public who are concerned with the

protection of our environment.

Finally, it is hoped that the work will act as a spur to students of all subjects mentioned and assist them in the challenge that awaits them in ensuring that the pollution of the environment is controlled so as to ensure that as we enter the new century we are left with a worthwhile environment to protect.

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T.R.Crompton
October 2001

Chapter 1

Introduction

1.1 Brief summary of methodologies

1.1.1 Titration method

The anions which can be determined by titration processes are listed below.

<i>Non saline waters:</i>	bicarbonate, bromide, carbonate, chlorate, chloride, hypochlorite, chlorite, iodide, nitrate, nitrite, polysulphide, sulphate, sulphide, thiosulphate.
<i>Sea water:</i>	alkalinity, bromide, chloride, iodide and sulphate.
<i>Surface, ground and pore waters:</i>	alkalinity and borate
<i>Potable water:</i>	alkalinity, chloride, chlorite, chlorate and hypochlorite.
<i>Waste waters:</i>	chloride, free cyanide, iodide.
<i>Trade effluents:</i>	chloride, free cyanide, polythionate, sulphate, sulphide and thiocyanate.
<i>High purity water:</i>	chloride and iodide.

Thus some 19 different anions can be determined in various types of water by this technique. As titration procedures are relatively insensitive compared to some other procedures, it is likely that they would only be applied to those types of water sample where the concentration of the determinand is relatively high, eg sewage and trade effluents and not, for example, to potable water samples.

The titration process has been automated so that batches of samples can be titrated non-manually and the data processed and reported via printouts and screens. One such instrument is the Metrohm 670 titroprocessor. This incorporates a built-in control unit and sample changer so that up to nine samples can be automatically titrated. The 670 titroprocessor offers incremental titrations with variable or constant volume steps (dynamic or monotonic titration). The measured value transfer in these titrations is either drift controlled (equilibrium titration) or effected after a fixed waiting time; pK determinations and fixed end points (eg for specified standard procedures) are naturally included. End-point titrations can also be carried out.

Sixteen freely programmable computational formulae with assignment of the calculation parameters and units, mean-value calculations and arithmetic of one titration to another (via common variables) are available. Results can be calculated without any limitations.

The 670 titroprocessor can also be used to solve complex analytical tasks. In addition

to various auxiliary functions, which can be freely programmed, up to four different titrations can be performed on a single sample.

In addition to the fully automated 670 system, Metrohm also supply simpler units with more limited facilities which nevertheless are suitable for more simple titrations. Thus the model 682 titroprocessor is recommended for routine titrations with automatic equivalence point recognition or to preset end points. The 686 titroprocessor is a lower-cost version of the above instrument, again with automatic equivalence point recognition and titration to preset end points.

Mettler produce two automatic titrators, the DL 40 GP memotitrator and the lower-cost DL 20 compact titrator. Features available on the DL 40 GP include absolute and relative end-point titrations, equivalence-point titrations, back-titration techniques, multi-method applications, dual titration, pH stating, automatic learn titrations, automatic determination of standard deviation and means, series titrations, correction to printer, acid balance analogue output for recorder and correction to the laboratory information system. Up to 40 freely definable methods can be handled and up to 20 reagents held in store. Six control principles can be invoked. The DL 20 can carry out absolute (not relative) end-point titrations and equivalence-point titrations, back-titration, series titrations, and correction to printer and balance and the laboratory information system. Only one freely definable method is available. Four control principles can be invoked.

The DL 40 GP can handle potentiometric, voltammetric or photometric titrations.

1.1.2 Spectrophotometric method

1.1.2.1 Visible spectrometry

This technique is only of value when the identity of the compound to be determined is known. There are also limitations on the sensitivity that can be achieved, usually milligrams per litre or occasionally, micrograms per litre.

The following 35 anions have been determined by this technique in a variety of types of water samples.

<i>Non saline waters:</i>	arsenate, borate, bromide, chloride, chromate, dichromate, free cyanide, dithionite, fluoride, iodate, nitrate, nitrite, phosphate, selenate, selenite, silicate, sulphate, sulphide, sulphite, tellurate, thiocyanate, titanate, uranate and vanadate, also ascorbate.
<i>Sea water:</i>	alkalinity, arsenate, arsenite, borate, bromate, bromide, fluoride, hypochlorite, iodate, iodide, nitrate, nitrite, phosphate, silicate and sulphate,
<i>Estuary water:</i>	nitrate, nitrite and phosphate.
<i>Aqueous precipitation:</i>	iodide, nitrate and sulphate.
<i>Surface, ground and porewaters:</i>	borate, nitrate, nitrite, iodide, phosphate
<i>Potable waters:</i>	alkalinity, bromide, fluoride, iodide, nitrate, nitrite, phosphate and sulphate.

<i>Waste waters:</i>	borate, chloride, chlorite, chromate, dichromate, cyanate, free cyanide, total cyanide, nitrate, nitrite, phosphate, sulphate, sulphide, sulphite, silicate and thiocyanate.
<i>Sewage effluents:</i>	nitrate, nitrite and phosphate.
<i>Trade effluents:</i>	free cyanide, complex cyanides, ferrocyanide, nitrate, nitrite, phosphate, silicate, sulphate, sulphide and thiocyanate.
<i>High purity waters:</i>	silicate and chloride.

Visible spectrophotometers are commonly used in the water industry for the estimation of colour in a sample or for the estimation of coloured products produced by reacting a colourless compound of the sample with a reagent, which produces a colour that can be evaluated spectrophotometrically.

Some commercially available instruments, in addition to visible spectrophotometers, can also perform measurements in the ultraviolet and near IR regions of the spectrum. These have not yet found extensive application in the field of water analysis.

Suppliers of visible spectrophotometers are reviewed in Table 1.1.

1.1.2.2 Ultraviolet spectrometry

This technique has found limited application (4 anions) in water analysis as indicated below:

<i>Non saline waters:</i>	nitrate, nitrite and nitroacetic acid.
<i>Seawater:</i>	nitrate and nitrite.
<i>Estuary waters:</i>	nitrite.
<i>Potable waters:</i>	nitrate.
<i>Wastewaters:</i>	phosphate.

Table 1.1 Visible-ultraviolet-near infrared spectrophotometers

<i>Spectral region</i>	<i>Range (nm)</i>	<i>Manufacturer</i>	<i>Model</i>	<i>Single or double beam</i>	<i>Cost range</i>
UV/visible	–	Philips	PU 8620 (optional) PU 8620 scanner)	Single	Low
Visible	325–900	Cecil Instruments	CE 2343 Optical Flowcell	Single	Low
Visible	280–900	Cecil Instruments	CE 2393 (grating, digital)	Single	High

Visible	280–900	Cecil Instruments	CE 2303 (grating, non-digital)	Single	Low
Visible	280–900	Cecil Instruments	CE 2373 (grating, linear)	Single	High
UV/visible	190–900	Cecil Instruments	CE 2292 (digital)	Single	High
UV/visible	190–900	Cecil Instruments	CE 2202 (non-digital)	Single	Low
UV/visible	190–900	Cecil Instruments	CE 2272 (linear)	Single	High
UV/visible	200–750	Cecil Instruments	CE 594 (microcomputer controlled)	Double	High
UV/visible	190–800	Cecil Instruments	CE 6000 (with CE 6606	Double	High
UV/visible	190–800	Cecil Instruments graphic plotter option)	5000 series (computerized and data station)	Double	High
UV/visible	–	Philips	PU 8800		High
UV/visible	–	Kontron	Unikon 860 (computerized with screen)	Double	High
UV/visible	–	Kontron	Unikon 930 (computerized with screen)	Double	High
UV/visible	190–1100	Perkin-Elmer	Lambda 2 (microcomputer electronics screen)	Double	High
UV/visible	190–750 or 190–900	Perkin-Elmer	Lambda 3 (microcomputer electronics)	Double	Low to High
UV/visible	190–900	Perkin-Elmer	Lambda 5 and Lambda 7 (computerized with screen)	Double	Double High
UV/visible	185–900 & 400–3200	Perkin-Elmer	Lambda 9 (computerized with screen)	UV/vis High	NIR
UV/visible	190–	Perkin-Elmer	Lambda Array 3840	Photodiode	High

Source: Own files

1.1.2.3 Fluorescence spectroscopy

Spectrofluorimetric methods have been described for the determination of the following 18 anions.

<i>Non saline waters:</i>	borate, bromide, free cyanide, fluoride, iodide, nitrate, nitrite, phosphate, selenite, silicate, sulphide, sulphite and vanadate. Also ascorbate, citrate, oxalate and tartrate.
<i>Estuary water:</i>	selenate and selenite.
<i>Aqueous precipitation:</i>	bromide and iodide.
<i>Potable waters:</i>	selenate and selenite.
<i>Trade effluents:</i>	free cyanide, selenate, selenite and sulphide.
<i>High purity waters:</i>	chloride.

Chemilumtnescence analysis has been applied to the determination of the following seven anions.

<i>Non saline waters:</i>	free cyanide, iodide, nitrate, nitrite, silicate, sulphite and vanadate.
<i>Seawater:</i>	nitrate.

Generally speaking, concentrations down to the microgram per litre level can be determined by this technique with recovery efficiencies near 100%.

Potentially, fluorometry is valuable in every laboratory, including water laboratories, for the performance of chemical analysis where the prime requirements are selectivity and sensitivity. While only 5–10% of all molecules possess a native fluorescence, many can be induced to fluoresce by chemical modification or tagged with a fluorescent module.

Luminescence is the generic name used to cover all forms of light emission other than that arising from elevated temperature (thermo-luminescence). The emission of light through the absorption of ultraviolet or visible energy is called photoluminescence, and that caused by chemical reactions is called chemiluminescence. Light emission through the use of enzymes in living systems is called bioluminescence, the only known application of which to water analysis is the determination of adenosine triphosphate. Photoluminescence may be further subdivided into fluorescence, which is the immediate release (10^{-8} s) of absorbed light energy, as opposed to phosphorescence, which is

delayed release (10^{-6} – 10^2 s) of absorbed light energy.

The excitation spectrum of a molecule is similar to its absorption spectrum, while the fluorescence and phosphorescence emissions occur at longer wavelengths than the absorbed light. The intensity of the emitted light allows quantitative measurement since, for dilute solutions, the emitted intensity is proportional to concentration. The excitation and emission spectra are characteristic of the molecule and allow qualitative measurements to be made. The inherent advantages of the technique, particularly fluorescence, are:

- 1 Sensitivity; picogram quantities of luminescent materials are frequently studied.
- 2 Selectivity, derived from the two characteristic wavelengths.
- 3 The variety of sampling methods that are available, ie dilute and concentrated samples, suspensions, solids, surfaces and combination with chromatographic methods, such as that used in the high performance liquid chromatography separation of *o*-phthalyl dialdehyde derivatised amino acids in natural and sea water samples.

Fluorescence spectrometry forms the majority of luminescence analysis. However, the recent developments in instrumentation and room-temperature phosphorescence techniques have given rise to practical and fundamental advances which should increase the use of phosphorescence spectrometry. The sensitivity of phosphorescence is comparable to that of fluorescence and complements the latter by offering a wider range of molecules of study.

The pulsed xenon lamp forms the basis for both fluorescence and phosphorescence measurement. The lamp has a pulse duration at half peak height of $10\mu\text{s}$. Fluorescence is measured at the instant of the flash. Phosphorescence is measured by delaying the time of measurement until the pulse has decayed to zero.

Several methods are employed to allow the observation of phosphorescence. One of the most common techniques is to supercool solutions to a rigid glass state, usually at the temperature of liquid nitrogen (77K). At these temperatures molecular collisions are greatly reduced and strong phosphorescence signals are observed.

Under certain conditions phosphorescence can be observed at room temperature from organic molecules adsorbed on solid supports such as filter paper, silica and other chromatographic supports.

Phosphorescence can also be detected when the phosphor is incorporated into an ionic micelle. Deoxygenation is still required either by degassing with nitrogen or by the addition of sodium sulphite. Micelle-stabilised room-temperature phosphorescence (MS RTP) promises to be a useful analytical tool for determining a wide variety of compounds such as pesticides and polyaromatic hydrocarbons.

Perkin-Elmer and Hamilton both supply luminescence instruments.

Perkin-Elmer LS-3B and LS-5B luminescence spectrometers

The LS-3B is a fluorescence spectrometer with separate scanning monochromators for excitation and emission, and digital displays of both monochromator wavelengths and signal intensity. The LS-5B is a ratioing luminescence spectrometer with the capability of measuring fluorescence, phosphorescence and bio- and chemiluminescence. Both instruments are equipped with a xenon discharge lamp source and have an excitation

wavelength range of 230–720nm and an emission wavelength range of 250–800nm.

These instruments feature keyboard entry of instrument parameters which combined with digital displays, simplifies instrument operation. A high-output pulsed xenon lamp, having low power consumption and minimal ozone production, is incorporated within the optical module.

Through the use of an RS 232C interface, both instruments may be connected to Perkin-Elmer computers for instrument control and external data manipulation.

With the LS-5B instrument, the printing of the sample photomultiplier can be delayed so that it no longer coincides with the flash. When used in this mode, the instrument measures phosphorescence signals. Both the delay of the start of the gate (t_d) and the duration of the gate (t_k) can be selected in multiples of 10 μ s from the keyboard. This corrects excitation and emission spectra. Delay times may be accurately measured by varying the delay time and noting the intensity at each value.

Specificity in luminescence spectrometry is achieved because each compound is characterised by an excitation and emission wavelength. The identification of individual compounds is made difficult in complex mixtures because of the lack of structure from conventional excitation or emission spectra. However, by collecting emission an excitation spectra for each increment of the other, a fingerprint of the mixture can be obtained. This is visualised in the form of a time-dimensional contour plot on a three-dimensional isometric plot.

Fluorescence spectrometers are equivalent in their performance to single-beam ultraviolet-visible spectrometers in that the spectra they produce are affected by solvent background and the optical characteristics of the instrument. These effects can be overcome by using software built into the Perkin-Elmer LS-5B instrument or by using application software for use with the Perkin-Elmer 3700 and 7700 computers.

Perkin-Elmer LS-2B micro filter fluorimeter

The model LS-2B is a low-cost easy-to-operate, filter fluorimeter that scans emission spectra over the wavelength range 390–700nm (scanning) or 220–650nm (individual interferences filters). The essentials of a filter fluorimeter are as follows:

- a source of ultraviolet/visible energy (pulsed xenon)
- a method of isolating the excitation wavelength
- a means of discriminating between fluorescence emission and excitation energy
- a sensitive detector and a display of the fluorescence intensity.

The model LS-2B has all these features arranged to optimise sensitivity for microsamples. It can also be connected to a highly sensitive 7 μ L liquid chromatographic detector for detecting the constituents in the column effluent. It has the capability of measuring fluorescence, time-resolved fluorescence and bio- and chemiluminescent signals. A 40-portion autosampler is provided. An excitation filter kit containing six filters—310, 340, 375, 400, 450 and 480nm—is available.

1.1.2.4 Infrared and Raman spectrometry

Both these techniques have only limited application to the analysis of water samples.

Infrared spectroscopy

Non saline waters: free cyanide.

Raman spectroscopy

Non saline waters: nitrate and nitrite.

Waste waters: free cyanide and nitrate.

A more recent development is Fourier transform infrared analysis.

Fourier transform Infrared spectrometry

Fourier transform infrared spectrometry, a versatile and widely used analytical technique, relies on the creation of interference in a beam of light. A source light beam is split into two parts and a continually varying phase difference is introduced into one of the two resultant beams. The two beams are recombined and the interference signal is measured and recorded, as an interferogram. A Fourier transform of the interferogram provides the spectrum of the detected light. Fourier transform infrared spectroscopy, a seemingly indirect method of spectroscopy, has many practical advantages, as discussed below.

A Fourier transform infrared spectrometer consists of an infrared source, an interference modulator (usually a scanning Michelson interferometer), a sample chamber and an infrared detector. Interference signals measured at the detector are usually amplified and then digitised. A digital computer initially records and then processes the interferogram and also allows the spectral data that result to be manipulated. Permanent records of spectral data are created using a plotter or other peripheral device.

The principal reasons for choosing Fourier transform infrared spectroscopy are: first, that these instruments record all wavelengths simultaneously and thus operate with maximum efficiency; and, second, that they have a more convenient optical geometry than do dispersive infrared instruments. These two facts lead to the following advantages.

- Fourier transform infrared spectroscopy spectrometers achieve much higher signal-to-noise ratios in comparable scanning times.
- They can cover wide spectral ranges with a single scan in a short scan time, thereby permitting the possibility of kinetic time-resolved measurements.
- They provide higher-resolution capabilities without undue sacrifices in energy throughput or signal-to-noise ratios.
- They encounter none of the stray light problems usually associated with dispersive spectrometers.
- They provide a more convenient beam geometry—circular rather than slit shaped—at the sample focus.

Conventional Raman spectroscopy cannot be applied directly to aqueous extracts of sediments and soils, although it is occasionally used to provide information on organic solvent extracts of such samples. Fourier transform Raman spectroscopy, on the other hand, can be directly applied to water samples. The technique complements infrared spectroscopy in that some functional groups, eg unsaturation, give a much stronger response in the infrared. Several manufacturers (Perkin-Elmer, Digilab, Bruker) now

supply Fourier transform infrared spectrometers.

1.1.3 Flow injection analysis

This technique has found a fairly extensive application (29 anions) in the determination of anions in various types of water.

<i>Non saline waters:</i>	arsenate, arsenite, bicarbonate, borate, bromide, carbonate, chlorate, perchlorate, free cyanide, fluoride, germanate, iodide, nitrate, nitrite, phosphate, polysulphide, pseudohalides, silicate, sulphide, sulphite, thiosulphate and triphosphate.
<i>Seawater:</i>	nitrate, nitrite, phosphate and silicate. bromide, chloride, nitrate, nitrite,
<i>Aqueous</i>	phosphate,
<i>precipitation:</i>	sulphate and thiocyanate.
<i>Surface and ground waters:</i>	sulphate.
<i>Potable waters:</i>	alkalinity, chlorate, chlorite, fluoride and nitrate.

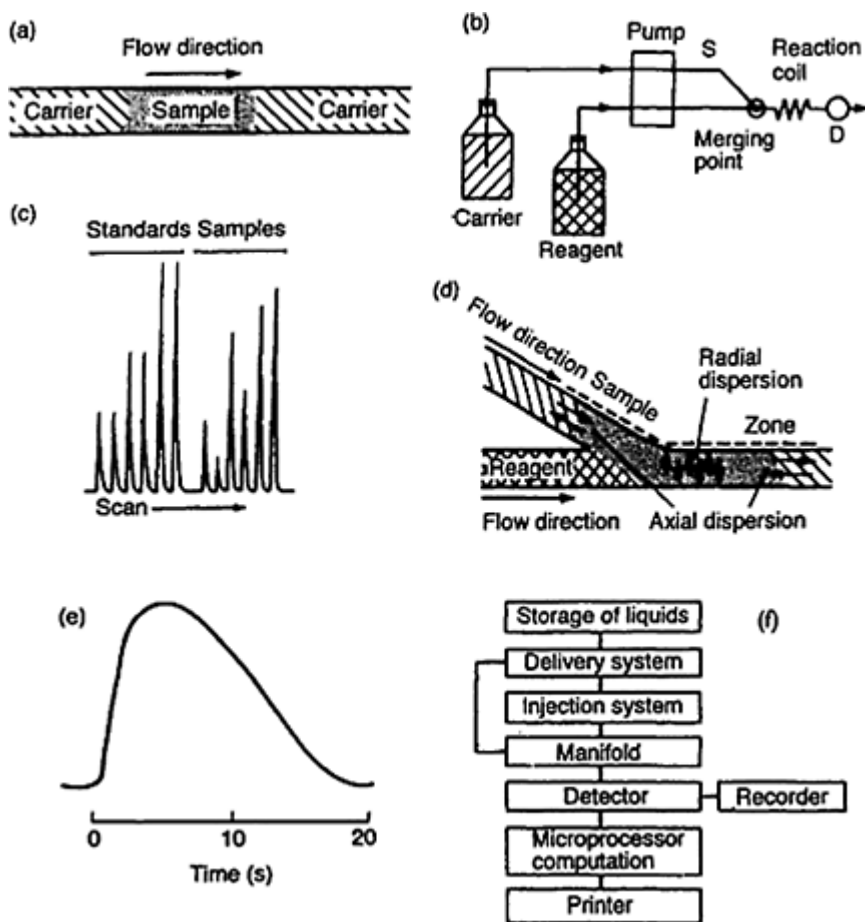


Fig. 1.1 (a) Schematic diagram of the flow pattern in an FIA system directly after injection of sample, (b) Simple FIA system for one reagent; S denotes the sample injection site and D is the flow-through detector, (c) Typical FIA peaks (detector output signals), (d) Radial and axial dispersion in an injected sample plug, (e) Rapid scan of an FIA curve, (f) Configuration of an FIA system.

Source: Own files

Waste waters: chloride, free cyanide and total cyanide.

Sewage effluents: phosphate.

Flow injection analysis (FIA) is a rapidly growing analytical technique. Since the introduction of the original concept by Ruzicka and Hansen [1] in 1975, about 1000 papers have been published.

Flow injection analysis is based on the introduction of a defined volume of sample into a carrier (or reagent) stream. This results in a sample plug bracketed by carrier (Fig. 1(a)). The carrier stream is merged with a reagent stream to obtain a chemical reaction between the sample and the reagent. The total stream then flows through a detector (Fig. 1.1(b)). Although spectrophotometry is the commonly used detector system in this application, other types of detectors have been used, namely fluorometric, atomic absorption emission spectrometry and electrochemical, eg ion selective electrodes.

The pump provides constant flow and no compressible air segments are present in the system. As a result the residence time of the sample in the system is absolutely constant. As it moves towards the detector the sample is mixed with both carrier and reagent. The degree of dispersion (or dilution) of the sample can be controlled by varying a number of factors, such as sample volume, length and diameter of mixing coils and flow rates.

When the dispersed sample zone reaches the detector, neither the chemical reaction nor the dispersion process has reached a steady state. However, experimental conditions are held identical for both samples and standards in terms of constant residence time, constant temperature and constant dispersion. The sample concentration can thus be evaluated against appropriate standards injected in the same manner as samples (Fig. 1.1(c)).

The short distance between the injection site and the merging point ensures negligible dispersion of the sample in this part of the system. This means that sample and reagent are mixed in equal proportions at the merging point.

The mixing technique can be best understood by having a closer look at the hydrodynamic conditions in and around the merging point (Fig. 1.1(d)). In Fig. 1.1(d) the hydrodynamic behaviour is simplified in order to explain the mixing process. Let us assume that there is no axial dispersion and that radial dispersion is complete when the sampler reaches the detector. The volume of the sample zone is thus 200 μ g after the merging point (100 μ L sample+100 μ L reagent as flow rates are equal). The total flow rate is 2.0ml min⁻¹. Simple mathematics then gives a residence time of 6s for the sample in the detector flow cell. In reality, response curves reflect some axial dispersion. A rapid scan curve is shown in Fig. 1.1(e). The baseline is reached within 20s. This makes it possible to run three samples per minute and obtain baseline readings between each sample (no carry-over), ie 180 samples per hour.

The configuration of an FIA system is shown schematically in Fig. 1.1(f). The (degassed) carrier and reagent solution(s) must be transported in a pulse-free transport system and at constant rate through narrow Teflon (Du Pont) tubing.

In a practical FIA system, peristaltic pumps are usually used since they have several channels, and different flow rates may be achieved by selection of a pump tube with a suitable inner diameter.

Table 1.2 Equipment for flow injector analysis

<i>Supplier</i>	<i>Model</i>	<i>Features</i>	<i>Detectors available</i>
Advanced	LCG 1	Relatively low-cost instrument, recorder	Colorimeter (other detectors

Medical Supplies		output. No computerization on data processing (8 channels)	can be used but are not linked in eg atomic absorption, fluorometer ion selective electrodes
Chemlab	–	Relatively low-cost, recorder output or data analysis by microprocessor (3 channels)	Colorimeter
Skalar	–	Relatively low-cost, recorder output on data analysis by microprocessor also carries out segmented flow analysis	Colorimeter, flow cells for fluorometer and ion selective electrodes available
Fiatron	Finlite 600	Laboratory process control and pilot plant instrument computerized	Colorimeter
	Fiatrode 400	Flow through analyser/controller, process control analyser	pH and ion selective electrode
	Fiatrode 410		
	Fiatrode 430		
Tecator	FIA star 5025	Relatively low cost manual instrument specifically designed for fluoride, cyanide, potassium, iodide, etc.	Specially designed for use with ion selective electrodes
	FIA star 5032	Relatively low-cost manual instrument (400–700 nm)	Spectrophotometer and/or photometer detectors
	Aquatec	Modular, semi-or fully automatic operation. Microprocessor controlled. A dedicated instrument designed for water analysis, i.e. dedicated method cassettes for phosphate and chloride, 600–100 samples h ⁻¹	Flow through Spectrophotometer (400–700nm)
	FIA star 5010	Modular, semi- or fully automatic operation. May be operated with process controller microprocessor. Can be set up in various combinations with 5017 sampler and superflow software which is designed to run on IBM PC/XT computer; 60–180 samples h ⁻¹ . Dialysis for in-line sample preparation and in-line solvent extraction. Thermostat to speed up reactions.	Spectrophotometer (400–700nm) or photometer can be connected to any flow through detector, e.g. UV/visible, inductively coupled plasma, atomic absorption spectrometer and ion selective electrodes

Source: Own files

A manifold provides the means of bringing together the fluid lines and allowing rinsing and chemical reaction to take place in a controlled way. Manifolds with several lines can be assembled as required. These manifolds are mounted on plastic trays and allow the use of different reaction coils.

Flow injection analysers available range from relatively low-cost unsophisticated instruments such as those supplied by Advanced Medical Supplies, Skalar and ChemLab to the very sophisticated instruments such as the FIA star 5010 and 5020 supplied by Tecator (Table 1.2).

1.1.4 Segmented flow analysis

This is a variant on flow injection analysis in which instead of injecting sample into a carrier reagent stream the reagents are injected into a sample stream. Some applications are listed below,

<i>Non saline waters:</i>	bicarbonate, carbonate, nitrite and nitrate.
<i>Seawater:</i>	bromide.
<i>Surface and ground waters:</i>	bromide.

Continuous flow analysis

<i>Non saline waters:</i>	nitrate, nitrite and sulphite.
<i>Sea water:</i>	nitrate and nitrite.
<i>Aqueous precipitation:</i>	bromide, chloride, nitrate, nitrite, phosphate, sulphate and thiocyanate.
<i>Potable water:</i>	nitrate and sulphate.
<i>Trade effluents:</i>	free cyanide.

1.1.5 Spectrometric methods

1.1.5.1 Atomic absorption spectrometric methods

Basically, the atomic absorption method was designed for the determination of cations. However, it has been applied to the indirect determination of some anions. If, for example, an excess of barium chloride solution is added to a sample containing sulphate and the precipitated barium sulphate filtered or centrifuged off then determination of excess barium ions by atomic absorption spectrometry enables the concentration of sulphate ions in the sample can be calculated indirectly.

Some 18 anions have been indirectly determined in water samples by this method.

<i>Non saline waters:</i>	arsenate, arsenite, borate, chloride, chromate, dichromate, free cyanide, total cyanide, molybdate,
	nitrate, phosphate, selenate, selenite, silicate and tungstate.
<i>Seawater:</i>	chromate, dichromate, selenate and selenite.

<i>Surface and ground waters:</i>	sulphate.
<i>Potable water:</i>	chromate, dichromate, fluoride and sulphate.
<i>Waste waters:</i>	chromate, dichromate, phosphate, silicate, free cyanide and total cyanide.
<i>Sewage effluents:</i>	free cyanide.
<i>Trade effluents:</i>	free cyanide, silicate, sulphate and thiosulphate.

Since shortly after its inception in 1955, atomic absorption spectrometry has been the standard tool employed by analysts for the determination of trace levels of metals in water samples. In this technique a fine spray of the analyte is passed into a suitable flame, frequently oxygen acetylene or nitrous oxide acetylene, which converts the elements to an atomic vapour. Through this vapour radiation is passed at the right wavelength to excite the ground state atoms to the first excited electronic level. The amount of radiation absorbed can then be measured and directly related to the atom concentration: a hollow cathode lamp is used to emit light with the characteristic narrow line spectrum of the analyte element. The detection system consists of a monochromator (to reject other lines produced by the lamp and background flame radiation) and a photomultiplier. Another key feature of the technique involves modulation of the source radiation so that it can be detected against the strong flame and sample emission radiation.

A limitation of this technique is its lack of sensitivity compared to that available by other techniques (eg inductively coupled plasma atomic emission spectrometry).

Suitable instrumentation is listed in Table 1.3.

1.1.5.2 Inductively coupled plasma atomic emission spectrometry

This technique has, in recent years, been found to be particularly useful for the determination in water of extremely low levels of a limited number of anions.

<i>Non saline waters:</i>	bromide, chloride, fluoride, iodate, iodide, nitrate, nitrite and tungstate.
<i>Seawater:</i>	sulphate.
<i>Surface and ground water:</i>	sulphide.

An inductively coupled plasma is formed by coupling the energy from a radiofrequency (1–3kW or 27–50MHz) magnetic field to free electrons in a suitable gas. The magnetic field is produced by a two- or three-turn water-cooled coil and the electrons are accelerated in circular paths around the magnetic field lines that run axially through the coil. The initial electron ‘seeding’ is produced by a spark discharge but, once the electrons reach the ionisation potential of the support gas, further ionisation occurs and a stable plasma is formed.

The neutral particles are heated indirectly by collisions with the charged particles upon which the field acts. Macroscopically the process is equivalent to heating a conductor by a radio-frequency field, the resistance to eddy-current flow producing joule heating. The field does not penetrate the conductor uniformly and therefore the largest current flow is at the periphery of the plasma. This is the so-called 'skin' effect and, coupled with a suitable gas-flow geometry, it produces an annular or doughnut-shaped plasma. Electrically, the coil and plasma form a transformer with the plasma acting as a one-turn coil of finite resistance.

The properties of an inductively coupled plasma closely approach those of an ideal source for the following reasons:

- The source must be able to accept a reasonable input flux of the sample and it should be able to accommodate samples in the gas, liquid or solid phases.
- The introduction of the sample should not radically alter the internal energy generation process or affect the coupling of energy to the source from external supplies.
- The source should be operable on commonly available gases and should be available at a price that will give cost-effective analysis.
- The temperature and residence time of the sample within the source should be such that all the sample material is converted to free atoms irrespective of its initial phase or chemical composition; such a source should be suitable for atomic absorption or atomic fluorescence spectrometry.
- If the source is to be used for emission spectrometry, then the temperature should be sufficient to provide efficient excitation of a majority of elements in the periodic table.
- The continuum emission from the source should be of a low intensity to enable the detection and measurement of weak spectral lines superimposed upon it.
- The sample should experience a uniform temperature field and the optical density of the source should be low so that a linear relationship between the spectral line intensity and the analyte concentration can be obtained over a wide concentration range.

Greenfield *et al.* [2] were the first to recognise the analytical potential of the annular inductively coupled plasma. Wendt and Fassel [3] reported early experiments with a 'tear-drop'-shaped inductively coupled plasma

Table 1.3 Available flame and graphite furnace atomic absorption spectrometers

Type instrument	Supplier	Model no and type	Microprocessor	Hydride and mercury attachment	Auto- sampler	Wavelength range
Flame (direct injection)	Thermo- electron	1 L 157 single channel 1 L 357 single	} -	Yes	Yes	-

		beam				
		1 L 457 single channel double beam	with graphics			
		Video 11 single channel single beam	with graphics			
		Video 12 single channel double beam	with graphics			
		Video 22 two double channels	computer interface			
Graphite furnace	Thermo-electron	IL 655 CTF	–	–	Yes	–
Direct injection	Perkin-Elmer	2280 single beam	Yes			
		2380 double beam	Yes (with automatic background correction)	–	–	190–870
Graphite furnace	Perkin-Elmer	100 single beam 2100 single path double beam	} Yes	–	–	190–870
Graphite furnace	Varian Associates	SpectrA A30+40 multi-element analysis	Yes	Yes	Yes	190–900
		Method storage				
		SpectrA A10 (low cost,	Yes (built-in VDU)	Yes	Yes	190–900

		single beam)	SpectrA A20 (medium cost, double beam)	Yes (built-in VDU)	Yes	Yes	190–900
Type instrument	Supplier	Model no and type	Microprocessor	Hydride and mercury attachment	Auto-sampler	Wavelength range	
Flame graphite furnace		SpectrA A300/400 multi-element analysis, centralized instrument control	Yes (with colour graphics and 90 elements on disk)	Yes	Yes	190–900	
		STA 95 and GTA 96 graphite tube atomizer units—compatible with all SpectrA A instruments	Furnace and programmable sample dispenser SpectrA A keyboard. Rapid interchange between flame and furnace operation				
Graphite furnace	GBC Scientific	903 single beam	Yes	Yes		176–900	
		Pty Ltd	902 double beam (both with impact head option)	Yes	Yes	170–900	
Flame (direct injection) graphite furnace	Shimadzu	AA670 double beam	Yes	Yes	Yes	190–900	
		AA670 G Double beam	Yes	Yes	Yes	190–900	

Source: Own files

but later described the medium power (1–3kW), 18mm annular plasma now favoured in modern analytical instruments [4].

The current generation of inductively coupled plasma emission spectrometers provide limits of detection in the range of $0.1\text{--}500\mu\text{g L}^{-1}$ in solution, a substantial degree of freedom from interference and a capability for simultaneous multi-element determination facilitated by a directly proportional response between the signal and the concentration of the analyte over a range of about five orders of magnitude.

The most common method of introducing liquid samples into the inductively coupled plasma is by using pneumatic nebulisation in which the liquid is dispensed into a fine aerosol by the action of a high-velocity gas stream. To allow the correct penetration of the central channel of the inductively coupled plasma by the sample aerosol, an injection velocity of about 7m s^{-1} is required. This is achieved using a gas injection with a flow rate of about $0.5\text{--}11\text{min}^{-1}$ through an injector tube of 1.5–2.0mm internal diameter. Given that the normal sample uptake is $1\text{--}2\text{ml min}^{-1}$ this is an insufficient quantity of gas to produce efficient nebulisation and aerosol transport. Indeed, only 2% of the sample reaches the plasma. The fine gas jets and liquid capillaries used in inductively coupled plasma nebulisers may cause inconsistent operation and even blockage when solutions containing high levels of dissolved solids, such as sea water or particulate matter, are used. Such problems have led to the development of a new type of nebuliser, the most successful being based on a principle originally described by Babington (US Patents). In these, the liquid is pumped from a wide-bore tube and thence conducted to the nebulising orifice by a V-shaped groove [5] or by the divergent wall of an over-expanded nozzle [6]. Such devices handle most liquids and even slurries without difficulty.

Nebulisation is inefficient and therefore not appropriate for very small liquid samples. Introducing samples into the plasma in liquid form reduces the potential sensitivity because the analyte flux is limited by the amount of solvent that the plasma will tolerate. To circumvent these problems a variety of thermal and electrothermal vaporisation devices have been investigated. Two basic approaches are in use. The first involves indirect vaporisation of the sample in an electrothermal vaporiser, eg a carbon rod or tube furnace or heated metal filament as commonly used in atomic absorption spectrometry [7–9]. The second involves inserting the sample into the base of the inductively coupled plasma on a carbon rod or metal filament support [10,11]. Available instrumentation is reviewed in Table 1.4.

1.1.6 Polarographic and electrochemical methods

1.1.6.1 Polarography

This technique has been applied to the following 20 determinations in water, all of which are capable of undergoing an oxidation reduction (ie redox).

<i>Non saline waters:</i>	arsenate, arsenite, iodate, iodide, nitrate, nitrite, phosphate, selenate, selenite, sulphide, also nitriloacetate.
<i>Seawater:</i>	bromate and sulphate.
<i>Aqueous precipitation:</i>	nitrate.
<i>Surface and ground waters:</i>	bromide and arsenate.
<i>Potable water:</i>	iodide, nitrate, nitrite, perchlorate and silicate.
<i>Waste waters:</i>	chromate, dichromate and sulphite.
<i>Trade effluents:</i>	free cyanide, selenate and selenite.

Differential pulse polarography has found limited applications.

Three basic techniques of polarography are of interest and the basic principles of these are outlined below.

Universal: Differential Pulse (DPN, DPI, DPR)

In this technique a voltage pulse is superimposed on the voltage ramp during the last 40ms of controlled drop growth with the standard dropping mercury electrode; the drop surface is then constant. The pulse amplitude can be preselected. The current is measured by integration over a 20ms period immediately before the start of the pulse and again for 20ms as the pulse nears completion. The difference between the two current integrals ($i_2 - i_1$) is recorded and this gives a peak-shaped curve. If the pulse amplitude is increased, the peak current value is raised but the peak is broadened at the same time.

Classical Direct Current (DCT)

In this direct current method, integration is performed over the last 20ms of the controlled drop growth (Tast procedure): during this time, the drop surface is constant in the case of the dropping mercury electrode. The resulting polarogram is step-shaped. Compared with classical DC polarography according to Heyrovsky, ie with the free-dropping mercury electrode, the DCT method offers great advantages; considerably shorter analysis times, no disturbance due to current oscillations, simpler evaluation and larger diffusion-controlled limiting current.

Table 1.4 Inductively coupled plasma optical emission spectrometers available on the market

<i>Supplier</i>	<i>Model</i>	<i>System</i>	<i>Number of elements claimed</i>	<i>Maximum analysis rate (elements min L⁻¹)</i>	<i>Micro-processor</i>	<i>Auto-sampler</i>	<i>Range (nm)</i>
Perkin-Elmer	Plasma II	Optimized	70	Up to 50	Yes	Yes	160–81

		sequential system					
Perkin-Elmer	ICP 5500	Sequential		15	Yes	Yes	170–90
Perkin-Elmer	ICP 5500B	Sequential		20	Yes	Yes	170–90
Perkin-Elmer	ICP 6500	Sequential		20	Yes	–	170–90
Perkin-Elmer	ICP 5000	Can be used for – flame and graphite furnace AAS and inductively coupled plasma atomic emission spectrometry (sequential)		Yes	Yes		175–900
Perkin-Elmer	Plasma 40	Lower-cost sequential		Personal computer	Yes		160–800
Labtam	Plasma Scan 8440	Simultaneous (polychromator or with optional monochromator for sequential)	60–70	Up to 64	Yes	Yes	170–800
Labtam	Plasma 8410	More than 70	–	Yes	Yes		170–820 Sequential
Thermoelectron	Plasma 300 (replacing the Plasma 200) (single (air) or double (air/vacuum) available)	Sequential	Up to 63	Up to 18 (single channel air); up to 24 (double channel air/vacuum)	Yes	Yes	160–90

<i>Supplier</i>	<i>Model</i>	<i>System</i>	<i>Number of elements claimed</i>	<i>Maximum analysis rate (elements min L⁻¹)</i>	<i>Micro-processor</i>	<i>Auto-sampler</i>	<i>Range (nm)</i>

Philips	PV 8050 series PV 8055 PV 8060 PV 8065	Simultaneous	56	–	Yes	Yes	165– 485 and 530– 860
Philips	PU 7450	Sequential	70	–	Yes	Yes	190– 800
Baird	Spectrovac PS3/4 plasma hydride device option	Simultaneous and sequential	Up to 60	Up to 80 samples h^{-1} each up to 60 elements	Yes	Yes	162– 766 and 162– 800
Baird	Plasmatest system 75	Simultaneous and sequential	Up to 64	–	Yes	Yes	176– 768 and 168– 800
Spectro Analytical Ltd	Spectroflame plasmahydride device option	Simultaneous and sequential	Up to 64	–	Yes	Yes	165– 800

Source: Own file

Rapid Square Wave (SQW)

Five square-wave oscillations of frequency around 125Hz are superimposed on the voltage ramp during the last 40ms of controlled drop growth; with the dropping mercury electrode the drop surface is then constant. The oscillation amplitude can be preselected. Measurements are performed in the second, third and fourth square-wave oscillation; the current is integrated over 2ms at the end of the first and at the end of the second half of each oscillation. The three differences of the six integrals (i_1-i_2 , i_3-i_4/i_5-i_6) are averaged arithmetically and recorded as one current value. The resulting polarogram is peak shaped.

Metrohm are leading suppliers of polarographic equipment. They supply three main pieces of equipment: the Metrohm 646 VA processor, the 647 VA stand (for single determinations) and the 675 VA sample changer (for a series of determinations). Some features of the 646 VA processor are listed below:

- Optimised data acquisition and data processing
- High-grade electronics for a better signal-to-noise ratio
- Automatic curve evaluation as well as automated standard addition for greater accuracy and smaller standard deviation
- Large, non-volatile methods memory for the library of fully developed analytical procedures
- Connection of the 675 VA sample changer for greater sample throughput
- Connection of an electronic balance

- Simple perfectly clear operation principle via guidance in the dialogue mode yet at the same time high application flexibility thanks to the visual display and alphanumeric keyboard
- Complete and convenient result recording with built-in thermal recorder/printer

The 675 VA sample changer is controlled by the 646 VA processor on which the user enters the few control commands necessary. The 646 VA processor also controls the 677 drive unit and the 683 pumps. With these auxiliary units, the instrument combination becomes a polarographic analysis station which can be used to carry out on-line measurements.

The 646 VA processor is conceived as a central compact component for automated polarographic and voltammetric systems. Thus, two independent 647 VA stands or a 675 VA sample changer can be added. Up to four multidosimats of the 665 type for automated standard additions and/or addition of auxiliary solutions can be connected to each of these wet-chemical workstations. Connection of an electronic balance for direct transfer of data is also possible.

Program-controlled automatic switching and mixing of these three electrode configurations during a single analysis via software commands occur. The complete electrode is pneumatically controlled. A hermetically sealed mercury reservoir of only a few millilitres suffices for approximately 200,000 drops. The mercury drops are small and stable, consequently there is a good signal-to-noise ratio. Mercury comes into contact only with the purest inert gas and plastic free of metal traces. Filling is seldom required and very simple to carry out. The system uses glass capillaries which can be exchanged simply and rapidly.

Up to 30 complete analytical methods (including all detailed information and instructions) can be filled in a non-volatile memory and called up. Consequently, a large extensive and correspondingly efficient library of analytical methods can be built up, comprehensive enough to carry out all routine determinations conveniently via call-up of a stored method.

The standard addition method (SAM) is the procedure generally employed to calculate the analyte content from the signal of the sample solution. The SAM is coupled directly to the determination of the sample solution so that all factors which influence the measurement remain constant. There would be no doubt that the SAM provides results that have proved to be accurate and precise in virtually every case.

The addition of standard solutions can be performed several times if need be (multiple standard addition) to raise the level of quality of the results still further.

Normally, a real sample solution contains the substances to be analysed in widely different concentrations. In a single multi-element analysis, however, all components must be determined simultaneously. The superiority of the facilities offered by segmented data acquisition in this respect is clear when a comparison is made with previous solutions. The analytical conditions were inevitably a compromise; no matter what type of analytical conditions were selected, such large differences could rarely be reconciled. In the recording, either the peaks of some of the components were shown meaningfully—each of the other two were either no longer recognisable—or led to gigantic signals with cut-off peak tips. And all too often the differences were still too large even within the two concentration ranges. Since the recorder sensitivity and also all other instrument and

electrode functions could only be set and adjusted for a single substance even automatic range switching of the recorder was of very little use.

The dilemma is solved with the 646 VA processor: the freedom to divide the voltage sweep into substance-specific segments and to adjust all conditions individually and independently of one and another within these segments opens up quite a new and, to date, unknown analytical possibility. Furthermore, it allows optimum evaluation of the experimental data.

Various suppliers of polarographs are summarised in Table 1.5.

Table 1.5 Suppliers of polarographs

<i>Supplier</i>	<i>Type</i>	<i>Model No.</i>	<i>Detection limits</i>
Metrohm	Differential pulse	646 VA processor	2–10 $\mu\text{g L}^{-1}$ quoted for nitroacetate
	Direct current	647 VA stand	
	Square wave	675 VA sample changer	
		665 Dosimat (motor driven piston burettes for standard additions)	
	Direct current normal pulse differential pulse 1st harmonic ac. 2nd harmonic ac. Kalousek	506 Polarecord	
	Direct current sampled differential pulse	DC 626 Polarecord	
Chemtronics Ltd	On-line voltammetric analyser for metals in effluents and field work	PDV 2000	$\sim 0.1 \mu\text{g L}^{-1}$
RDT Analytical Ltd	Differential pulse anodic stripping on-line voltammetric analyser for metals in effluents and field work	ECP 100 plus ECP 1 04 programmes ECP 140 PDV 200	
	On-line voltammetric analyser for continuous measurement of metals in effluents and water	OVA 2000	
EDT Analytical Ltd	Cyclic voltammetry differential pulse voltammetry linear scan voltammetry, square-wave voltammetry, single- and double-step chronopotentiometry and chronocoulometry	Cipress Model CYSY-1B (basic system) CY57-IH- (high-sensitivity system)	

Source: Own files

1.1.6.2 Potentiometry

This technique has been applied to the determination of iodide and free cyanide in non saline waters and nitrate in aqueous precipitation.

1.1.6.3 Chronopotentiometry

This technique has been applied to the determination of chloride in seawater.

1.1.6.4 Amperometry

This technique has been applied to the determination of nitrate and nitrite in non saline waters and nitrite in trade effluents.

1.1.6.5 Anodic stripping voltammetry

This technique has been applied to the determination of selenite, hypochlorite, chlorite and phosphate in non saline waters, and polysulphide, sulphate and thiosulphate in waste waters.

1.1.6.6 Cathodic stripping voltammetry

This technique has been applied to the determination of iodate, iodide, nitrite and chloride in non saline waters and iodide and nitrate in seawater and sulphide in waste waters.

1.1.7 Ion selective electrodes

Ion selective electrode technology is based on the simple measuring principle consisting of a reference electrode and a suitable sensing or indicator electrode sample solution (for the ion being dipped) dipped in the sample solution and connected by a sensitive voltmeter. The sensing electrode responds to a difference between the composition of the solution inside and outside the electrode and requires a reference electrode to complete the circuit.

The Nernst equation, $E = E_0 + S \log C$, which gives the relationship between the activity or concentration (C) contains two terms which are constant for a particular electrode. These are E_0 (a term based on the potentials which remain constant for a particular sensing/reference electrode pair) and the slope S (which is a function of the sign and valency of the ion being sensed and the temperature). In direct potentiometry, it has to be assumed that the electrode response follows the Nernst equation in the sample matrix and in the range of measurement. E_0 and slope are determined by measuring the electrode potential in two standard solutions of known composition and the activity of the ion in the unknown sample is then calculated from the electrode potential measured in the sample.

Reference electrodes of interest to the water chemist are of two types—single function

and double function. Indicating or sensing electrodes are of four types:

- solid state determination of Br^{1-} , Cd^{2+} , Cl^{1-} , Cu^{2+} , CN^{1-} , F^{1-} , I^{1-} , Pb^{2+} , Redox, silver/sulphide $^{1-}$, Na^+ , CNS^{1-}
- liquid membrane Ca^{2+} , divalent (hardness), fluoroborate, NO_3^{1-} , K^{1+} , ClO_4^{1-} , HF, surfactants
- residual chlorine
- glass sodium

Applications of ion selective electrodes to the determination of 16 anions in various types of water are listed below.

Non saline waters: sulphate, sulphite, thiocyanate, iodate, iodide, nitrate, nitrite and palmitate, bromate, bromide, chloride, free cyanide, total cyanide and fluoride.

Seawater: bromide, chloride and fluoride.

Aqueous precipitation: fluoride and sulphate.

Surface and ground waters: free cyanide and nitrate.

Potable waters: fluoride.

Waste waters: chloride, sulphate, sulphide, free cyanide, total cyanide, nitrate.

Sewage effluents: chloride, nitrate and sulphide.

Trade effluents: sulphate, sulphide and thiocyanate.

High purity water: chloride.

Variables which effect precise measurement by ion selective electrodes are the following:

- concentration range
- ionic strength—an ionic strength adjuster is added to the samples and standards to minimise differences in ionic strength
- temperature
- pH
- stirring
- interferences
- complexation

Traditionally electrodes have been used in two basic ways, direct poten-tiometry and potentiometric titration. Direct potentiometry is usually used for pH measurement and for measurement of ions like sodium, fluoride, nitrate and ammonium, for which good selective electrodes exist.

Direct potentiometry is usually done by manually preparing ionic activity standards

and recording electrode potential in millivolts, using a high-impedance millivoltmeter and plotting a calibration graph on semilogarithmic graph paper (or using a direct reading pH/ion meter which plots the calibration graph internally).

In potentiometric titration techniques, the electrode is simply used to determine the end-point of a titration, much as a coloured indicator would be used.

Direct potentiometry is an accurate technique but the precision and repeatability are limited because there is only one data point. Electrodes drift and potential can rarely be reproduced to better than $\pm 0.5\text{mV}$ so that the best possible repeatability in direct measurement is usually considered to be $\pm 2\%$.

Orion, the leading manufacturers of ion selective electrodes, supply equipment for both direct potentiometry (EA 940, EA 920, SA 720 and SA 270 meters) and potentiometric titration (Orion 90 autochemistry system).

Ion selective electrode equipment: Orion direct potentiometry meters

A review of these four meters, in Table 1.6, shows that only the EA 940 has a facility for multiple point calibration and this places it at the top of their range of direct-potentiometry meters. This instrument automatically prints out results. It has a memory for storing calibration information for all the electrodes.

The EA 920 is a lower-priced instrument for two-step calibration. It also has a memory for storing calibration information. The SA 720 and the portable SA 270 are relatively inexpensive bottom of range instruments with more limited capabilities.

The Orion 960 autochemistry system (direct potentiometry—potentiometric titration)

This is the top-of-the-range instrument. In addition to direct potentiometry and potentiometric titrations it has other features not previously incorporated in potentiometric analysers.

The 960 uses 12 basic analytical techniques. To do an analysis one of techniques is chosen and modified to suit the requirements of the particular sample. The memory will accommodate up to 20 methods.

KAP™ analysis is a time-saving technique that eliminates sample preparation and calibration. Simply weigh sample into a beaker, add water and measure. Aliquots of one standardising solution or reagent are added automatically to the sample and sample concentration is determined from the changes in potential observed after each addition. Every step is performed in one beaker.

Results from KAP analysis are automatically verified in two ways. First a check for electrode drift and noise is performed at the beginning of each

Table 1.6 Orion pH/ISE meter features chart

Feature	Orion pH/Se meters			
	EA	EA	SA	SA
	940	920	720	270
H ⁺	✓	✓	✓	
P				

Direct concentration readout in any unit	✓	✓	✓	✓
mV	✓	✓	✓	✓
RelmV	✓	✓	✓	
Temperature	✓	✓	✓	✓
Oxygen	✓	✓		✓
Redox	✓	✓	✓	✓
Dual electrode inputs	✓	✓		
Expandable/upgradable	✓	✓		
Automatic anion/cation electrode recognition	✓	✓	✓	✓
Multiple point calibration	✓			
Incremental analytical techniques	✓	✓ ¹		
Multiple electrode memory	✓	✓		
Prompting	✓	✓	✓	✓
Ready indicator	✓	✓	✓	
Resolution and significant digit selection	✓	✓	✓	✓
pH autocal	✓	✓	✓	
Blank correction	✓	✓		
Multiple print option	✓	✓		
Recorder output	✓	✓	✓	
RS-232C output	✓	✓	✓	
Adjustable ISO	✓	✓	✓	✓
Automatic temperature compensation-line	✓	✓	✓	✓
and battery operation			✓	✓

¹With PROM upgrade

Source: Own files

analysis. Second, each sample is spiked with standard as part of the analysis and recovery of the spike is calculated.

GAP™ analysis is a faster way to perform many titrations. GAP analysis actually predicts the location of the end point so there is no need to titrate all the way. And GAP analysis allows titrations to be performed at low levels when conventional techniques yield very poor end-point breaks or asymmetrical curves.

HELP analysis is a diagnostic technique in which the instrument studies the data collected and recommends the optimum procedure for repetitive analysis of similar samples.

The heart of the Orion 960 autochemistry system is the EA 940 expendable analyser—an advanced pH/ISE meter.

Orion supply both electrodes and measuring equipment. Ingold, on the other hand, supply only electrodes. EDT Analytical (UK) also manufacture ion selective electrodes.

1.1.8 X-ray methods

1.1.8.1 X-ray spectrometry

The application of this technique is limited to the determination of traces of bromide in seawater.

1.1.8.2 X-ray fluorescence spectroscopy

This technique has been applied to the determination of seven anions as indicated below.

<i>Non saline waters:</i>	selenate, selenite and phosphate.
<i>Seawater:</i>	bromide.
<i>Aqueous precipitation:</i>	chloride, bromide and iodide.
<i>Waste waters:</i>	phosphate.
<i>Trade effluents:</i>	selenate and selenite.

1.1.8.3 Energy-dispersive X-ray fluorescence spectrometry

Energy-dispersive X-ray fluorescence (EDXRF) spectrometry is an instrumental analytical technique for non-destructive multi-elemental analysis. The use of modern-day technologies coupled with the intrinsic simplicity of X-ray fluorescence spectra (as compared for instance with optical emission (OE) spectra) means that the powerful EDXRF technique can be used routinely. The EDXRF spectrum for iron is a clearly resolved doublet, while the optical emission spectrum contains more than 4000 lines. This simplicity is a direct consequence of the fact that XRF spectra are a result of inner shell electron transitions which are possible only between a limited number of energy levels for the relatively few electrons. Optical emission spectra, on the other hand, arise from electron transitions in the outer, valence shells which are closer together in energy, more populated than the inner shells and from which it is easier to promote electron transitions.

In order to generate X-ray spectra, we may excite the elements in the specimen with any one of the following:

- X-ray photons
- High-energy electrons
- High-energy charged particles
- Gamma rays
- Synchrotron radiation.

The term XRF is generally applied when X-ray photons are used to generate

characteristic X-rays from the elements in the specimen. The most commonly used source of such X-rays (in the 2–100keV range) are radioisotopes and X-ray tubes. An EDXRF spectrometer such as the XR300 uses a compact, low power (10–100W typical) X-ray tube capable of delivery of X-ray photons with a maximum energy of 30 or 50keV.

Why is the technique referred to as ‘energy-dispersive’ XRF?

The classical XRF spectrometer which has been commercially available since the 1950s uses crystal structures to separate (resolve) the X-rays emanating from the fluorescence process in the irradiated specimen. These crystals diffract the characteristic X-rays from the elements in the specimen, allowing them to be separated and measured. The characteristic fluorescent X-rays are said to have been separated from each other by the process of ‘wavelength dispersion’ (WDXRF). Each element emits characteristic lines which can be separated by WDXRF before being individually counted. For each line and diffracting crystal, we can set a detector at a particular angle (from the Bragg equation) and collect X-rays, which are primarily from the selected element.

The EDXRF system uses the Si(Li) (lithium-drifted silicon) detector to simultaneously collect all X-ray energies emitted from the specimen. Each detected X-ray photon gives rise to a signal from the detector. The magnitude of this signal is proportional to the energy of the detected X-ray and when amplified and digitised can be passed to a multi-channel analyser which displays a histogram of number of X-rays (intensity) against energy. The incident photons, therefore, have been electronically separated (dispersed) according to their energy. The energy of each of the X-rays from all the elements is readily accessible from published tables.

Due to the simple spectra and the extensive element range (sodium upwards) which can be covered using the Si(Li) detector and a 50kV X-ray tube, EDXRF spectrometry is perhaps unparalleled for its quantitative element analysis power.

Qualitative analysis is greatly simplified by the presence of few peaks which occur in predictable positions and by the use of tabulated element/ line markers which are routinely available from the computer-based analyser.

To date, the most successful method of combined background correction and peak deconvolution is to use the method of digital filtering and least squares (FLS) fitting of reference peaks to the unknown spectrum [13]. This method is robust, simple to automate and is applicable to any sample type.

The combination of the digital filtering and least squares peak deconvolution method and empirical correction procedures has application throughout elemental analysis. This approach is suitable for specimens of all physical types and is used in a wide selection of industrial applications.

1.1.8.4 Total reflection X-ray fluorescence spectrometry

The major disadvantage of conventional energy dispersive X-ray fluorescence spectrometry has been poor elemental sensitivity, a consequence of high background noise levels resulting mainly from instrumental geometries and sample matrix effects. Total reflection X-ray fluorescence (TXRF) is a relatively new multi-element technique with the potential to be an impressive analytical tool for trace-elemental determinations

for a variety of sample types. The fundamental advantage of TXRF is its capability to detect elements in the picogram range in comparison to the nanogram levels typically achieved by traditional energy-dispersive X-ray fluorescence spectrometry.

The problem in detecting atoms in the nanogram per litre or submicrogram per litre level is basically one of being able to obtain a signal which can be clearly distinguished from the background. The detection limit being given typically as the signal which is equivalent to three times the standard deviation of the background counts for a given unit of time. In energy-dispersive X-ray fluorescence spectrometry the background is essentially caused by interactions of radiation with matter resulting from an intense flux of elastic and Compton-scattered photons. The background, especially in the low-energy region (0–20keV), is due in the main to Compton scattering of high-energy Bremsstrahlung photons from the detector crystal itself. In addition, impurities on the specimen support will contribute to the background. The Auger effect does not contribute to an increased background, as the emitted electrons, of different but low energy, are absorbed either in the beryllium foil of the detector entrance windows or in the air path of the spectrometer.

A reduction in the spectral background can be effectively achieved by X-ray total reflection at the surface of a smooth reflector material such as quartz. X-ray total reflection occurs when an X-ray beam impinges on a surface at less than the critical angle of total reflection. If a collimated X-ray beam impinges onto the surface of a plane smooth and polished reflector at an angle less than the critical angle, then total reflection occurs. In this case the angle of incidence is equal to the angle of reflection and the intensities of the incident and totally reflected beams should be equal.

The principles of TXRF were first reported by Yaneda and Horiuchi [14] and further developed by Aiginger and Wodbrauschek [15]. In TXRF the exciting primary X-ray beam impinges upon the specimen prepared as a thin film on an optically flat support at angles of incidence in the region of 2–5min of arc below the critical angle. In practice the primary radiation does not (effectively) enter the surface of the support but skims the surface, irradiating any sample placed on the support surface. The scattered radiation from the sample support is virtually eliminated, thereby drastically reducing the background noise. A further advantage of the TXRF system, resulting from the new geometry used, is that the solid-state energy-dispersive detector can be accommodated very close to the sample (0.3mm), which allows a large solid angle of fluorescent X-ray collection, thus enhancing a signal sensitivity and enabling the analysis to be carried out in air at atmospheric pressure.

The sample support or reflector is a 3cm diameter wafer made of synthetic quartz or perspex. The water sample can be placed directly onto the surface. The simplest way to prepare liquid samples is to pipette volumes between 1 and 50 μ L directly onto a quartz reflector and allow them to dry. For aqueous solutions the reflector can be made hydrophobic (eg by silicon treatment) in order to hold the sample in the centre of the plate. Suitable elements for calibration can be achieved by a simple standard addition technique.

Since Yaneda and Horiuchi [13] first reported the use of TXRF various versions have been developed [15–18]. Recently an X-ray generator with a fine focus tube and multiple reflection optics has been developed by Seifert & Co and coupled with an energy-

dispersive spectrometer fitted with an Si(Li) detector and multi-channel analyser supplied by Link Analytical. The new system, which will be described later, known as the EXTRA II, represents the first commercially available TXRF instrument.

The attractive features of TXRF can be summarised as follows:

- An inherent universal calibration curve is obtained as a smooth function of atomic number
- The use of internal single-element standardisation eliminates the need for matrix-matched external standards
- Only small sample volumes are required (5–50 μL).
- The technique requires only a simple sample preparation methodology.

The attractive features of the TXRF technique outlined above suggest that TXRF has the potential to become a very powerful analytical tool for trace-elemental determinations applicable to a wide range of matrix types and may, indeed, compete with the inductively coupled plasma mass spectrometry.

Various suppliers of energy-dispersive and energy-reflection instruments are listed in Table 1.7.

Table 1.7 Energy dispersive and total reflection X-ray fluorescence spectrometers

<i>Supplier</i>	<i>Model</i>	<i>Type</i>	<i>Sample types</i>	<i>Computer</i>	<i>Handling of peak overlaps</i>	<i>Element range</i>	<i>Detector</i>
Link Analytical	XR 200/300	Energy dispersive	Solid and liquid	Yes	Filtered least squares technique	Atomic numbers 15–55 (Mo–Ba)	10mm ² 155eV resolution Si (Li) detector
Pye Instruments (Philips)	PW 1404	Energy dispersive sequential	Solid and liquid	Yes	Various techniques	B–U	Argon flow scintillation
Seifert	Extra III	Energy dispersive and multiple total reflection	Solid and liquid	Yes	No correction for matrix effects required except for those in the range sodium to phosphorus	All elements beyond sodium	80mm ² 165eV Si (Li) detector

Source: Own files

Philips PW 1404 energy-dispersive X-ray fluorescence spectrometer

The Philips PW 1404 is a powerful versatile sequential X-ray spectrometer system developed from the PW 1400 series and incorporating many additional hardware and

software features that further extend its performance. All system functions are controlled by powerful microprocessor electronics, which make routine analysis a simple push-button exercise and provide extensive safeguards against operator error. The microprocessor also contains sufficient analytical software to permit stand-alone emergency operation, plus a range of self-diagnostic service-testing routines.

The main characteristics of this instrument are as follows:

- Identifies all elements from boron to uranium
- Choice of side window X-ray tubes allows optimum excitation for all applications
- New detectors and crystals bring improved light-element performance
- 100kV programmable excitation enhances heavy-element detection
- Special calibration features give more accurate results:
 - auxiliary collimator provides high resolution
 - programmable channel mask reduces background
 - fast digital scanning speeds data collection
 - high angular accuracy aids positive identification
- Powerful software includes automatic peak labelling
- Compact one-cabinet system
- Distributed intelligence via five microprocessors
- High-frequency generator cuts running costs and improves stability
- New high-speed electronics allows operation at one million counts per second
- System self-selects analytical programs for unknowns
- Surface-down sample presentation aids accurate analysis of liquids
- Small airlock speeds sample throughput, cuts helium costs
- Designed for laboratory automation
- Front panel continuously displays system status
- New generation software for DEC computers
- Computer dialogue in English, French, German and Spanish
- Colour graphics simplify results interpretation
- Extensive programming, reporting, editing facilities available.

The layout of the Philips PW 1404 instrument is shown in Fig. 1.2.

Unique among XRF instruments the EXTRA II TXRF spectrometer yields lower limits of detection in the region of 10pg (1pg=10⁻¹²g) for more than 60 elements, eg 5–10pg for chlorine, 10–30pg for phosphorus and sulphur and 30–100pg for silicon.

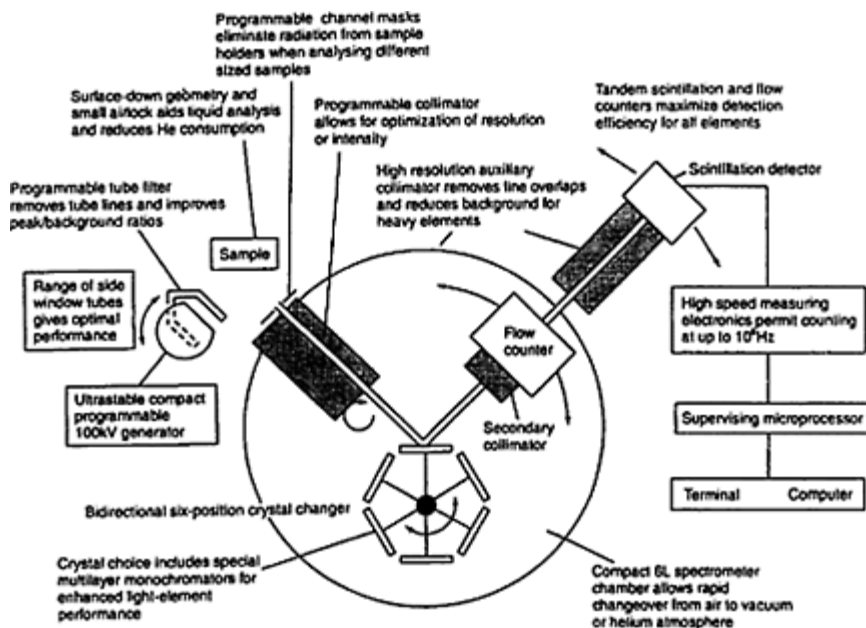


Fig. 1.2 Layout of Philips PW 1404 energy-dispersive X-ray fluorescence spectrometer

Source: Own files

All elements upwards from sodium ($z=11$) in the periodic table may be determined. The inclusion of twin excitation sources, which may be switched electronically within a few seconds, assures optimum sensitivity for all detectable elements. The applicable concentration range is from per cent to below $1\mu\text{g L}^{-1}$. As little as $1\mu\text{g}$ of sample is sufficient to determine elements at the milligram per litre level; calibration is necessary only once and is carried out during installation. The calibration will remain unchanged for a period of at least 12 months. Quantitative analysis is simple and uses the method of internal standardisation. No external standards are necessary. The method requires no correction of matrix effects for all elements except those in the range sodium to phosphorus. Empirical absorption-enhancement correction models may be applied to these light elements. Sample preparation for solutions and dispersions is very simple, requiring only a micropipette.

1.1.9 Neutron activation analysis

This is a very sensitive technique whose application in water has been limited to the determination of iodide in non saline water and bromide in aqueous precipitation. Due to the complexity and cost of the technique, no water laboratory in the UK has its own facility for carrying out neutron activation analysis. Instead, samples are sent to one of the organisations that possess the facilities, eg the Atomic Energy Research

Establishment at Harwell, or the Joint Manchester-Liverpool University Reactor located at Risley.

The technique's extreme sensitivity makes it suitable for use when a referee analysis is required on a material which has become a standard for checking out other methods. Another advantage of the technique is that a foreknowledge of the elements present is not essential. It can be used to indicate the presence and concentration of entirely unexpected elements, even when present at very low concentrations.

In neutron activation analysis, the sample in a suitable container, often a pure polyethylene tube, is bombarded with slow neutrons for a fixed time together with standards. Transmutations convert analyte elements into radioactive elements, which are either different elements or isotopes of the original analyte.

After removal from the reactor the product is subject to various counting techniques and various forms of spectrometry to identify the elements present and their concentration.

1.1.10 Photo activation analysis

The application of this technique is limited to the determination of fluoride in seawater.

1.1.11 Isotope dilution analysis

This technique has very limited applications in the determination of anions, viz selenate, selenite, chloride and iodide in non saline water and bromide in aqueous precipitation.

1.1.12 Enzymic assay

Again there are very few applications, viz sulphate, nitrate, phosphate, chromate, dichromate and free cyanide in non saline waters.

1.1.13 Chromatographic methods

The identification and determination of traces of organic and organic substances in water samples is a subject that has made tremendous advances in recent years. The demands made on water chemists in terms of specificity and sensitivity in carrying out these analyses have become greater and greater with the increasing realisation that organic substances from industrial sources are permeating the ecosystem and identification and measurements of minute traces of these are required in potable, river and ground waters and even in rain water. At the same time, measurements in industrial effluent outfalls are necessary in order to control the rate of release of these substances.

For the more volatile components of water samples, ie those with boiling points up to about 250°C, gas chromatography has been a favoured technique for several decades. However, with the realisation that retention time measurements alone are insufficient to identify organics there has been an increasing move in recent years to connect a gas chromatograph to a mass spectrometer in order to provide unequivocal identifications. Element-specific detectors are another recent development.

A limitation of gas chromatography is that it cannot handle less volatile compounds and these comprise a high proportion of the total organics content of the sample. For this reason increasing attention is being paid to the application of high-performance liquid chromatography in water analysis. Again, when positive identifications are required, a mass spectrometer is connected to the outlet of the chromatograph.

Supercritical fluid chromatography is a recent development which may find increasing use in water analysis.

A major breakthrough in recent years for the determination of anions is ion chromatography and, even more recently, electrostatic ion chromatography.

1.1.13.1 Ion chromatography

This technique developed by Small *et al.* in 1975 [19] is usually extensively employed for the separation and determination of mixtures of 31 inorganic anions in water. However, applications have also been found for the determination of some 50 organic anions in water.

The technique uses specialised ion exchange columns and chemically suppressed conductivity detection. Advances in column and detection technologies have expanded this capability to include wider ranges of anions as well as organic ions. These recent developments, discussed below, provide the chemist with a means of solving many problems that are difficult, if not impossible, using other instrumental methods. Ion chromatography can analyse a wide variety of organic and inorganic anions more easily than either atomic absorption spectrometry or inductively coupled plasma techniques.

At the heart of the ion chromatography system is an analytical column containing an ion exchange resin on which various anions (and/or cations) are separated before being detected and quantified by various detection techniques, such as spectrophotometry, atomic absorption spectrometry (metals) or conductivity (anions).

Ion chromatography is not restricted to the separate analysis of only anions or cations, and, with the proper selection of the eluent and separator columns, the technique can be used for the simultaneous analysis of both anions and cations.

The original method for the analysis of mixtures of anions used two columns attached in series packed with ion exchange resins to separate the ions of interest and suppress the conductance of the eluent, leaving only the species of interest as the major conducting species in the solution. Once the ions were separated and the eluent suppressed, the solution entered a conductivity cell, where the species of interest were detected.

The analytical column is used in conjunction with two other columns, a guard column which protects the analytical column from troublesome contaminants, and a preconcentration column. The intended function of the preconcentration column is twofold. First, it concentrates the ions present in the sample, enabling very low levels of contaminants to be detected. Second, it retains non-complexed ions on the resin, while allowing complexed species to pass through.

Dionex Series 400001 Ion Chromatographs

Some of the features of this instrument are:

- chromatography module;

- up to six automated valves made of chemically inert, metal-free material eliminate corrosion and metal contamination;
- liquid flow path is completely compatible with all high performance liquid chromatography solvents;
- electronic valve switching, multi-dimensional, coupled chromatography or multi-mode operation;
- automated sample clean up or pre-concentration;
- environmentally isolates up to four separator columns and two suppressors for optimal results;
- manual or remote control with Dionex Autoion 300 or Autoion 100 automation accessors;
- individual column temperature control from ambient to 100°C optional.

Dionex Ion-Pac Columns

Features are:

- polymer ion exchange columns are packed with new pellicular resins for anion or cation exchange applications;
- 4 μ polymer ion exchange columns have maximum efficiency and minimum operating pressure for high-performance ion and liquid chromatography applications;
- new ion exclusion columns with bifunctional cation-exchange sites offer more selectivity for organic acid separations;
- neutral polymer resins have high surface area for reversed-phase ion-pair and ion-suppression applications without pH restriction;
- 5 and 10 μ silica columns are optimised for ion-pair, ion suppression and reversed phase applications.

Micromembrane suppressor

The micromembrane suppressor makes possible detection of non-ultraviolet absorbing compounds such as inorganic anions and cations, surfactants, antibiotics, fatty acids and amines in ion exchange and ion-pair chromatography. Two variants of this exist: the anionic (AMMS) and the cationic (CMMS) suppressor. The micromembrane suppressor consists of a low dead volume eluent flow path through altering layers of high-capacity ion exchange screens and ultra-thin ion exchange membranes. Ion exchange sites in each screen provide a site-to-site pathway for eluent ions to transfer to the membrane for maximum chemical suppression.

Dionex anion and cation micromembrane suppressors transform eluent ions into less conducting species without affecting sample ions under analysis. This improves conductivity detection, sensitivity, specificity and baseline stability. It also dramatically increases the dynamic range of the system for inorganic and organic ion chromatography. The high ion exchange capacity of the MMS permits changes in eluent composition by orders of magnitude, making gradient ion chromatography possible.

In addition, because of the increased detection specificity provided by the MMS sample, preparation is dramatically reduced, making it possible to analyse most samples after filtering and dilution.

Conductivity detector

Features include:

- high-sensitivity detection of inorganic anions, amines, surfactants, organic acids, Group I and II metals, oxy-metal ions and metal cyanide complexes (used in conjunction with MMS);
- bipolar-pulsed excitation eliminates the non-linear response with concentration found in analogue detectors;
- microcomputer-controlled temperature compensation minimises the baseline drift with changes in room temperature.

UVVis detector

Important factors are:

- high-sensitivity detection of amino acids, metals, silica, chelating agents, and other ultraviolet absorbing compounds using either post-column reagent addition or direct detection;
- non-metallic cell design eliminates corrosion problems;
- filter-based detection with selectable filters from 214 to 800nm;
- proprietary dual wavelength detection for ninhydrin-detectable amino acids and PAR-detectable transition metals.

Optional detectors

In addition to the detectors shown, Dionex also offer visible fluorescence and pulsed amperometric detectors for use with the series 4000i. Dionex also supply a wide range of alternative instruments, eg single channel (2010i) and dual channel (2020i). The latter can be upgraded to an automated system by adding the Autoion 100 or Autoion 300 controller to control two independent ion chromatograph systems. They also supply a 2000i series equipped with conductivity pulsed amperometric, ultraviolet-visible and refractometric detectors.

Applications of ion chromatography

Non saline waters: pyrophosphate, selenate, selenite, silicate, sulphide, sulphite, thiocyanate, thiosulphate, hypochlorite, chlorite, hypophosphite, iodide, metal cyanide complexes, nitrate, nitrite, phosphate, arsenate, arsenite, bicarbonate, borate, borofluoride, bromate, bromide, carbonate, chlorate, chloride, chromate, dichromate, free cyanide, total cyanide, dithionite, fluoride.

Also, protocatechaute, propionate, pyruvate, quinate, resorcyate, salicylate, succinate, sulphonates, tartrate, transaconitate, trifluoroacetate, valerate, gallate, gluconate, gluconurate, glycollate, glyoxylate, hexane sulphonate, hydroxybenzoate, isobutyrate, isocitrate, α -hydroxybutyrate, isobutyrate, isocitrate, α -ketoglutarate, lactate, malate, malonate, mono-chloroacetate, octane sulphate, octane sulphonate, oxalacetate, oxalate, phthalate, anisate, carboxylates, chlorobenzoate, cis aconitate, citrate, decane sulphonate, dichloroacetates, dimethyl benzoate, decane sulphate, decane sulphonate, formate, fumarate and galactonurate.

<i>Seawater.</i>	bromide, iodide, nitrate, nitrite, phosphate and sulphate. Also acetate, acrylate, benzoate, butyrate, carboxylate, pyruvate and valerate.
<i>Aqueous precipitation:</i>	bromate, bromide, chloride, fluoride, iodide, nitrate, nitrite, phosphate, sulphate, sulphite, thiocyanate. Also hydroxymethane sulphonate.
<i>Surface and ground waters:</i>	chloride, bromide, nitrate, nitrite, phosphate, sulphate, arsenite, arsenate, selenate and selenite. Also formate.
<i>Waste waters:</i>	borate, bromide, foil cyanide, phosphate, nitrite, chloride, fluoride, sulphate, sulphite, sulphide, thiocyanate, thiosulphate, nitriloacetate, ethylene diamine tetracetate.
<i>Potable water:</i>	arsenate, arsenite, bicarbonate, bromide, chloride, chlorate, chlorite, fluoride, nitrate, nitrite, phosphate, selenate, selenite, sulphate, sulphite and sulphide.
<i>Trade effluents:</i>	borate, bromide, chloride, free cyanide, dithionite, fluoride, nitrate, nitrite, phosphate, sulphate and sulphide.
<i>High purity waters:</i>	carbamate, chloride, nitrite, sulphate, phosphate and sulphite.

1.1.13.2 Electrostatic ion chromatography

Application of this recently developed technique have, so far, been limited to the determination of chloride bromide and iodide in seawater.

1.1.13.3 High performance liquid chromatography

This technique is now finding fairly extensive applications in the analysis of mixtures of inorganic (28 anions) and organic (13 anions) in various types of water sample.

<i>Non saline waters:</i>	phosphite, polyphosphate, selenite, selenate, sulphate, silicate, sulphite, thiocyanate and thiosulphate, iodate, iodide, mixed halides, nitrate, nitrite, phosphate, arsenate, borate, borofluoride, bromide, chlorate, chloride, chromate, dichromate, condensed phosphates, fluoride and monofluorophosphate, perchlorate. Also propionate, pyrenyl palmitate, glycolate, a-hydroxy valerate, isobutyrate, lactate, palmitate, acetate, ascorbate, butyrate, dichloroacetate and ethylene diamine tetraacetate.

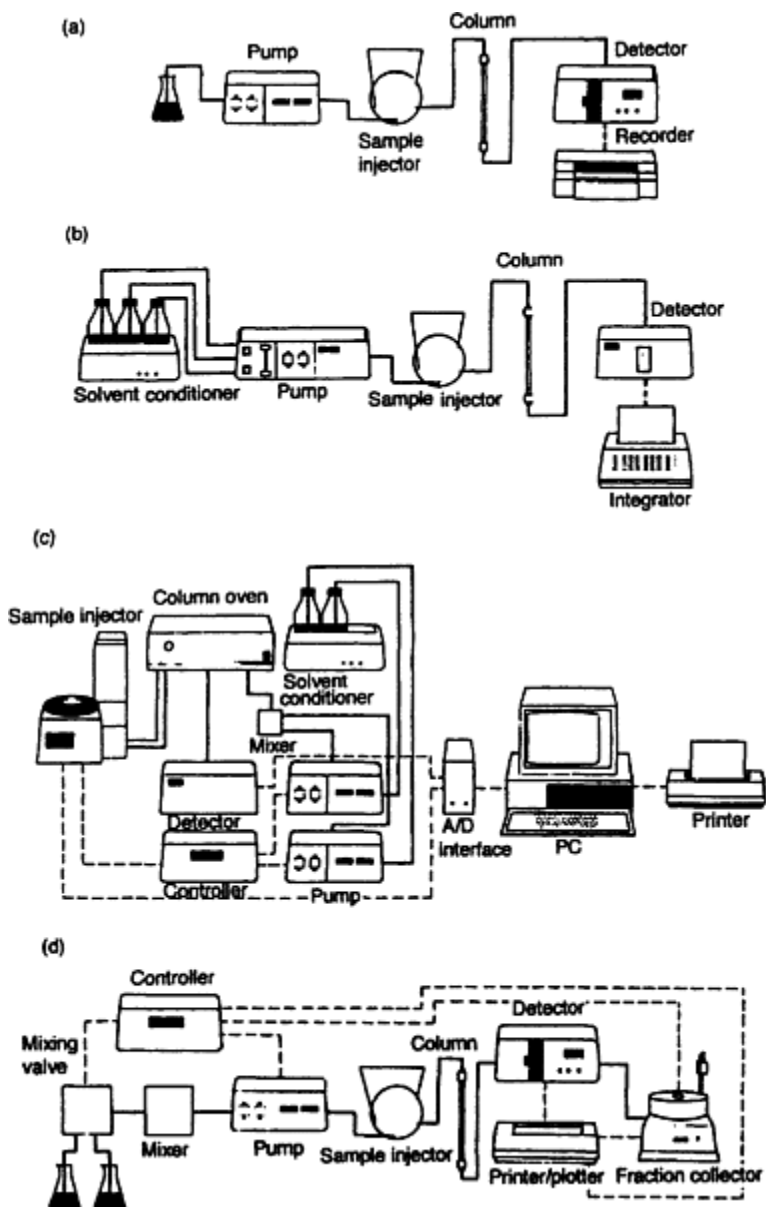


Fig. 1.3 Elution systems supplied by LKB, Sweden (a) isocratic bioseparation system; (b) basic system; (c) advanced chromatography system; (d) inert system.

Source: Own files

Seawater: iodide and formate.

<i>Aqueous precipitation:</i>	chloride, iodide, nitrate and thiocyanate. Also formate, bromate, bromide, chromate, dichromate, chloride, chlorate, iodate and iodide.
<i>Potable waters:</i>	phosphate.
<i>Waste waters:</i>	ethylene diamine tetracetate.
<i>Sewage effluents:</i>	phosphate.
<i>Trade effluents:</i>	fluoride, polythionate and thiosulphate.

There has, in recent years, been a growing interest in applying high performance liquid chromatography which is not subject to this temperature limitation, to the determination of the not only volatile compounds, such as aliphatic and polyaromatic hydrocarbons, saturated and unsaturated aliphatic and polyaromatic hydrocarbons, saturated and unsaturated aliphatic halogen compounds, haloforms and some esters, phenols and others but also non-volatile components of water.

Modern high performance liquid chromatography has been developed to a very high level of performance by the introduction of selective stationary phases of small particle sizes, resulting in efficient columns with large plate numbers per litre.

There are several types of chromatographic columns used in high performance liquid chromatography.

Four basic types of elution system are used in high performance liquid chromatography. This is illustrated below by the systems offered by LKB, Sweden.

The isocratic system

This consists of a solvent delivery for isocratic reversed-phase and gel filtration chromatography. The isocratic system (Fig. 1.3) provides an economic first step into high performance liquid chromatography techniques. The system is built around a high performance, dual-piston, pulse-free pump providing precision flow from 0.01 to 5 mL min⁻¹.

Any of the following detectors can be used with this system:

- fixed wavelength ultraviolet detector (LKB Unicord 2510);
- variable ultra violet-visible (190–600nm);
- wavelength monitor (LKB 2151);
- rapid diode array spectral detector (LKB 2140);
- refractive index detector (LKB 2142);
- electrochemical detector (LKB 2143);
- wavescan EG software (LKB 2146).

Basic gradient system

This is a simple upgrade of the isocratic system with the facility for gradient elution techniques and greater functionality (Fig. 1.3(b)). The basic system provides for manual operating gradient techniques such as reversed-phase, ion exchange and hydrophobic interaction chromatography. Any of the detectors listed above under the isocratic system can be used.

Advanced gradient system

For optimum functionality in automated systems designed primarily for reversed-phase chromatography and other gradient techniques, the LKB advanced-gradient system is recommended (Fig 1.3(c)). Key features include the following:

- a configuration that provides the highest possible reproducibility of results;
- a two-pump system for highly precise and accurate gradient formation for separation of complex samples;
- separation of complex samples;
- full system control and advanced method development provided from a liquid chromatography controller;
- precise and accurate flows ranging from 0.01 to 5ml min⁻¹.

This system is ideal for automatic method for development and gradient optimisation.

The inert system

By a combination of the use of inert materials (glass, titanium, and inert polymers) this system offers totally inert fluidics. Primary features of the system include (Fig. 1.3(d)):

- the ability to perform isocratic or gradient elution by manual means;
- full system control from a liquid chromatography controller;
- precise and accurate flows from 0.01–5mL min⁻¹.

This is the method of choice when corrosive buffers, eg those containing chloride or aggressive solvents, are used.

Chromatographic detector

Details concerning the types of detectors used in high-performance liquid chromatography are given in Table 1.8. The most commonly used detectors are those based on spectrophotometry in the region 185–400nm, visible ultraviolet spectroscopy in the region 185–900nm, post-column derivatisation with fluorescence detection (see below), conductivity and those based on the relatively new technique of multiple wavelength ultraviolet detectors using a diode array system detector (described below). Other types of detectors available are those based on electrochemical principles, refractive index, differential viscosity and mass detection.

Electrochemical detectors

These are available from several suppliers (Table 1.8). PSA supply the model PS 5100A coulochem multi-electrode electrochemical detector. Organics, anions and cations can be detected by electrochemical means.

The Gilson Aspec automatic sample preparation system is a fully automated system for solid-phase extraction on disposable columns and on-line high performance liquid chromatography analysis. The Aspec system offers total automation and total control of the entire sample preparation process including clean-up and concentration. In addition, Aspec can automatically inject prepared samples into on-line high performance liquid chromatographic systems.

Aspec is designed to receive up to 108 samples. The system is compatible with most

standard disposable extraction columns, Analytichem Bond-Elut Baker SPE, Supelco Supelclean, Alltech Extract Clean, etc. There is a choice of more than 20 different stationary phases.

Spectrofluorimetric detectors

A spectrofluorimeter has been used as a detector in the high performance liquid chromatographic separation of polyaromatic hydrocarbons in water samples. A great improvement in sensitivity and specificity can be obtained by the correct wavelengths.

Amino acid analysers

This is an example of a dedicated application of high performance liquid chromatography. Measurements of amino acids have been performed in lake water and sea water. Also, measurements of total protein or amino acids are required in river waters and effluents.

The most popular current techniques for amino acid analysis rely on liquid chromatography and there are two basic analytical methods. The first is based on ion exchange chromatography with post-column derivatisation. The second uses pre-column derivatisation followed by reversed-phase high performance liquid chromatography. Derivatisation is necessary because amino acids, with very few exceptions, do not

Table 1.8 Detectors used in high performance liquid chromatography

<i>Type of detector</i>	<i>Wavelength range (nm)</i>	<i>Supplier</i>	<i>Detection part no</i>	<i>HPLC instrument part no</i>
Spectrophotometric (variable wavelength)	190–390	Perkin-Elmer	LC-90	–
	193–350	Kontron	735 LC	Series 400
	195–350	Shimadzu	SPD-7A	LC-7A
	195–350	Shimadzu	SPD-6A	LC-8A
	195–350	Shimadzu	SPD-6A	LC-6A
	206–405	LKB	2510Uvicord SD	–
	(choice of seven fixed wavelengths)			
	190–370	Cecil Instruments	Model 1937	Chrom-A-Scope
	190–400		CE 1220	Series 100
Variable wavelength UV-visible	190–600	Varian	2550	2500
	190–600	LKB	2151	Uvicord SD

190–700	Kontron	432	Series 400
190–800	Kontron	430	Series 400
185–900	Kontron	720 LC	Series 400
200–570	Kontron	740 LC	Series 400
190–800	Dionex	VDM II	Series 400
190–750	Isco	V4	} Microbo system
214–660 (18 preset wavelengths)	Isco	USA and 228	
195–700	Shimadzu	SPD 7A	
195–700	Shimadzu	SPD–6A	V LC-8A
195–700	Shimadzu	SPD–6AV	LC–6A
195–700	Hewlett Packard	Programmably variable wavelength detector	9050 series
380–600	Cecil Instruments	CE 1200	Series 1000

<i>Type of detector</i>	<i>Wavelength range (nm)</i>	<i>Supplier</i>	<i>Detection</i>	<i>HPLC instrument</i>
Conductivity	190–800	Applied Chromatography systems	750/1 6 and 5750/11	–
	–	Dionex	CDM II	4500i
	–	Roth Scientific	–	Chrom-A- Scope
Electrochemical detector	–	Dionex	PAD–11	4500i
	–	LKB	2143	Wave-scan EG
	–	Roth Scientific	–	Chrom-A- Scope
	–	Cecil Instruments	CE 1500	–
	–	PSA Inc	5100A	–
	–	Applied Chromatography systems	650*350*06	–
Refractive index	–	LKB	2142	Wavescan EG

detector	Roth Scientific	–	Chrom-A-Scope
	Cecil Instruments	CE 1400	Series 1000
Differential viscosity	Roth Scientific	–	Chrom-A-Scope
mass detection	Applied	750/14	Scope
(evaporative)	Chromatography system		–
Diode array	Varian	9060	200L and 5001 5500 series
	Perkin-Elmer	LC 135, LC 235 and LC 480	–
	LKB	2140	
	Hewlett Packard	Multiple wavelength detector	1050 series

Source: Own files

absorb in the ultraviolet-visible region, nor do they possess natural fluorescence. Each of the major methods has its own particular advantages and disadvantages. Since the variety of available chemistries can be confusing, the method itself should govern the choice that meets requirements, rather than the equipment or systems offered. The optimal method is best selected by a comprehensive and objective review of all commonly used techniques.

Overriding criteria which will influence the selection are resolution, sensitivity and speed. While the very best chromatogram for any given method will inevitably be a compromise, only the fullest evaluation of all the alternatives offered will guarantee a correct selection.

Certainly, a vast amount of experience has been gained by the widespread use of conventional amino acid analysers. They offer high reliability, accuracy, reproducibility and can separate complex samples. Because conventional analysers can be fully automated, they are widely used in routine analysis. However, the method is limited by the sensitivity which can be achieved using ninhydrin as the derivatising agent. Sensitivity can be increased by using *ortho*-phthaldialdehyde (OPA) instead, but where extremely high sensitivity is required, high performance liquid chromatography is the method of choice.

The other reagents used in high performance liquid chromatography are 9-fluorenyl methoxycarbonyl chloride (FMOC) and phenyliso-thiocyanate (PITC). Fluorenyl methoxycarbonyl chloride is becoming increasingly popular in protein chemistry research because it reacts with secondary amines and also offers rapid analysis of protein hydrosylates.

One aspect governing the choice of method is the sensitivity required. If only a small amount of sample is available, then for the LKB Alpha Plus and the LKB high

performance liquid chromatography instruments, the greatest sensitivity is obtained using the Alpha Plus instrument with ion exchange separation and post-column derivatisation with OPA reagent (108µg) or the high performance liquid chromatography instrument using reversed-phase chromatography and pre-column derivatisation with OPA, or fluorenyl methoxycarbonyl chloride reagents (30–33ng).

One leading supplier, LKB, is discussed below. LKB supply two instruments, the LKP 4150 Alpha HPLC, and for analysis requiring higher sensitivity and faster run times the LKB 4151 Alpha Plus.

LKB 4150 Alpha

This system is a reversed-column chromatograph equipped for pre-column derivatisation. The column is made of glass and has solid-state heating. The detection system comprises a dual-channel photometer with a high-temperature reaction coil. A single low-volume long-pathlength flow cell is employed. A fluorescence detector is available to

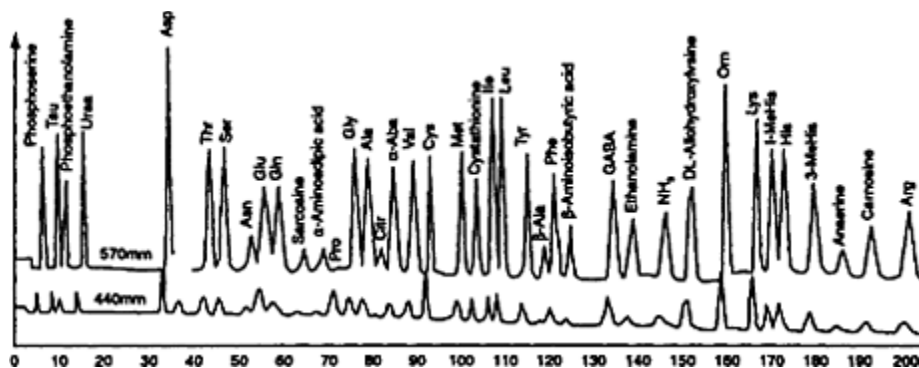


Fig. 1.4 Chromatogram of amino acid mixture: sample physiological fluid amino acid standard, 10nmol amino acid in 40µL column—LKB 4418–550 high-resolution column, 270×4.6mm packed with lithium from exchange resin; buffers—physiological fluid buffer system (five lithium buffers); flow rate—20mol h⁻¹ ninhydrin; detection—vis. 570nm and 440nm, 1.0AUFS

Source: Own files

provide an approximately 10-fold increase in sensitivity over ninhydrin detection. Refrigerated sample capsule loading is supplied. Powerful programming capability permits the storage of up to 200 methods. Storage facilities for six buffers is supplied.

LKB 4151 Alpha Plus

Alpha Plus is a fully automated and dedicated analyser. This turnkey system has been carefully designed to give a truly robust chromatography. Stepwise elution with up to five buffers plus flexible temperature control guarantees optimal separations from even the most complex samples. The versatile programmer monitors and controls all instrument functions and a complete fault-detection system assures absolutely safe operation while

preserving the integrity of samples.

The analysis time for protein hydrolysates is 85 min using standard columns. For extra-high resolution a high-resolution lithium cation exchange column is recommended which achieves baseline separation of virtually all 40 amino acids (Fig. 1.4).

Reversed-phase chromatography

The most commonly used chromatographic mode in high performance liquid chromatography is reversed-phase chromatography. Reversed-phase chromatography is used for the analysis of a wide range of neutral compounds such as carbohydrates and polar organic compounds. Most common reversed-phase chromatography is performed using bonded silica-based columns, thus inherently limiting the operating pH range to 2.0–7.5. The wide pH range (0–14) of some columns (eg Dionex Ion Pac NSI and NS 1–5 μ columns) removes this limitation, and consequently they are ideally suited for ion-pairing and ion-suppression reversed-phase chromatography, the two techniques which have helped extend reverse-phase chromatography to ionisable compounds.

High-sensitivity detection of non-chromophoric organic ions can be achieved by combining the power of suppressed conductivity detection with these columns. Suppressed conductivity is usually a superior approach to using refractive index or low-ultraviolet-wavelength detection.

Reversed-phase ion-pairing chromatography

Typically, reversed-phase ion-pairing chromatography is carried out using the same stationary phase as reversed-phase chromatography. A hydrophobic ion of opposite charge to the solute of interest is added to the mobile phase. Samples which are determined by reversed-phase ion-pairing chromatography are ionic and thus capable of forming an ion pair with the added counter ion. This form of reversed-phase chromatography can be used for anion and cation separations and for the separation of surfactants and other ionic types of organic molecules. An unfortunate drawback to using silica-based columns is that ion-pairing reagents increase the solubility of silica in water, leading to loss of bead integrity and drastically reducing column life. Some manufacturers (eg Dionex) employ neutral macroporous resins, instead of silica, in an attempt to widen the usable pH range and eliminate the effect of ion-pairing reagents. The technique has been applied to the analysis of phosphorus-containing insecticides in water. This technique has been used for the determination of free cyanide in non saline waters.

Ion exclusion chromatography

The following anions have been determined by this technique.

<i>Non saline waters:</i>	arsenate, arsenite, chloride, condensed phosphates, sulphate, sulphide, sulphite, nitrite, phosphate. Also tartrate, glycolate, malate, malonate, carboxylates, citrate, formate and fumarate.
<i>Sea water:</i>	silicate.
<i>Potable waters:</i>	bicarbonate.

Waste chloride, carbonate and phosphate.
water:

Unlike the pellicular packings used for ion exchange, the packings used in ion exclusion are derived from totally sulphonated polymeric materials. Separation is dependent upon three different mechanisms: Donnan exclusion, steric exclusion and adsorption/partitioning. Donnan exclusion causes strong acids to elute in the void volumes of the column. Weak acids which are partially ionised in the eluent are not subject to Donnan exclusion and can penetrate into the pores of the packing. Separation is accomplished by differences in acid strength, size and hydrophobicity. The major advantage of ion exclusion lies in the ability to handle samples that contain both weak and strong acids. A good example of the power of ion exclusion is the routine determination of organic acids in sea water. Without ion exclusion, the high chloride ion concentration would present a serious interference.

Ion suppression chromatography

Ion suppression is a technique used to suppress the ionisation of compounds (such as carboxylic acids) so they will be retained exclusively by the reversed-phase retention mechanism and chromatographed as the neutral species. Column packings with an extended pH range are needed for this application as strong acids or alkalis are used to suppress ionisation. In addition to carboxylic acids, the ionisation of amines can be suppressed by the addition of a base to the mobile phase, thus allowing chromatography of the neutral amine.

Micelle exclusion chromatography

This technique has found limitations in the determination of bromide mixed halides, iodide, iodate, nitrite, nitrate, sulphide, sulphite, thiocyanate, thiosulphate and isobutyrate in non saline waters.

1.1.13.4 Ion exchange chromatography

This technique has been used to determine the following types of organic compounds in water.

<i>Non saline waters:</i>	sulphate, nitrite, nitrate, bromide, chloride and fluoride.
<i>Aqueous precipitation:</i>	chloride, bromide.
<i>Potable water:</i>	nitrate and nitrite.

Ion exchange chromatography is based upon the differential affinity of ions for the stationary phase. The rate of migration of the ion through the column is directly dependent upon the type and concentration of ions that constitute the eluent. Ions with low or moderate affinities for the packing generally prove to be the best eluents. Examples are hydroxide and carbonate eluents for anion separations.

The stationary phases commonly used in high performance liquid chromatography are typically derived from silica substrates. The instability of silica outside the pH range 2 to 7.5 represents one of the main reasons why ion exchange separations have not been extensively used in high performance liquid chromatography. To overcome this, some manufacturers (eg Dionex) supply columns under the trade name Ion-Pac which contain a packing which is derived from cross-linked polystyrene which is stable throughout the entire pH range. This pH stability allows eluents of extreme pH values to be used so that weak acids such as carbohydrates (and bases) can be ionised.

1.1.13.5 Gas chromatography

The numerous anions that have been determined by gas chromatography or gas chromatography-mass spectrometry are listed below.

<i>Non saline waters:</i>	arsenate, bromide, chloride, free cyanide, total cyanide, fluoride, iodide, nitrate, nitrite, phosphate, selenate, selenite, sulphide and thiosulphate. Also aminoacetate, carboxylates, hexane carboxylate, malonate, octane dithioate and octanethioate.
<i>Sea water:</i>	sulphide.
<i>Aqueous precipitation:</i>	bromide, chloride, nitrate, phosphate and sulphate
<i>Surface and ground waters:</i>	iodide.
<i>Potable water:</i>	bromide, chloride, iodide and chlorolignosulphonate.
<i>Waste waters:</i>	thiocyanate, free cyanide; total cyanide.
<i>Trade effluents:</i>	free cyanide, polysulphide and sulphide.

The basic requirements of a high performance gas chromatograph are:

- the sample is introduced to the column in an ideal state, ie uncontaminated by septum bleed or previous sample components, without modification due to distillation effects in the needle and quantitatively, ie without hold-up or adsorption prior to the column;
- the instrument parameters that influence the chromatographic separation are precisely controlled;
- sample components do not escape detection; ie highly sensitive, reproducible detection and subsequent data processing are essential.

There are two types of separation column used in gas chromatography: capillary columns and packed columns.

Packed columns are still used extensively, especially in routine analysis. They are essential when sample components have high partition coefficients and/or high concentrations. Capillary columns provide a high number of theoretical plates, hence a very high resolution, but they cannot be used in all applications because there are not many types of chemically bonded capillary columns. Combined use of packed columns

of different polarities often provides better separation than with a capillary column. It sometimes happens that a capillary column is used as a supplement in the packed-column gas chromatograph. It is best, therefore, to house the capillary and packed columns in the same column oven and use them routinely and the capillary column is used when more detailed information is required.

Conventionally, it is necessary to use a dual-column flow line in packed-column gas chromatography to provide sample and reference gas flows. The recently developed electronic base-line drift compensation system allows a simple column flow line to be used reliably.

Recent advances in capillary column technology presume stringent performance levels for the other components of a gas chromatograph as column performance is only as good as that of the rest of the system. One of the most important factors in capillary column gas chromatography is that a high repeatability of retention times be ensured even under adverse ambient conditions. These features combine to provide ± 0.01 min repeatability for peaks having retention times as long as 2 h (other factors being equal).

Another important factor for reliable capillary column gas chromatography is the sample injection method. Various types of sample injection ports are available. The split/splitless sample injection port unit series is designed so that the glass insert is easily replaced and the septum is continuously purged during operation. This type of sample injection unit is quite effective for the analysis of samples having high-boiling-point compounds as the major components.

In capillary column gas chromatography, it is often required to raise and lower the column temperature very rapidly and to raise the sample injection port temperature. In one design of gas chromatography, the Shimadzu GC 14-A, the computer-controlled flap operates to bring in the external air to cool the column oven rapidly—only 6 min from 500°C to 100°C. This computer-controlled flap also ensures highly stable column temperature when it is set to a near-ambient point. The lowest controllable column temperature is about 26°C when the ambient temperature is 20°C.

Some suppliers of gas chromatography are listed in Table 1.9.

Instrumentation

Shimadzu gas chromatographs

This is a typical high performance gas chromatograph version (see Table 1.9 for further details). The inner chamber of the oven has curved walls

Table 1.9 Commercial gas chromatographs

<i>Manufacturer</i>	<i>Model</i>	<i>Packed column</i>	<i>Capillary column</i>	<i>Detectors</i>	<i>Sample injection point system</i>	<i>Keyboard control</i>	<i>Link to computer</i>	<i>Vis display</i>
Shimadzu	GC-	Yes	Yes	FID	1 Split-	Yes	Yes	No

	14A			ECD FTD FPD TCD (all supplied)	splitless Yes 2 Glass insert for single column 3 Glass insert to dual column 4 Cool on column system unit 5 Moving needle system 6 Rapidly ascending temperature vaporiser			
Shimadzu	GC 15A	Yes	Yes	FID ECD FTD FPD TCD	1 Split- splitless 2 Direct sample injection (capillary column) 3 Standard sample injector (packed column) 4 Moving pre-column system (capillary columns) 5 On- column (capillary columns)	No	Yes	Yes

<i>Manu- facturer</i>	<i>Model</i>	<i>Packed</i>	<i>Capillary</i>	<i>Detectors</i>	<i>Sample</i>	<i>Keyboard</i>	<i>Link to</i>	<i>Visual</i>	<i>F</i>
		<i>column</i>	<i>column</i>		<i>injection</i>	<i>control</i>	<i>computer</i>	<i>display</i>	
					<i>point</i>				

system

Shimadzu	GC 16A		Yes	FID FCD FTD FPD TCD (all supplied)	1 Split-splitless	Yes	Yes	Yes	Y
Shimadzu	GC8A	Yes	Yes	FID FCD FPD TCD Single detector for instruments (detector chosen on purchase)	1 Point for packed columns 2 Point for capillary columns 3 Split-splitless	Yes Not built in	Optional	No	C

<i>Manufacturer</i>	<i>Model</i>	<i>Packed column</i>	<i>Capillary column</i>	<i>Detectors</i>	<i>Sample injection point system</i>	<i>Keyboard control</i>	<i>Link to computer</i>	<i>V</i>

Perkin- Elmer	8410	Yes	Yes	Single detector instrument (detector chosen on purchase) FID ECD FTD FPD TCD	1 Flash vaporisation 2 Split-splitless injector 3 Manual or automatic gas sampling valves 4 Manual or automatic liquid sampling valves	No	No	1
Perkin—Elmer	8420	No	Yes	Single detector	1 Programmable	No	No	1

instrument temperature
(chosen vaporiser
on 2 Split-
purchase) splitless
FID injector
ECD 3 Direct on
FTD column
FPD injector
TCD

<i>Manufacturer</i>	<i>Model</i>	<i>Packed column</i>	<i>Capillary column</i>	<i>Detectors</i>	<i>Sample injection point system</i>	<i>Keyboard control</i>	<i>Link to computer</i>
Perkin- Elmer	8400 and 8500	Yes	Yes	Dual detector instrument (detector chosen from following) FID ECD FTD FPD FPD TCD	Can be fitted with any combination of above injection systems	Yes	Yes
Perkin- Elmer	8700	Yes	Yes	FID ECD FPD TCD Hall E.C. photo-ionisation dual detector instrument. (Detectors chosen from above list)	1 Flash vaporisation 2 Split-splitless 3 Programmable temperature vaporiser 4 Gas sampling valve 5 Liquid sampling valve	Yes	Yes
<i>Manu-</i>	<i>Model</i>	<i>Packed</i>	<i>Capillary</i>	<i>Detectors</i>	<i>Sample</i>	<i>Keyboard</i>	<i>Link to</i>

<i>facturer</i>		<i>column</i>	<i>column</i>		<i>injection point system</i>	<i>control</i>	<i>compute</i>
Nordion	Micromat HRCG 412	No	Yes	Dual simultaneous detector combinations from the following: FID ECD FTD Photoionisation Hall E.C.	1 Split- splitless 2 On-column injector	Yes	Yes
Siemens	SiChromat 1-4 (single oven) SiChromat 2-8 (dual oven) for multi- dimensional GC)	Yes	Yes	FID ECD FTD FPD TCD Helium detector	1 Liquid- liquid packed columns 2 Split- splitless 3 Temperature programmable 4 On-column 5 Liquid injector valve on-line 6 Gas injection valve 7 Rotary as injection valve	No	No

Source: Own files

for smooth circulation of air; the radiant heat from the sample injection port units and the detector oven is completely isolated. These factors combine to provide demonstrably uniform temperature distribution. (The temperature variance in a column coiled in a diameter of 20cm is less than $\pm 0.75\text{K}$ at a column temperature of 250°C).

When the column temperature is set to a near ambient temperature, external air is brought into the oven via a computer-controlled flap, providing rigid temperature control stability. (The lowest controllable column temperature is 24°C when the ambient temperature is 18°C and the injection port temperature is 250°C. The temperature fluctuation is less than $\pm 0.1\text{K}$ even when the column temperature is set at 50°C.)

This instrument features five detectors (Table 1.9). In the flame ionisation detector, the high-speed electrometer, which ensures a very low noise level, is best suited to trace analysis and fast analysis using a capillary column.

Samples are never decomposed in the jet, which is made of quartz.

Carrier gas, hydrogen, air and make-up gas are separately flow-controlled. Flow rates are read from the pressure flow-rate curves.

In the satellite system, one or more satellite gas chromatographs (GC 14 series) are controlled by a core gas chromatograph (eg GC 16A series). Since the control is made externally, the satellite gas chromatographs are not required to have control functions (the keyboard unit is not necessary).

When a GC 16A series gas chromatograph is used as the core, various laboratory-automation-oriented attachments such as barcode reader and a magnetic-card reader become compatible: a labour-saving system can be built, in which the best operational parameters are automatically set. Each satellite gas chromatograph (GC 14A series) operates as an independent instrument when a keyboard unit is connected.

The IC card-operated gas chromatography system consists of a GC 14A series gas chromatograph and a C-R5A Chromatopac data processor. All of the chromatographic and data processing parameters are automatically set simply by inserting the particular IC card. This system is very convenient when one GC system is used for the routine analysis of several different types of samples.

One of the popular trends in laboratory automation is to arrange for a personal computer to control the gas chromatograph and to receive data from the GC to be processed as desired. Bilateral communication is made via the RS 232C interface built in a GC 14A series gas chromatograph. A system can be built to meet requirements.

A multidimensional gas chromatography system (multi-stage column system) is effective for analysis of difficult samples and can be built up by connecting several column ovens, ie tandem GC systems, each of which has independent control functions such as for temperature programming.

The Shimadzu GC 15A and GC 16A systems are designed not only as independent high performance gas chromatographs but also as core instruments (see above) for multi-gas-chromatography systems (ie several gas chromatographs in the laboratory linked to a central management system) or computerised laboratory automation systems. The GC 16A has a keyboard, the GC 15A does not. Other details of these instruments are given in Table 1.9. The Shimadzu GC 8A range of instruments do not have a range of built-in detectors but are ordered either as temperature programmed instruments with TCD, FID or FPD detectors, or as isothermal instruments with TCD, FID or ECD detectors (Table 1.9).

Perkin-Elmer

Perkin-Elmer supply a range of instruments including the basic models 8410 for packed and capillary work and the 8420 for dedicated capillary work, both supplied on purchase with one of the six different types of detection (Table 1.9). The models 8400 and 8500 are more sophisticated capillary column instruments capable of dual detection operation with the additional features of keyboard operation, screen graphics method storage, host computer links, data handling and compatibility with laboratory automation systems.

Perkin-Elmer supply a range of accessories for these instruments including an autosampler (AS-8300), an infrared spectrometer interface, an automatic headspace accessory (HS101 and HS-6), an autoinjector device (AI-I), also a catalytic reactor and a pyroprobe (CDS 190) and automatic thermal desorption system (ATD-50) (both useful for examination of sediments).

The Perkin-Elmer 8700, in addition to the features of the models 8400 and 8500, has the ability to perform multi-dimensional gas chromatography.

The optimum conditions for capillary chromatography of material heart-cut from a packed column demand a highly sophisticated programming system. The software provided with the model 8700 provides this, allowing methods to be linked so that pre-column and analytical column separations are performed under optimum conditions. Following the first run, in which components are transferred from the pre-column to the on-line cold trap, the system will reset to a second method and, on becoming ready, the cold trap is desorbed and the analytical run automatically started.

Other applications of the model 8700 system include fore-flushing and back-flushing of the pre-column, either separately or in combination with heart cutting, all carried out with complete automation by the standard instrument software.

There are many other suppliers of gas chromatography equipment, some of which are discussed further in Table 1.9.

1.1.14 Column coupling capillary isotachoelectrophoresis

This technique has found limited applications to the determination of anions in water. The technique offers many similar advantages to ion chromatography, namely multiple-ion analysis, little or no sample pretreatment, speed, sensitivity and automation.

<i>Non saline waters:</i>	chloride, fluoride, nitrate, nitrite and aminoacetate.
<i>Sea water:</i>	bromide and sulphide.
<i>Aqueous precipitation:</i>	chloride, fluoride and nitrate.
<i>Waste water:</i>	chlorite, free cyanide, nitrate and nitrite.

Separation capillary columns are made in fluorinated ethylene-propylene copolymer. Detection is achieved by conductivity cells and an a.c. conductivity mode of detection is used for making the separations visible. The driving current is supplied by a unit enabling independent currents to be preselected for the preseparation and final analytical stages. The run of the analyser is controlled by a programmable timing and control unit. The zone lengths from the conductivity detector, evaluated electronically, can be printed on a line printer.

To satisfy the requirements for the properties of the leading electrolyte applied in the first stage and, consequently, to decide its composition, two facts had to be taken into account: the pH value of the leading electrolyte needs to be around 4 or less and at the same time the separations of the macroconstituents need to be optimised by means other than adjusting the pH of the leading electrolyte (anions of strong acids).

The choice of the leading electrolyte for the second stage, in which the

microconstituents were finally separated and quantitatively evaluated, was straightforward, involving a low concentration of the leading constituent (low detection limit) and a low pH of the leading electrolyte (separation according to pK values).

1.2 Rationale, analysis of water samples

Tables 1.10(a–j) review the methods used for the determination of various anions in various types of waste samples, eg natural, sea, estuary, aqueous precipitation (rain, snow and ice), ground and surface waters, potable water, waste waters, sewage and trade effluents and high purity waters (eg boiler feed).

In these tables analytical techniques are cross-referenced with anion determined, the type of water sample and the section number in the book. If the reader finds that a method is not listed for determining a particular anion in the particular type of water sample, then by examination of the table he or she may find a method that is listed under another type of

Table 1.10(a) Determination of anions in natural waters

<i>Anion</i>	<i>Titration</i>	<i>Spectro- photometric</i>	<i>Spectro- fluorimetric</i>	<i>Chemilum- inescence</i>	<i>Segmented flow analysis</i>	<i>Flow injection analysis</i>	<i>Conti flow analy</i>
Acetate	2.1.1						
Arsenate		2.4.1				2.4.2	
Arsenite						2.5.1	
Ascorbate		2.6.1	2.6.2				
Bicarbonate	2.8.1				2.8.2	2.8.3	
Borate		2.9.1	2.9.2			2.9.3	
Bromide	2.12.1	2.12.1	2.12.3			2.12.4	
Carbonate alkalinity	2.14.2.1				2.14.2.2	2.14.1.1 2.14.2.3	
Chlorate	2.16.1					2.16.2	
Chloride	2.17.1	2.17.2				2.17.3	
Chlorite	2.47.1						
Chromate/ dichromate		2.19.1				2.19.2	
Citrate			2.21.1				
Cyanide free		2.23.1	2.23.2	2.23.3		2.23.5	
Cyanide, total		2.28.1					
Dithionate							
Fluoride		2.31.1	2.31.2			2.31.3	
Germanate						2.37.1	
Hypochlorite	2.47.1						
Iodate		2.49.1					
Iodide	2.50.1	2.50.2	2.50.3	2.50.4.		2.50.5	
<i>Anion</i>	<i>Titration</i>	<i>Spectro- photometric</i>	<i>Spectrofluorimetric</i>	<i>Chemiluminescence</i>	<i>Segmented flow analysis</i>		
Nitrate	2.64.1	2.62.1, 2.64.2	2.62.2	2.62.3 2.64.3		2.64.5	

Nitriloacetate					
Nitrite	2.64.1	2.63.1, 2.64.2	2.63.2	2.63.3, 2.64.3	2.64.5
Oxalate			2.71.1		
Phosphate		2.75.1	2.75.2		
Polysulphide	2.78.1				
Pseudohalide					
Selenite		2.89.1	2.89.2		
Silicate		2.91.1	2.91.2	2.91.3	
Sulphate	2.93.1	2.93.2	2.93.3		
Sulphide	2.94.1	2.94.2	2.94.3		
Sulphite	2.95.1	2.95.2	2.95.3	2.95.4	
Tartrate			2.97.1		
Tellurate		2.99.1			
Thiocyanate		2.100.1			
Thiosulphate	2.101.1				
Titanate		2.102.1			
Triphosphate					
Uranate		2.107.1			
Vanadate		2.109.1	2.109.2	2.109.3	

Source: Own files

Table 1.10(a) Determination of anions in natural waters

Anion	Atomic absorption spectrometry	Inductively coupled plasma AES	Polarography	Potentiometry	Amperometry	Anodic strip, volta
Arsenate	2.4.3		2.4.4			
Arsenite	2.5.2		2.5.3			
Borate	2.9.4					
Bromide		12.12.5 2.12.9				
Chloride	2.17.4	2.17.5 2.17.10				

Chlorite				2.47.
Chromate/ dichromate	2.19.3			
Cyanide free	2.23.4		2.23.6	
Cyanide, total	2.24.1			
Iodate	2.49.2	2.49.4		
Iodide	2.50.6	2.50.8	2.50.9	
Fluoride	2.31.4			
Hypochlorite				
Mixed halide				
Molybdate	2.59.1			

<i>Anion</i>	<i>Atomic absorption spectrometry</i>	<i>Inductively coupled plasma AES</i>	<i>Polarography</i>	<i>Potentiometry</i>	<i>Amperometry</i>	<i>Anode strip voltammetry</i>
Nitrate	2.62.6	2.64.13 2.62.7	2.64.7		2.64.8	
Nitrite		2.64.13	2.63.6 2.64.7		2.64.8	
Nitriloacetate			2.65.1			
Palmitate						
Phosphate	2.75.4		2.75.5			2.75.
Selenate	2.90.1		2.88.1, 2.90.2			
Selenite	2.90.1		2.89.3, 2.90.2			
Silicate	2.91.5					
Sulphate	2.93.7	2.93.8				
Sulphide			2.94.5			
Sulphite						
Thiocyanate						
Thiosulphate						2.10.
Tungstate	2.98.1	2.98.2				

Source: Own files

Table 1.10(a) Determination of anions in natural waters

<i>Anion</i>	<i>Neutron activation analysis</i>	<i>Isotope dilution</i>	<i>Enzymic assay</i>	<i>Ion chromatography</i>	<i>High performance liquid chromatography</i>	<i>Ion pairing chromato- graphy</i>
Acetate				2.1.2	2.1.3	
Anisate				2.3.1		
Arsenate				2.4.5	2.4.6	
Arsenite				2.5.4		
Ascorbate					2.6.3	
Benzoate				2.7.1		
Bicarbonate				2.8.4		
Borate				2.9.6	2.9.7	
Borofluoride				2.10.1	2.10.2	
Bromate				2.11.1	2.11.2	
Bromide				2.12.10	2.12.1 1	
Butyrate				2.13.1	2.13.2	
Carbonate				2.14.1.2		
Carboxylate				2.15.1	2.15.2	
Chloride		2.17.1 1		2.17.3	2.17.4	
Chlorate				2.16.3	2.16.4	
Chlorite				2.47.3		
Chloro- benzoate				2.18.1		
Chromate/ dichromate			2.19.5	2.19.6	2.19.7	
Cis aconitate				2.20.1		
Citrate				2.21.2		
Condensed phosphate					2.22.1	

<i>Anion</i>	<i>Neutron activation analysis</i>	<i>Isotope dilution</i>	<i>Enzymic assay</i>	<i>Ion chromatography</i>	<i>High performance liquid chromatography</i>	<i>Ion pairing chromato- graphy</i>
Cyanide free			2.23.9	2.23.10		2.23.11
Cyanide, total				2.24.3		
Decane sulphate				2.29.1		
Decane sulphonate				2.25.1		
Dichloro- acetate				2.26.1	2.26.2	
Dimethyl benzoate				2.27.1		
Dithionate				2.28.2		
Dodecane sulphonate				2.30.1		
Ethylene- diamine tetracetate					2.32.1	
Fluoride				2.31.7	2.31.8	
Formate				2.33.1	2.33.2	
Fumarate				2.34.1		
Galactonurate				2.35.1		
Gallate				2.36.1		
Gluconate				2.38.1		
Gluconurate				2.39.1		
Glycollate				2.40.1	2.40.2	
Glyoxylate				2.41.1		

<i>Anion</i>	<i>Neutron activation analysis</i>	<i>Isotope dilution</i>	<i>Enzymic assay</i>	<i>Ion chromatography</i>	<i>High perform- ance liquid chromatography</i>	<i>Ion pairing chromato- graphy</i>	<i>Ion exclu- chro- graphy</i>
Hexane sulphonate				2.43.1			
Hydroxy-				2.44.1			

benzoate							
Hydroxy- butyrate				2.45.1	2.45.2		
α -hydroxy valerate				2.46.1			
Hypochlorite				2.47.3			
Hypophosphite				2.48.1			
Iodate					2.49.6		
Iodide	2.50.11	2.50.12		2.50.13	2.50.14		
Isobutyrate				2.51.1	2.51.2		
Isocitrate				2.52.1			
α -ketoglutarate				2.53.1			
Lactate				2.54.1	2.54.2		
Maleate				2.55.1		2.55.2	
Malonate				2.56.1			2.56.2
Metal cyanide complexes				2.57.1			
Mixed halides					2.58.2		
Monochloro- acetate				2.60.1			
Monofluoro- phosphate					2.61.1		

<i>Anion</i>	<i>Neutron activation analysis</i>	<i>Isotope dilution</i>	<i>Enzymic assay</i>	<i>Ion chromat- ography</i>	<i>High perform- ance liquid chromatography</i>	<i>Ion pairing chromato- graphy</i>	<i>Ion exclu- chron graph</i>
Nitrate			2.62.12	2.62.13 2.64.14	2.62.14 2.64.15		
Nitrite				2.63.9 2.64.14	2.63.10 2.64.15		2.63.1
Octane sulphate				2.67.1			
Octane sulphonate				2.68.1			
Oxalacetate				2.70.1			
Oxalate					2.71.2		

Palmitate			2.72.1	
Perchlorate			2.73.2	
Phosphite			2.76.1	
Pyrenyl palmitate				2.82.1
Phthalate		2.74.1		
Phosphate	2.75.9	2.75.10	7.75.11	2.75.1
Polyphosphate			2.77.1	
Propionate		2.80.1	2.80.2	
Protocateuate		2.79.1		
Pyrophosphate		2.83.1		
Pyruvate		2.84.1		
Quinate		2.85.1		
Resorcylate		2.86.1		

<i>Anion</i>	<i>Neutron activation analysis</i>	<i>Isotope dilution</i>	<i>Enzymic assay</i>	<i>Ion chromatography</i>	<i>High performance liquid chromatography</i>	<i>Ion pairing chromato graphy</i>
Salicylate				2.87.1		
Selenate			2.90.4	2.88.2 2.90.5	2.90.6	
Selenite		2.90.4		2.89.5 2.90.5	2.90.6	
Silicate				2.91.6	2.91.7	
Succinate				2.92.1		
Sulphide				2.94.7		
Sulphate				2.93.11	2.93.12	
Sulphite			2.95.8	2.95.9	2.95.10	
Sulphonate					2.96.1	
Tartrate				2.97.2		
Thiocyanate				2.100.3	2.100.4	
Thiosulphate				2.101.4	2.101.5	
Transaconitate				2.103.1		
Trifluoro-				2.104.1		

acetate

Valerate 2.108.1

Source: Own files

Table 1.10(a) Determination of anions in natural waters

Anion	Micelle exclusion chromatography	Gas chromatography	Isotachoelect- rophoresis	X-ray spectrometry	Pre
Aminoacetate		2.2.2	2.2.1		
Arsenate		2.4.8			2.4.
Arsenite					2.5.
Borate					2.9.
Bromide	2.12.13	2.12.14		2.12.8	2.12
Carboxylate		2.15.4			
Chloride		2.17.17	2.17.7		
Chromate/dichromate					2.15
Cyanide free		2.23.12			
Cyanide, total		2.24.4			
Fluoride		2.31.10	2.31.5		
Hexane carboxylate		2.42.1			
Iodate	2.49.7				2.45
Iodide	2.50.15	2.50.16			2.50
Malonate		2.56.3			
Metal cyanide complexes					2.57
Mixed halides	2.58.3				
Molybdate					2.55
Nitrate	2.62.16, 2.64.17	2.62.17	2.62.8, 2.64.9		
Nitrite	2.63.12, 2.64.17	2.63.13	2.63.7.2.64.9		
Octanedithioate		2.66.1			
Octanoate		2.69.1			
Phosphate		2.75.13	2.75.7		2.75
Selenate		2.90.7			2.85

Selenite		2.89.6, 2.90.7	2.85
Silicate			2.91
Sulphate		2.93.9	
Sulphide	2.94.9	2.94.10	2.94
Sulphite	2.95.12		
Thiocyanate	2.100.5	2.100.6	
Thiosulphate	2.101.6		2.10
Vanadate			2.10
Tungstate			2.95

Source: Own files

Table 1.10(b) Determination of anions in seawater

Anion	Titration	Spectrophotometry	Chemiluminescence	Segmented flow analysis	Flow injection analysis	Continuous flow analysis	Ultraviolet
Alkalinity	3.3.1	3.3.2					
Arsenate		3.4.1, 3.32.1					
Arsenite		3.5.1, 3.32.1					
Borate		3.8.1					
Bromate		3.9.1					
Bromide	3.10.1			3.10.2			
Chloride	3.12.1						
Fluoride		3.14.					
Hypochlorite		3.16.					
Iodate		3.17.					
Iodide	3.18.1	3.18.2					
Nitrate		3.20.1 3.22.1	3.20.3		3.20.5 3.22.4	3.20.4 3.22.3	3.2 3.2
Nitrite		3.21.1 3.22.1			3.21.2 3.22.4	3.22.2	3.2
Phosphate		3.32.1, 3.24.1			3.24.2		
Silicate		3.28.1			3.28.2		
Sulphate	3.29.1	3.29.2					

Sulphide 3.32.1

Source: Own files

Table 1.10(b) Determination of anions in seawater

Anion	Atomic absorption spectrometry	Inductively coupled plasma AES	Polarography	Chrono- potentiometry	Cathodic stripping voltammetry	Ion selective electrode
Bromate			3.9.1			
Bromide						3.10.4
Chloride				3.12.3		3.12.2
Chromate/ dichromate	3.13.1					
Fluoride						3.14.3
Iodide					3.18.3	
Molybdate	3.19.1					
Nitrate					3.20.6	
Sulphate		3.29.3	3.29.4			

Source: Own files

Table 1.10(b) Determination of anions in seawater

Anion	X-ray fluorescence spectrometry	Photon activation analysis	Ion chromato- graphy	Electrostatic ion chromato- graphy	High performance liquid chromat- ography	Ion exclusion chromatography
Acetate			3.1.1			
Acrylate			3.2.1			
Benzoate			3.6.1			
Bromide	3.10.7				3.22.2 3.10.7	
Butyrate			3.7.1			
Carboxyate			3.11.1			

Fluoride	3.14.2			
Formate				3.15.1
Iodide	3.18.4	3.32.2	3.18.5	
		3.18.6		
Nitrate	3.20.7	3.32.2	3.22.5	
Nitrite				3.22.5
Phosphate	3.24.3			
Propionate	3.25.1			
Pyruvate	3.26.1			
Silicate				3.28.3
Sulphate	3.29.5			
Valerate	3.31.1			

Source: Own files

Table 1.10(b) Determination of anions in seawater

<i>Anion</i>	<i>Gas chromatography</i>	<i>Isotachoelectrophoresis</i>	<i>Spectro-fluorometry</i>	<i>Preconcentration</i>
Bromide		3.10.3		
Molybdate				3.19.2
Perrhenate				3.23.1
Phosphate				3.24.4
Selenate			3.27.1	
Selenite			3.27.1	
Sulphide	3.30.2	3.30.1		

Source: Own files

Table 1.10(c) Determination of anions in estuary waters

<i>Anion</i>	<i>Spectro-photometric</i>	<i>Spectro-fluorometric</i>	<i>Ultraviolet spectorscopy</i>
Nitrate	4.2.1, 4.6.1		4.1.1
Nitrite	4.2.1		
Phosphate	4.3.1 4.6.1		

Selenate	4.4.1
Selenite	4.4.1
Sulphate	4.5.1, 4.6.1

Source: Own files

Table 1.10(d) Determination of anions in aqueous precipitation

Anion	Titration	Spectro- photometric	Spectrofluorimetric	Flow injection analysis	Continuous flow analysis	Emission spectrometry
Alkalinity	5.2.1.1					
Bromide			5.1.2.1	5.1.2.3	5.1.2.2, 5.1.14.1	
Chloride				5.1.3.2 5.1.14.4	5.1.3.1 5.1.14.1	
Fluoride						
Iodide		5.1.6.1				
Nitrate		5.1.7.1 5.2.4.1		5.1.7.3 5.1.14.4	5.1.7.2	
Nitrite				5.1.8.2	5.1.8.1	5.1.14.4
Phosphate				5.1.10.2 5.1.14.4	5.1.10.1 5.1.14.1	
Sulphate		5.1.11.1 5.2.5.1		5.1.11.3 5.1.14.4	5.1.11.2 5.1.14.1	5.1.11.4

Source: Own files

Table 1.10(d) Determination of anions in aqueous precipitation

Anion	X-ray fluorescence spectrometry	Neutron activation analysis	Isotope dilution	Ion chromat- ography	High performance liquid chromatography	Ion exchange chromat- ography	Gas chrc ogrc
Bromide	5.1.2.4	5.1.2.5	5.2.2.1	5.1.2.6, 5.1.14.3	5.1.2.7 5.1.2.8	5.1.2.9	
Bromate				5.1.1.1, 5.1.14.3			

Chloride	5.1.3.4	5.1.3.5	5.1.3.6, 5.1.14.3	5.1.3.7 5.1.3.8	5.1.3.9	5.1.3
Fluoride			5.1.4.3, 5.1.14.3			
Formate				5.1.5.1		
Hydroxy methane sulphonate			5.2.3.1			
Iodide	5.1.6.4	5.1.6.2		5.1.6.3		
Nitrate			5.1.7.7 5.1.9.1, 5.1.14.3	5.1.7.8 5.1.9.2	5.1.7.9	5.1.7
Nitrite			5.1.8.3, 5.1.9.1, 5.1.14.3	5.1.8.4 5.1.9.2		
Phosphate			5.1.10.4 5.1.14.3			5.1.1
Sulphate			5.1.11.7 5.1.14.3			5.1.1
Sulphite			5.1.12.1 5.1.14.3			
Thiocyanate				5.1.13.1		

Source: Own files

Table 1.10(e) Determination of anions in surface (s), ground (g), mineral (m), borehole (b) and porewaters (p)

<i>Anion</i>	<i>Titration</i>	<i>Spectrophotometric</i>	<i>Segmented flow analysis</i>	<i>Flow injection analysis</i>	<i>Ultraviolet spectrometry</i>	<i>Atomic absorption spectrometry</i>
Alkalinity	6.1.1.1 6.2.1.1(s)					
Arsenate						
Arsenite						
Borate	6.3.1.1(s)	6.1.2.2(s)				
Bromide			6.2.3.1(g)			

Chloride

Cyanide,
free

Fluoride

Iodide 6.2.4.1(g)
6.4.1.1(s)Nitrate 6.1.5.1 6.3.4.1.(b)
6.3.4.1(m)Nitrite 6.3.4.1 6.3.4.1
(m) (m)Phosphate 6.2.6.1(g)
6.4.2.1(b)

Selenate

Selenite

Sulphate 6.1.8.1(s) 6.1.8.2(s)

Sulphide

Sulphite

Thiosulphate

Uranyl

 Source: Own files

Table 1.10(f) Determination of anions in potable water

<i>Anion</i>	<i>Titration</i>	<i>Spectro- photometric</i>	<i>Spectrofluorimetric</i>	<i>Flow injection analysis</i>	<i>Continuous flow analysis</i>	<i>Ultraviolet spectroscopy analysis</i>
Alkalinity	7.1.1	7.1.2		7.1.3		
Bromide		7.6.1				
Chlorate	7.9.1			7.9.2		
Chloride	7.8.1					
Chlorite	7.10.1			7.10.2		
Fluoride		7.13.1 7.13.6		7.13.2		
Hypochlorite	7.14.1					
Iodide		7.16.1				
Nitrate		7.18.1 7.20.1		7.18.4	7.18.3	7.18.2
Nitrite		7.19.1 7.20.1				
Phosphate		7.22.1				
Selenate			7.23.1			
Selenite			7.23.1			
Sulphate		7.25.1 7.25.2		7.25.4	7.25.3	

Source: Own files

Table 1.10(f) Determination of anions in potable waters

<i>Anion</i>	<i>Atomic absorption spectroscopy</i>	<i>Polarography</i>	<i>Ion selective electrodes</i>
Chromate/ dichromate	7.7.1		
Fluoride	7.13.3		7.13.4
Iodide		7.16.2	
Nitrate		7.18.5, 7.18.9, 7.20.2	7.18.9

Nitrite		7.20.2	
Perchlorate		7.21.1	
Silicate		7.24.1	
Sulphate	7.25.5		7.25.6

Source: Own files

Table 1.10(f) Determination of anions in potable water

<i>Anion</i>	<i>Ion chromatography</i>	<i>High performance liquid chromatography</i>	<i>Ion exchange chromatography</i>	<i>Ion exclusion chromatography</i>
Arsenate	7.2.1			
Arsenite	7.3.1, 7.28.2			
Bicarbonate	7.4.2			7.4.3
Bromate		7.5.1		
Bromide	7.6.2	7.6.3		
Chlorate	7.9.3	7.9.4		
Chloride	7.8.2, 7.28.2	7.8.3		
Chlorite	7.10.3			
Cyanide, free	7.12.1			
Fluoride	7.13.5, 7.28.2			
Iodide		7.16.3		
iodate		7.15.1		
Nitrate	7.18.6, 7.28.2, 7.20.3	7.18.7	7.18.8, 7.20.4	
Nitrite	7.19.2, 7.28.2, 7.20.3		7.20.4	
Phosphate	7.22.2, 7.28.2			
Selenate	7.23.2, 2.28.2			
Selenite	7.23.2, 7.28.2			
Sulphate	7.25.7, 7.28.2			
Sulphide	7.27.1			
Sulphite	7.26.1			

Source: Own files

Table 1.10(f) Determination of anions in potable water

<i>Anion</i>	<i>Gas chromatography</i>	<i>Preconcentration</i>	<i>Miscellaneous</i>
Bromide	7.6.4, 7.28.3		
Chloride	7.8.4		
Chloroligno-sulphonate	7.11.1		
Fluoride			7.13.6
Iodide	7.16.4, 7.28.3		
Molybdate		7.17.1	
Nitrate	7.20.5		7.18.9
Nitrite	7.20.5		

Source: Own files

Table 1.10(g) Determination of anions in waste waters

<i>Anion</i>	<i>Titration</i>	<i>Spectro- photometric</i>	<i>Flow injection analysis</i>	<i>Ultraviolet spectroscopy</i>	<i>Raman spectroscopy</i>
Borate		8.1.1			
Chloride		8.3.1	8.3.2	8.3.3	
Chlorite		8.4.1			
Chromate/dichromate		8.6.1			
Cyanate		8.7.1			
Cyanide, free	8.8.1	8.8.2			
Cyanide, total		8.9.1	8.9.2		
Iodide	8.13.1				
Nitrate		8.14.1			8.14.4
Nitrite		8.15.1			8.15.3
Phosphate		8.17.1		8.17.2	
Silicate		8.23.1			
Sulphate		8.20.1 8.26.1			

Sulphide	8.21.1 8.26.1
Sulphite	8.22.1 8.26.1
Thiocyanate	8.24.1

Source: Own files

Table 1.10(g) Determination of anions in waste waters

<i>Anion</i>	<i>Atomic absorption spectrometry</i>	<i>Polarography</i>	<i>Chronopotential- iometry</i>	<i>Anodic stripping voltammetry</i>	<i>Cathodic stripping voltammetry</i>
Chloride					
Chromate/dichromate	8.6.2	8.6.3			
Cyanide, free	8.8.4		8.8.5		
Cyanide, total	8.9.3				
Nitrate					
Phosphate	8.17.3				
Polysulphide				8.19.1	
Silicate	8.23.2				
Sulphate					
Sulphide					8.21.2
Sulphite		8.22.2			
Thiosulphate				8.25.1 14.8.1.1	

Source: Own files

Table 1.10(g) Determination of anions in waste waters

<i>Anion</i>	<i>X-ray fluorescence spectrometry</i>	<i>Ion chromat- ography</i>	<i>High perform- ance liquid chromato- graphy</i>	<i>Ion chromat- graphy</i>	<i>Ion exclusion chromat- ography</i>

Borate	8.1.2		
Bromide	8.2.1		
Carbonate			8.5.1
Chloride	8.3.5, 8.26.2		8.3.6
Cyanide, free	8.10.1		
Cyanide, total	8.10.1		
Ethylene diamine tetra acetate		8.11.1	
Fluoride	8.12.2, 8.26.2		
Nitrate	8.26.2		
Nitroacetate		8.16.1	
Nitrite	8.15.4, 8.26.2		
Phosphate	8.17.4 8.26.2	8.17.6	8.17.5
Phosphite	8.18.1		
Sulphate	8.20.4 8.26.2	8.20.5	
Sulphide	8.21.4		8.21.5
Sulphite	8.22.3 8.26.2		
Thiocyanate	8.24.2		
Thiosulphate	8.25.2		

Source: Own files

Table 1.10(g) Determination of anions in waste waters

<i>Anion</i>	<i>Gas chromat-ography</i>	<i>Isotacho electrophoresis</i>	<i>Miscellaneous</i>
Chlorite			8.26.3
Chromate/ dichromate			8.6.4
Cyanate			8.7.3
Cyanide, free	8.8.7		8.8.8
Cyanide, total	8.9.5		8.9.6

Nitrate		8.14.2	8.26.3, 8.15.5
Nitrite		8.14.2	8.15.5, 8.26.3
Sulphate		8.20.2	
Thiocyanate	8.24.3		8.24.4

Source: Own files

Table 1.10(h) Determination of anions in sewage effluents

<i>Anion</i>	<i>Spectro- photometric</i>	<i>Flow injection analysis</i>	<i>Atomic absorption spectrometry</i>	<i>Ion selective electrodes</i>	<i>High performance liquid chromatography</i>	<i>Miscellaneous</i>
Borate	9.1.1					
Chloride				9.2.1		9.2.2
Cyanide, free	9.3.1		9.3.2			9.3.3
Fluoride	9.4.1			9.4.2		
Nitrate	9.5.1 9.7.1			9.5.2		9.5.3
Nitrite	9.7.1					9.6.1
Phosphate	9.8.1	9.8.2			9.8.3	9.8.4
Sulphide				9.9.2		9.9.1

Source: Own files

Table 1.10(i) Determination of anions in trade effluents

<i>Anion</i>	<i>Titration</i>	<i>Spectro- photometric</i>	<i>Spectrofluorometric</i>	<i>Atomic absorption spectrometry</i>	<i>Polarography An</i>
Borate		10.1.1			
Chloride	10.3.1				
Cyanide, free	10.4.1	10.4.2	10.4.3	10.4.5	10.4.6
Complex cyanides		10.5.1			

Ferrocyanide	10.7.1				
Nitrate	10.10.1				
Nitrite	10.11.1				10
Phosphate	10.12.1				
Polythionate	10.14.1				
Selenate/ selenite		10.15.1		10.15.2	
Silicate	10.16.1			10.16.2	
Sulphate	10.17.1	10.17.2		10.17.3	
Sulphide	10.18.1	10.18.2	10.18.3		10.18.4
Thiocyanate	10.20.1	10.20.2			
Thiosulphate	10.21.1			10.21.2	

Source: Own files

Table 1.10(i) Determination of anions in trade effluents

<i>Anion</i>	<i>X-ray fluorescence spectrometry</i>	<i>Ion chromatography</i>	<i>High performance liquid chromatography</i>	<i>Ion pairing chromatography</i>
Borate		10.1.2		
Bromide		10.2.1 10.22.1		
Chloride		10.3.2 10.22.1		
Cyanide, free		10.4.10		
Complex cyanide		10.5.2		
Dithionate		10.6.1		
Fluoride		10.8.1 10.22.1	10.8.2	
Iodide		10.9.2		
Nitrate		10.10.2 10.22.1		
Nitrite		10.11.3 10.22.1		
Phosphate		10.12.2		

		10.22.1	
Polysulphide		10.13.1	
Polythionate			10.14.2
Selenate/ selenite	10.15.3		
Sulphate		10.17.5	
Sulphide		10.18.5	
Sulphite		10.19.1	
Thiosulphate		10.22.1	10.21.3

Source: Own files

Table 1.10(i) Determination of anions in trade effluents

<i>Anion</i>	<i>Gas chromatography</i>	<i>Miscellaneous</i>	<i>Ion sensing optrodes</i>
Cyanide, free	10.4.9	10.4.11 10.4.8	
Iodide			10.9.1
Nitrite		10.11.4	
Sulphide	10.18.6		

Source: Own files

Table 1.10(j) Determination of anions in high purity (h), boiler feed (b) and nuclear reactor cooling waters (n)

<i>Anion</i>	<i>Titration</i>	<i>Spectro- photometric</i>	<i>Spectrofluorimetric</i>	<i>Ion selective electrodes</i>	<i>Ion chromatography</i>	<i>Molec emiss. cavity analy.</i>
Carbonate					11.1.1.1(h)	
Chloride	11.2.1.1 (b)	11.2.1.2(b)	11.1.2.1(h)	12.2.1.3(b)	11.2.1.4(b) 12.1.2.2(h)	
Nitrite	11.3.1.1 (n)				11.1.3.1(h) 11.2.2.1(b)	
Phosphate					11.2.3.1(b)	
Silicate		11.1.5.1(h)				

11.2.4.1(b)

Sulphate	11.1.4.2(h)	11.1.4
	11.2.5.1(b)	
Sulphite	11.2.6.1(b)	

Source: Own files

water sample that is applicable to the type of sample of interest. Thus, if a method is not available for determining a particular anion in say non saline water, he or she may find one is listed under potable water. Obviously this approach will not always be applicable, thus a method listed under trade effluents is not likely to be applicable to the ultra low-level analysis of potable, natural or sea waters.

The various methods of determining anions are discussed below in order of the number of applications found for each technique.

1.2.1 Chromatographic techniques

By far the most extensively used techniques are chromatographic techniques such as ion chromatography, high performance liquid chromatography, gas chromatography and other chromatographic techniques.

Ion chromatographic and high performance liquid chromatographic techniques have been obvious advantages of good sensitivity, specificity, multicomponent analysis and automation of the analytical procedure.

In all 85 anions have been determined by ion chromatography of which 31 are inorganic anions and 54 are organic anions. The relatively new technique of electrostatic ion chromatography has, to date, only found application in the determination of bromide application in iodide and nitrite.

Some 40 anions have been determined by high performance liquid chromatography; 25 inorganic and 15 organic anions. Ion exclusion chromatography has been applied to some 19 anions; 11 inorganic and eight organic.

Similarly, micelle chromatography has been applied to the determination of 10 anions. Ion pairing chromatography has very few applications to date (two inorganic anions). Ion exchange chromatography has been applied to the determination of six inorganic anions.

Gas chromatographic methods are limited by the need for appropriate chemistry to convert anions to a volatile form. Methods of achieving this have been described in the cases of arsenate, bromide, chlorite, cyanide, fluoride, iodide, nitrate, nitrite, phosphate, sulphate, selenate, selenite, sulphide and thiocyanide.

1.2.2 Titration techniques

Titration procedures have been developed for 19 anions. These generally lack in sensitivity and specificity. They should be used only when analysis is required at the mg L⁻¹ level and when the possible interference effects by other anions or cations present in the sample is fully understood.

1.2.3 Spectroscopic techniques

Spectrophotometric procedures have been employed for the determination of 35 anions. However, in general, these procedures lack in sensitivity. Additionally, interference effects can be a problem and it is necessary to exhaustively examine the effect of potential interferants which consider using these methods.

In many cases spectrofluorimetric (19 anions) are surprisingly sensitive. Chemiluminescence techniques have been applied to the determination of some seven anions (cyanide, iodide, nitrite, nitrate, silicate, sulphite and vanadate).

The application of ultraviolet spectroscopy is extremely limited *viz* nitrite, nitrate, phosphate and nitriloacetate, while the application of infrared spectroscopy and Raman spectroscopy are limited to the determination of one anion (cyanide) and two anions (nitrite and nitrate) respectively.

1.2.4 Flow analysis techniques

Other techniques which are frequently coupled with Spectrophotometric or atomic procedures include absorption spectrometric flow injection analysis (26 anions), segmented flow analysis (seven anions) and continuous flow analysis (nine anions). These techniques all have the advantage of automation but suffer the same limitations as direct spectrophotometry as regards sensitivity and selectivity.

1.2.5 Spectrometric techniques

The application of atomic absorption spectrometry and, more recently, inductively coupled plasma atomic emission spectrometry to the determination of anions has involved a variety of techniques. Some 16 anions have been determined by atomic absorption techniques listed below.

- (a) Formation of ion pair complexes with malalite green and subsequent atomic absorption spectrometry of the complex, phosphate, arsenate and arsenite.
- (b) Formation of complex with benzoin oxime (tungstate) or diethyldithiocarbamate (selenate, selenite, chromate and dichromate) followed by extraction of complex with methyl isobutyl ketone and analysis of extract by atomic absorption spectrometry.
- (c) Reaction of chloride ions with phenyl mercuric nitrite to produced phenyl mercuric chloride and chloroform extraction of this compound, followed by atomic absorption spectrometry of complex.
- (d) Preconcentration columns of anion exchange resin for tungstate, or cupric sulphide for cyanide, followed by desorption from the column of the tungstate or cuprocyanide complexes and analysis by atomic absorption spectrometry.
- (e) Formation of volatile derivative of anion eg reaction of borate with methanol to form methyl borate and subsequent atomic absorption spectrometry of the solution. To determine nitrate this anion is reduced to ammonia using Ti^{III} sulphate and the ammonia is swept by an air current prior to gas phase molecular absorbance measurements with an atomic absorption spectrometer.

- (f) Formation of aluminium fluoride complex in a graphite furnace followed by molecular absorption spectrometry at 227.45nm.
- (g) Conversion of silicate to silicon tetrafluoride with hydrofluoric acid/ nitric acid and analysis of silicon tetrafluoride solution by atomic absorption spectrometry.
- (h) Indirect determination of sulphate by addition of excess barium chloride to form barium sulphate, followed by determination of excess barium ions by atomic absorption spectrometry.

Similar, and other, techniques have been employed for the determination of 10 anions (sulphate, sulphide, bromide, chloride, fluoride, iodide, iodate, nitrite, nitrate and tungstate) used in conjunction with an inductively coupled plasma atomic emission spectrometric finish.

1.2.6 Electrochemical techniques

Electrochemical methods have been employed fairly extensively and include direct polarography (18 anions), anodic scanning voltammetry (seven anions) and cathodic scanning voltammetry (7 anions), amperometry (nitrate and nitrite), potentiometry (citrate and iodide) and chronopotentiometry (chloride and cyanide). Between them these techniques cover some 24 anions:

<i>Polarography:</i>	arsenate, arsenite, bromide, chromate, citrate, iodate, iodide, nitrate, nitrite, phosphate, selenate, selenite, silicate, sulphate, sulphide, sulphite, bromate, perchlorate.
<i>Anodic scanning voltammetry:</i>	bromide, phosphate, sulphate, chlorite, hypo-chlorite, polysulphide and thiosulphate.
<i>Cathodic scanning voltammetry:</i>	bromide, iodate, iodide, nitrate, nitrite, sulphide and chloride.
<i>Amperometry:</i>	nitrate and nitrite.
<i>Chrono-</i>	
<i>potentiometry:</i>	Chloride and cyanide.
<i>Potentiometry:</i>	iodide and citrate.

In general, electrochemical methods offer the possibility of speciation of anions. Thus arsenite and arsenate and selenate and selenite can be resolved. Ion selective electrodes now have a reasonably larger number of applications, including borate, bromide, fluoride, free and total cyanide, chlorite, iodate, nitrate, nitrite, sulphate, sulphide, sulphite and thiocyanate.

Isotachoelectrophoresis is more limited in its range of applications which include chlorite, hypochlorite, fluoride, nitrate, nitrite and sulphate.

1.2.7 Enzymic techniques

Enzymic assay methods have limited applications in the determination of anions

including chromate, cyanide, nitrate, phosphate, selenate and selenite.

1.2.8 Miscellaneous techniques

Other miscellaneous techniques which have found very limited applications in the determination of anions in waters include the following:

- X-ray spectrometry, bromide
- Neutron activation analysis, bromide and iodide
- Photoactivation analysis, fluoride
- Cavity analysis, sulphate
- Emission spectrometry, sulphate
- X-ray fluorescence spectroscopy, bromide, chloride, iodide, phosphate, selenate and selenite
- Ion sensing optodes, iodide.

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Chapter 2

Anions in non saline waters

2.1 Acetate

2.1.1 Titration method

Hasson *et al.* [1] have used a potentiometric gas sensing probe for the selective potentiometric determination of acetate in non saline waters.

2.1.2 Ion chromatography

The determination of acetate by this procedure is discussed under multianion analysis in sections 12.2.4 and 12.2.5.

2.1.3 High performance liquid chromatography

The determination of acetate by this procedure is discussed under multianion analysis in section 13.1.1.5.

2.2 Amino-acetate

2.2.1 Electrophoresis

Yu and Dovichi [2] used capillary zone electrophoresis with thermo-optical absorbance detection to determine sub $\mu\text{g L}^{-1}$ concentrations of 18 amino acids.

2.2.2 Gas chromatography

Gardner and Lea [3] preconcentrated free and combined amino acid from lake water on an ion exchange column, prior to desorption with a small volume of acid followed by conversion to N-trifluoroacetyl methyl esters and gas chromatography.

2.3 Anisate

2.3.1 Ion chromatography

The determination of anisate by this technique is discussed under multianion analysis in section 12.2.5.

2.4 Arsenate

2.4.1 Spectrophotometric methods

Matsuhara *et al.* [4] have described a rapid method for the determination of trace amounts of arsenate (and phosphate) in water by Spectrophotometric detection of their heteropolyacid-malachite green aggregates following preconcentration by membrane filtration.

The determination of arsenate is discussed under multianion analysis in section 14.2.2.1.

2.4.2 Flow injection analysis

This technique has been applied to the determination of arsenate in non saline waters [5].

The determination of arsenate is discussed under multianion analysis in section 14.4.1.5.

2.4.3 Atomic absorption spectrometry

Arsenate (and arsenite and phosphate) have been determined in non saline waters by a technique based on flotation spectrophotometry and extraction—indirect atomic absorption spectrometry using malachite green as an ion-pair reagent [6].

2.4.4 Polarography

An indirect polarographic method has been used to determine traces of arsenate in mineral waters [7]. In this method arsenate is converted to uranyl arsenate which is filtered off and excess uranyl ion is determined by polarography at -3.60V . Phosphates interfere in this procedure.

Chakraborti *et al.* [8] determined arsenate by differential pulse polarography on acidic aqueous solutions containing polyhydroxy compounds such as D-mannitol. Peak heights measured at -0.55V in a medium containing 2M aqueous perchloric acid and 4.5g mannitol in a 50ml solution gave linear calibration curves over the range $20\text{--}160\mu\text{g L}^{-1}$. Arsenite could be similarly determined at -0.34V or -0.42V with or without mannitol respectively, the method of measurement at -0.42V being used where arsenite occurred in the presence of arsenate. Detection limits were approximately $10\mu\text{g}$ arsenic for both forms. Examples of results obtained for arsenite and arsenate recovery in a river water sample are given.

2.4.5 Ion chromatography

This technique has been applied to the determination of arsenate (and sulphite) in non saline waters [9] and is discussed further under multianion analysis in sections 12.2.2, 12.2.4 and 12.2.5.

2.4.6 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.4.7 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.2.

2.4.8 Gas chromatography

Fukai *et al.* [10] have described a procedure based on gas chromatography of 2,3 mercaptopropanol complexes for the determination of arsenate, arsenite and monomethylarsonic acid in non saline waters. The 2,3 mercaptopropanol is extracted with benzene and introduced into a gas chromatograph equipped with a flame-photometric detector for the determination of sulphur. One aliquot of sample is treated with stannous chloride solution and potassium iodide solution to reduce arsenate and monomethylarsonic acid, then 2,3 mercaptopropanol is added and the complexes are extracted with benzene. The extract is analysed for total inorganic arsenic plus monomethylarsonic acid. Magnesia mixture and phosphate solution are added to another aliquot to remove arsenate by co-precipitation with magnesium ammonium phosphate. The precipitate is filtered off and arsenite determined in the filtrate. The detection limits are 0.02ng of arsenic for arsenate and arsenite and 0.04ng of arsenic for monomethylarsonic acid.

2.4.9 Miscellaneous

2.4.9.1 Determination of arsenate and arsenite

In the method of Johnson and Pilson [11], one aliquot of sample arsenite is oxidised to arsenate, in a further aliquot arsenate is reduced to arsenite and a third aliquot is untreated. Each aliquot is submitted to a molybdenum blue procedure. The first gives a value for phosphate plus arsenate plus arsenite, the second for phosphate and the third a value for phosphate plus arsenate. The content of each anion is calculated from these results. The method is applicable at the $3\mu\text{mol L}^{-1}$ level.

Johnson [12] has also described a spectrophotometric method for the determination of arsenate and phosphate in non saline water in which total arsenate-plus phosphate are determined by classical molybdenum blue procedure [13]. Arsenate is then reduced to arsenite which does not form a coloured complex with molybdic acid. A difference technique then enables the separate determination of phosphate and arsenate.

2.4.10 Preconcentration

The preconcentration of arsenate is discussed in section 5.1.13.

2.5 Arsenite

2.5.1 Flow injection analysis

The application of this technique is discussed under multianion analysis in section 14.4.1.5.

2.5.2 Atomic absorption spectrometry

Arsenite (and arsenate and phosphate) have been determined in non saline waters by a technique based on flotation spectrophotometry and extraction—indirect atomic absorption spectrometry using malachite green as an ion-pair reagent [14].

2.5.3 Differential pulse polarography

Reed and Stolzberg [15] used differential pulse polarography for the direct determination of arsenite in the presence of other arsenic species but there was significant interference as a result of overlapping polarographic waves of lead, thallium and tin. Details are given of procedure for removal of divalent lead and thallium by chromatography on a chelating ion exchange resin. The presence of strong ligands could interfere with the removal of lead but this interference could be prevented by the addition of divalent copper to dissociate the lead complex. Since the interfering ions are removed from solution, large amounts of lead and thallium could be tolerated.

2.5.4 Ion chromatography

Urasa and Ferede [16] used direct current plasma as an element-selective detector for the simultaneous ion chromatographic determination of arsenic(III) and arsenic(V) in the presence of other common anions. Matrix effects were eliminated, and a wide range of element compositions can be used without experiencing detector limitations.

The application of this technique is also discussed under multianion analysis in section 12.2.2.

2.5.5 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.2.

2.5.6 Preconcentration

The preconcentration of arsenite is discussed in section 15.1.1.

2.6 Ascorbate

2.6.1 Spectrophotometric method

Norwitz and Keliher [17] have discussed the determination of ascorbic and isoascorbic acids by the Spectrophotometric diazotisation coupling technique.

2.6.2 Spectrofluorometric method

Ascorbate at the nmol^{-1} level has been determined by a kinetic fluorometric method [18].

2.6.3 High performance liquid chromatography

Kishida *et al.* [19] derivatised ascorbic acid with 2,4-dinitrophenyl hydrazine to ascorbic acid bis (dinitrophenyl) hydrazone (osazone) prior to separation from other sample constituents by high performance liquid chromatography.

2.7 Benzoate

2.7.7 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.8 Bicarbonate

2.8.1 Titration method

Feij and Smeenk [20] and Colin [21] discuss the titrimetric determination of bicarbonate.

2.8.2 Segmented flow analysis

This technique can be applied to the determination of bicarbonate in the concentration range $0\text{--}0.5\text{mg L}^{-1}$ as (CO_2) in water.

2.8.3 Flow injection analysis

Basson and Van Staden [22] have described a single point titration system for the determination of total alkalinity in surface waters, ground and domestic waters, based on

flow injection analysis. Water samples are injected automatically into the flow system using a flow injection sampling unit. A sampling cycle of 30s allows 120 samples per hour to be analysed. The sample is reacted with an acid linear response buffer solution and the pH of the resulting solution is measured with a glass electrode in a flow through assembly.

Reagents

Unless otherwise specified all reagents are of analytical grade quality. Carrier stream, 0.1mol L⁻¹ sodium chloride solution. Dissolve 5.844g sodium chloride in 1L distilled water. Buffer solution. Prepare the following buffer component solutions.

- (a) Add 6.01 g diethylmalonate to 7ml concentrated hydrochloric acid solution and dilute to 500ml with distilled water.
- (b) Weigh 7.88g citric acid and dilute to 500ml with distilled water.
- (c) Weigh 5.22g p-nitrophenol and dilute to 500ml with distilled water.
- (d) Weigh 3.87g diethylbarbituric acid and dilute to 500ml with distilled water.
- (e) Weigh 2.32g boric acid, dissolve and dilute to 500ml with distilled water.
- (f) Weigh 3.53g phenol, dissolve and dilute to 500ml with distilled water.

Prepare a stock buffer solution by mixing 50ml of solution (a), 50ml of solution (b), 59ml of solution (c), 150ml of solution (d), 50ml of solution (e) and 50ml of solution (f). This solution is made 0.10 mol L⁻¹ with respect to sodium chloride.

Apparatus

Peristaltic pump turning at 30rpm, scientific flow-injection sampler

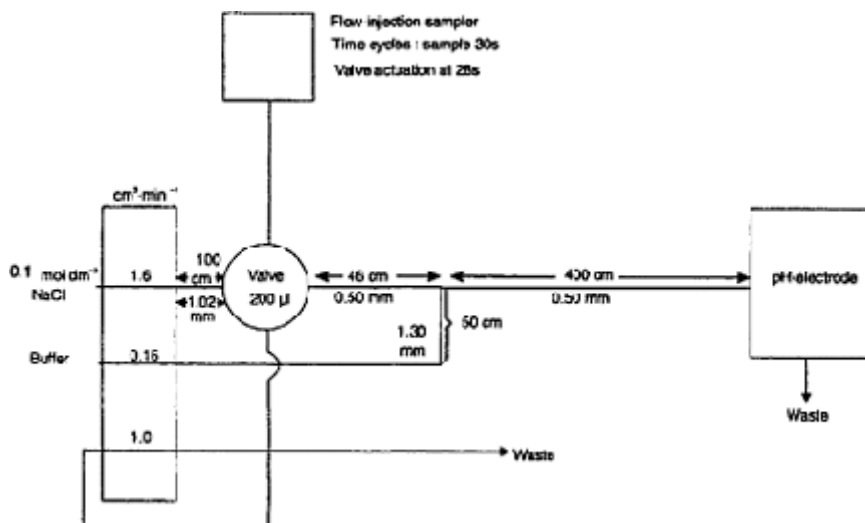


Fig. 2.1 Flow system for the determination of total alkalinity. Sampling rate 120 samples h⁻¹. Tube length and diameters are given in cm and mm
Source: Reproduced with permission from United Trades Press [22]

(Breda), Orion model 601 pH meter, Beckman micro blood electrode consisting of a micro sensor assembly (Beckman Part No 580621), and a pH-electrode (Beckman Part No. 39045), Hitachi model QPD 53 potentiometric recorder.

Procedure

A schematic flow diagram for the system is shown in Fig. 2.1. Tygon tubing of 0.50mm diameter was used and all connectors were made from Perspex. The tube lengths used are as indicated in Fig. 2.1.

Automatically inject water samples into the flow system by using a flow injection sampling unit. Use a sampling cycle of 30s between successive samples giving a capacity of 120 samples per h. Actuate the valve system on a time basis which is correlated with the sampler unit. The sampling valve actuates every 28 s after movement of the sampler to the next sample.

Fig. 2.2 shows the appearance of recorder tracing as well as calibration curves when analysing a series of standards in the range 20–300mg L⁻¹ bicarbonate solution. Although the calibration curve is not linear over the complete concentration range, experimental results indicate linearity in the range 30–75 mg L⁻¹.

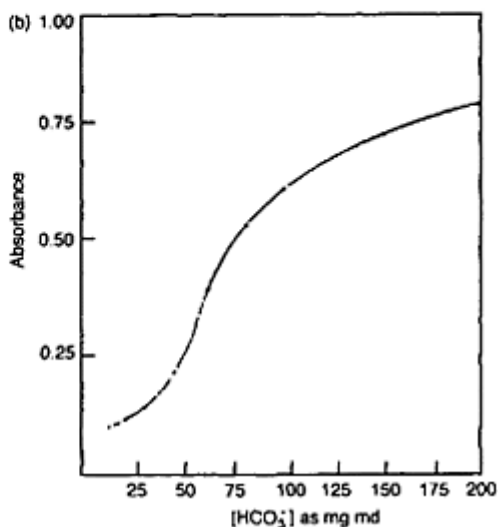
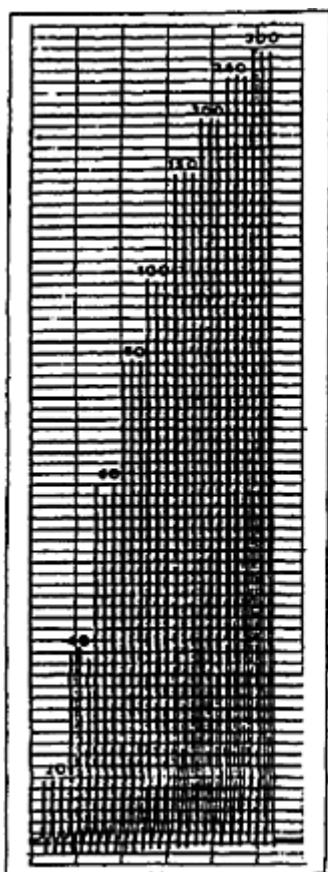


Fig. 2.2 (a) Calibration peaks obtained with 10cm^2 buffer solution diluted to 100cm^3 with distilled water. The values on top of the peaks represent mg L^{-1} bicarbonate ions, (b) Corresponding calibration graph
Source: Reproduced with permission from United Trades Press [22]

In Table 2.1 a comparison is made of results obtained by the above flow injection method, by an electrometric titration method, and by an automated bromocresol green indicator method.

Flow injection results compare favourably with a standard electrometric method and in some instances better results were obtained when compared to the automated bromocresol green method. This is probably due to colour interferences from these water specific samples. Students' t-test was applied in comparing both sets of results with the manual electrometric method. Table 2.1 reflects these calculations. Both procedures give results that differ to a statistically insignificant extent when compared to the electrometric procedure. However, the difference between the procedures is smaller than the difference between the continuous flow procedure and the electrometric procedure.

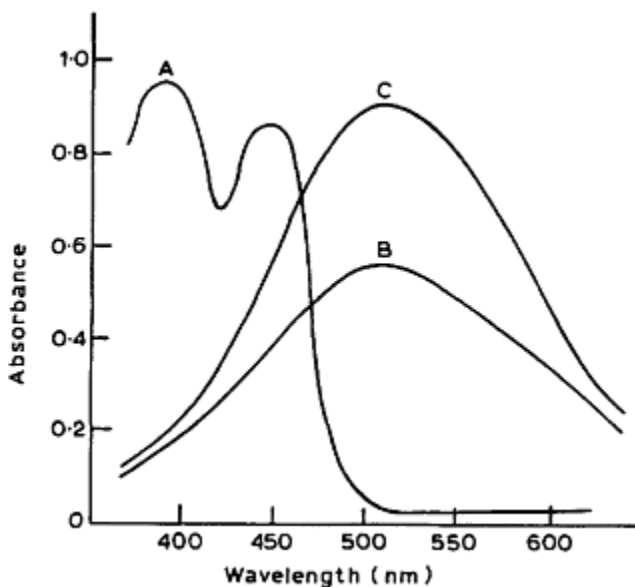


Fig. 2.3 Absorption spectra of A, reagent blank solution measured against TBMK as reference; B, boron-curcumin compound against reagent blank, $3\mu\text{g mL}^{-1}$ of boron; and C, as B, $5\mu\text{g mL}^{-1}$ of boron
Source: Reproduced with permission from the Royal Society of Chemistry [23]

2.8.4 Ion chromatography

This technique has been applied to the determination of bicarbonate in non saline waters

[24,25].

The application of this technique is also discussed under multianion analysis in sections 12.2.1 and 12.2.5.

2.8.5 Combustion method

Harmsen *et al.* [26] have described a rapid method for the determination of bicarbonate in ground water and surface water. Using the inorganic channel of the Beckmann total organic carbon analyser these workers determined the TOC content of a 2.0 μ L water sample. Since the total inorganic carbon is dependent on the pH of the water, use of a determined pH value allows determination of the total bicarbonate based on the equilibrium equations of carbonic acid in water. Calculation in terms of mg L⁻¹ is also possible. These workers tabulate the percentages of carbon dioxide, bicarbonate ion and carbonate ion and total organic carbon in water at 20°C as a function of pH over the range pH 7.0 to 8.0 at 0.1 pH unit intervals. The method is rapid (2–3 min) and has an accuracy of better than 2%, is insensitive to other weak acids and requires only small sample volumes.

Table 2.1 Comparison of results obtained by the FIA-method, the electrometric method and the automated segmented bromecresol green method*

Sample	Automated segmented method (HCO ₃ ⁻) in mg L ⁻¹	Electrometric method [HCO ⁻] in mg L ⁻¹	FIA-method [HCO ₃ ⁻] in mg L ⁻¹	Coefficient of variation
1	226	268	248	0.99
2	485	546	532	0.46
3	266	298	305	0.98
4	266	306	313	0.56
5	213	232	236	0.71
6	250	276	288	0.66
7	120	142	135	0.98
8	160	259	287	0.48
9	267	291	324	0.31
10	480	317	332	0.56
11	107	120	110	0.26
12	117	123	110	0.27
13	119	123	112	0.24
14	120	125	113	0.31
15	113	109	110	0.42

16	113	117	108	0.55
17	96	98	95	0.30
18	138	142	132	0.22
19	178	201	187	0.28
20	183	204	199	0.35
21	174	194	193	0.21
22	174	196	186	0.48
23	167	186	178	0.21
24	65	68	66	0.30
25	30	28	26	1.10

*15 tests were carried out on each sample

Source: Reproduced with permission from United Trades Press [22]

2.9 Borate

2.9.1 Spectrophotometric methods

Choi and Chen [27] have developed a curcumin method using a 20% v/v 2-ethyl-1,3-hexanediol, a boron complexing agent, in methyl isobutyl ketone as an extracting solvent. A 5cm cylindrical quartz cell is used to measure absorbance against 100% ethyl alcohol at a wavelength of 550nm. This method eliminates inconvenient time-limits and the interference of fluorides, or nitrates. Using a 5cm cylindrical cell, the detectable range of boron is approximately 0.25–3.0 mg L⁻¹ with less than 5% error.

There is no significant interference from magnesium, calcium, and fluoride and nitrate ions in this method. The detection limit of this method is approximately 0.2 mg L⁻¹ borate.

In this method 1ml of water sample is transferred into a 10ml polypropylene tube (17×100mm) with a friction-fit closure. 2ml of 1N hydrochloric acid and 3 ml of 20 vol % 2-ethyl-1,3-hexanediol in methyl isobutyl ketone is added and the solution shaken vigorously for 2min. 1ml aliquot from the upper organic solvent layer of the extract is transferred into a 50ml polypropylene centrifuge tube with a screw cap. 2ml of curcumin reagent (0.375g 100 mL⁻¹ glacial acetic acid) is added and then 0.5ml of concentrated sulphuric acid. The centrifuge tube is closed immediately after the addition of concentrated sulphuric acid and the bottle swirled until the yellowish colour turns to a dark purple colour. The reaction may be terminated at any time under 23h by adding 50 ml of 100% ethyl alcohol. The absorbance of the solution is measured against 100% ethyl alcohol at a wavelength 550nm with a 5cm cylindrical quartz cell (glass and quartz function equally well in the visible portion of the spectrum). The absorbance of the solution can be measured 60min after the addition of alcohol. The time span between the addition of alcohol and the measurement of absorbance can be arranged according to the

number of samples, but better accuracy is achieved when the intervals are relatively close.

The results obtained from the study of interference from fluoride, magnesium, calcium and nitrate ions show clearly that there is no significant interference from any of these ions.

Aznarez *et al.* [23] have described a sensitive spectrophotometric method based on the curcumin complex. In this method the boron is extracted into isobutyl methyl ketone with methylpentanediol.

The absorption spectrum of the boron-curcumin compound in isobutyl methyl ketone obtained following the above procedure exhibits maximum absorbance at 510nm when measured against a reagent blank solution, as shown in Fig. 2.3.

The calibration graph at 510nm obtained in the curcumin method is a straight line and Beer's law is obeyed from 0.5 to $5\mu\text{g mL}^{-1}$ of boron in the final measured solution (corresponding to 10–110 μg of boron in the aqueous phase).

In this method 50ml of non saline water (containing 10–100 μg boron) with hydrochloric acid (1+1) is transferred to a 100ml calibrated flask and the solution extracted with three 10ml volumes of methyl isobutyl ketone to eliminate iron interference, 10ml of 20% volume methyl pentane diol in methyl isobutyl ketone is added and the mixture shaken for 5min. The organic phase is then dried with 1g anhydrous sodium sulphate.

3ml of the organic phase is pipetted into a polyethylene test tube with a hermetic cap, and 2ml of curcumin solution (0.1% w/v in glacial acetic acid), 2ml of concentrated phosphoric acid are added. The sealed test tube is shaken for 2min and heated at $70\pm 3^\circ\text{C}$ for 1h in a thermostated bath. After rapid external cooling to room temperature, the absorbance of the solution is measured at 510nm against a reagent blank solution within 45min.

Prepare a calibration graph as follows. To different volumes of standard solution containing 10–100 μg of boron add an equal volume of hydrochloric acid (1+1) and extract with 10ml of extraction solution according to the above extraction procedure. Pipette 3ml of the organic phase and carry out the same spectrophotometric procedure.

The Department of the Environment UK [28] have discussed four alternative methods for the determination of boron comprising the curcumin method, automated and manual methods based on azomethine H, with measurements of absorbance of the complexes formed, and a mannitol titration method suitable for a wide range of boron concentrations from 0.5 to 1000 mg L^{-1} . Interference by nitrate is discussed.

A further chromogenic reagent that has been used for the determination of borate is azomethine [29–31] which forms a yellow complex with borate. Randow [30] evaluated the Azomethine H method for several non saline water samples and also for model solutions containing humic acids with standard amounts of boron added to the sample. The effects of illumination, temperature and time on the colour development were examined, together with other factors such as the initial colour of the sample and the container materials. Over the temperature 12–24 $^\circ\text{C}$ the absorbance maximum was reached within 1h and remained stable for 1h afterwards. The sample colour intensity necessitated a proportionate correction to the observed value. Recoveries of added boron ranged from 86 to 104% for concentrations between 20 and 200 $\mu\text{g L}^{-1}$. The limit point of

determination was $16\mu\text{g L}^{-1}$ glass vessels were only suitable for brief contact during operations such as pipetting or dilution; all other operations should be performed in polythene beakers or flasks.

Bilikova [31] executed microgram level determinations of boron in non saline waters by two methods, namely the modified curcumin method with rosocyanin, and the Azomethine method. Both methods allowed determination of boron in water at between 0.1 and $1.6\mu\text{g}$ in 50 and 100 ml volumes respectively. Dryssen *et al.* [32] also used curcumin to determine boron in non saline waters.

Other chromogenic reagents that have been employed for the spectrophotometric determination of borate include crystal violet which forms a complex with boron, having an adsorption maximum of 600nm [33], ferroin [34], carmine [35], chromotropic acid [36]–[39], various diketones [40], 1,8-dihydroxynaphthalene-4-sulphonic acid [41], dianthrinamide [42], Azomethine H. Detection limits claimed are down to $10\mu\text{g L}^{-1}$ (dianthrimide method).

Spectrofluorometric reagents that have been used include 4'-chloro-2-hydroxy-4-methoxybenzophenone [43,44].

Yoshimura *et al.* [39] determined boron in non saline waters after specific adsorption on Sephadex gel.

Lussier *et al.* [45] determined borate in light and heavy water by a method based on flow injection analyses with indirect ultraviolet-visible spectrophotometric detection.

2.9.2 Spectrofluorometric methods

Aznarez *et al.* [23] have described a sensitive fluorometric method based on molecular fluorescence with dibenzoylmethane. In this method the boron is extracted into isobutyl methyl ketone with methylpentanediol.

In this method a Pye Unicam SP8 100 spectrophotometer or equivalent with special equipment for fluorescence measurements was used. Glass materials must be avoided in order to eliminate boron contamination. PTFE, polyethylene or platinum materials are recommended.

50ml of non saline water is diluted with hydrochloric acid (1+1) to 100ml in a calibrated flask. A measured volume of sample solution containing 0.5–5 μg of boron is placed in a separating funnel and extracted three times with 10ml volumes of isobutyl methyl ketone in order to eliminate any iron interference. 10ml of 20 vol % methylpentanediol in methyl isobutyl ketone solution is added and the mixture shaken for about 5min with a mechanical shaker. The organic phase is dried with 1g of anhydrous sodium sulphate.

3ml of the organic extraction phase is placed into a polyethylene test tube with a hermetic cap and 2ml of 0.1% w/v benzoylmethane in glacial acetic acid added and 2ml of concentrated phosphoric acid. The sealed test tube is shaken for 2min and heated at $80\pm 3^\circ\text{C}$ for 30min in a thermostated bath. After rapid external cooling to room temperature, the relative fluorescence intensity of the solution is measured at 400nm with excitation at 390nm and quinine sulphate solution as reference, within 45min.

A calibration graph is prepared as follows. To different volumes of standard solution containing 0.5–5 μg of boron, add an equal volume of hydrochloric acid (1+1) and extract

with 10ml of extraction solution according to the above extraction procedure. Pipette 3ml of the organic phase and carry out the same fluorometric procedure.

The absorption spectrum of the boron-curcumin compound in isobutyl methyl ketone obtained following the above procedure exhibits maximum absorbance at 510nm when measured against a reagent blank solution.

The fluorescent excitation spectrum of the boric acid dibenzoylmethane compound in isobutyl methyl ketone against quinine sulphate solution is shown in Fig. 2.4. The wavelength of the maximum excitation

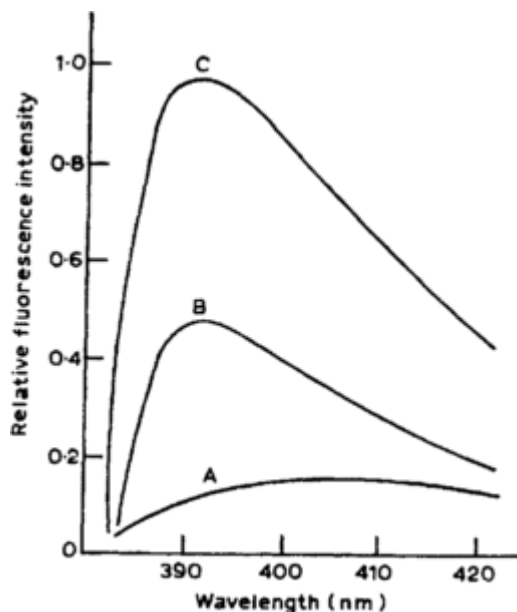


Fig. 2.4 Fluorescence excitation spectra against quinine sulphate solution as reference: A, reagent blank solution, B, boron-DBM, $50\mu\text{g mL}^{-1}$ of boron; and C, boron-DBM, $100\mu\text{g mL}^{-1}$ of boron

Source: Reproduced with permission from the Royal Society of Chemistry [23]

radiation was 390nm. The maximum relative fluorescence intensity was measured at 400nm or by using a Kodak 2B cut-off filter (400nm cut-off).

The precision of the method for 10 replicate determinations was 0.6%. The corresponding detection limit in the fluorometric method was $1\mu\text{g L}^{-1}$ (as boron). Interference effects in both methods are illustrated in Table 2.2. The interference of iron at concentrations greater than $7 \times 10^{-5} \text{ mol L}^{-1}$ can be eliminated by removing iron as the chloro complex by extraction with isobutyl methyl ketone. The total elimination of iron was not necessary as the phosphoric acid masked the residual iron in the boric acid-curcumin reaction.

Boron recoveries in some non saline waters were in the range 97.5–101%.

A large number of fluorometric reactions are known for the determination of borate anion. Some of them involve its previous distillation as methylborate [46,47] to isolate it from interfering species.

In spite of the fact that benzoin is a widely used fluorometric reagent for the determination of boron, special precautions must be taken with this method as benzoin in alkaline solution is oxidised by the oxygen of the air and nitrogen must be bubbled through the solution [48]. Also, benzoin undergoes photodecomposition when exposed to radiation.

2-hydroxy-4-methoxy-4'-chlorobenzophenone is a sensitive fluorometric reagent for borate and has been applied satisfactorily in the

Table 2.2 Effect of foreign ions on boron determination

Foreign ion	Maximum concentration tested without giving interference mol L ⁻¹	
	<i>Spectrophotometric method</i> ^a	<i>Fluorometric method</i> ^b
Cl ⁻	7.2	7.2
SO ₄ ²⁻	2.5	2.5
NH ₄ ⁺	1.0	0.8
Na ⁺	0.2	0.2
K ⁺ , Ca ²⁺ , Al ³⁺	0.5	0.4
NO ₃ ⁻ , NO ₃ ⁻ , Cr ³⁺	0.2	0.2
Mg ²⁺ , HCO ₃ ⁻ , CO ₃ ²⁻	0.05	0.05
Mn ²⁺	0.05	0.01
F ⁻	0.02	0.01
Cu ²⁺ , Zn ²⁺ , Ni ²⁺	4×10 ⁻³	4×10 ⁻³
Sr ²⁺ , PO ₄ ³⁻ , SiO ₃ ²⁻ , Br ⁻	3×10 ⁻³	3×10 ⁻³
Fe ³⁺	7×10 ^{-5c}	7×10 ^{-5c}
Fe ³⁺ (by elimination with three 10ml IBMK washes)	0.1	0.01

^aDetermination of 58.3µg of boron by the spectrophotometric method.

^bDetermination of 2.38µg of boron by the fluorometric method.

^cTolerance limit (M) as the concentration level at which the interferent causes an error of not more than ±2% (spectrophotometric method) or ±3% (fluorometric method)

Source: Reproduced with permission from the Royal Society of Chemistry [23]

determination of this anion in several samples. Monier *et al.* [49] studied the action of 41 ions on the fluorescence of the complex and none interfered in the determination of borate. The fluoride ion interfered only at ratios of fluorine to boron of 100:1 (m/m) or

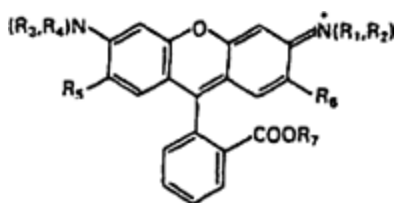
greater.

Most of these methods for the determination of borate are highly sensitive. The method using dibenzoylmethane [50,51] (0.5ng ml^{-1}), quercetin [52,53] (0.3ng ml^{-1}) or 2-hydroxy-4-methoxy-4'-chlorobenzophenone [54] (0.4ng ml^{-1}) are the most sensitive.

These methods are based on the formation of an ion association ternary or binary anionic complex associated with a basic dye cation that generally belongs to the family of the rhodamines, (see formula p.108).

Haddad [55] published an extensive review on the application of ternary complexes to spectrofluorometric analysis.

Several rhodamines (Rhodamine S, Rhodamine 6G and Butylrhodamine B) were compared as reagents for the determination of boron [56] by measurement of the luminescence of their compounds with BF_4 in benzene solution. Butylrhodamine B was the best reagent The addition



Name

Substituent	Rhodamine B	Butylrhodamine B	Rhodamine 6G
R ₁	C ₂ H ₅	C ₂ H ₅	H
R ₂	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
R ₃	C ₂ H ₅	C ₂ H ₅	H
R ₄	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
R ₅	H	H	CH ₃
R ₆	H	H	CH ₃
R ₇	H	C ₄ H ₉	C ₂ H ₅

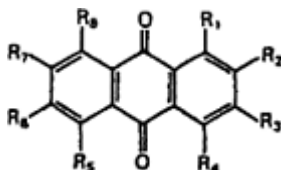
of acetone to the benzene extract increased the luminescence considerably in determinations with Butylrhodamine B, and the addition of acetone to the aqueous phase before the extraction with benzene increased the intensity of luminescence of the extract in determinations with Rhodamine 6G. In a further paper Babko *et al.* [57] used the same method with Butylrhodamine B but having previously removed the cations with an ion exchange resin in the acidic form.

Boron has been determined with salicylic acid and Rhodamine 6G [58, 59]. The excess of salicylic acid was removed, after evaporating the solution to dryness, by complexing it with iron(III). The complex of boron was extracted into benzene. The data were used for the development of a luminescence method for the determination of boron in waters [60].

In methods based on formation of complexes, the anion reacts with either one or two

reagents, giving rise to a binary or ternary fluorescent complex. Borate is the most common anion determined by this methodology. Neither of these methods is based on the phenomenon of quenching.

Although many anthraquinones have been described as photometric reagents of borate, only a few have been applied to the fluorometric analysis of this anion. Some of these anthraquinones are shown below.



Name

Substituent	Carminic acid	Quinizarin	Alizarin Red S
R ₁	OH	OH	H
R ₂	CO(CHOH) ₄ CH ₃	H	SO ₃ Na
R ₃	OH	H	OH
R ₄	OH	OH	OH
R ₅	COOH	H	H
R ₆	OH	H	H
R ₇	H	H	H
R ₈	CH ₃	H	H

1-Amino-4-hydroxyanthraquinone was the first anthraquinone tested for the qualitative fluorometric determination of boron. The complex shows up an intense orange-brown fluorescence in daylight in concentrated sulphuric acid [61,62].

A method for the determination of boron with carminic acid in buffered neutral solution has been described [63], with a standard deviation of 0.03 µg mL⁻¹. Initially the method involves the use of cochineal, a preparation obtained from the dried female insect *Coccus cacti* L., and of its chief active constituent, carminic acid [64].

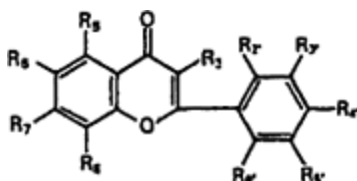
Holme [65] carried out a systematic investigation of complex formation in concentrated sulphuric acid between boric acid and a series of hydroxyanthraquinones (1,4-dihydroxy-, 1,5-dihydroxy-, 1,8-dihydroxy-, 1,2,3-trihydroxy-, 1,2,4-trihydroxy-, and 1,2,3,5,6,7-hexahydroxyanthraquinone). He found that quinizarin (1,4-dihydroxyanthraquinone) was the only reagent to produce a fluorescent complex and he described the determination of boron with this reagent.

Alizarin Red S changes its yellow fluorescence to pinkish red in the presence of boron [66,67]. A chelate ester with a six-membered ring is formed in the reaction. Boron can be determined with this reagent in the presence of a 1000-fold excess of most cations and anions; only iodides, chlorates, antimony and iron interfere. The interference of iodides is

eliminated by the addition of powdered silver sulphate, that of chlorates by the introduction of 30% formaldehyde solution, that of antimony by chlorine water and that of iron by reduction with tin(II) chloride powder.

Further fluorinated methods are based on the formation of binary or ternary hydroxy flavone or ketone complexes with boron. The hydroxy flavones used are shown below.

Murata and Yamauchi [68] described the determination of boron with morin based on the Taubock test [69]. A yellowish green fluorescence is produced in acetone solution. The authors verified that the intensity of the fluorescence increased in the presence of organic acids such as oxalic, malonic, succinic and phthalic acid. This method is applicable to the analysis of non saline waters without the separation of boron.

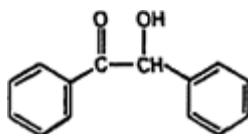


Name

Substituent	Flavonol	Quercetin	Kaempferol	Morin
R ₂ .	H	H	H	OH
R ₃ .	OH	OH	OH	OH
R ₃ .	H	OH	H	H
R ₄ .	H	OH	OH	OH
R ₅ .	H	OH	OH	OH
R ₅ .	H	H	H	H
R ₆	H	H	H	H
R ₆	H	H	H	H
R ₇	H	OH	OH	OH
R ₈	H	H	H	H

Ketones

Benzoin (i) is a fluorometric reagent widely used for the qualitative [70–73] and quantitative [46,48,74–78] determination of boron.



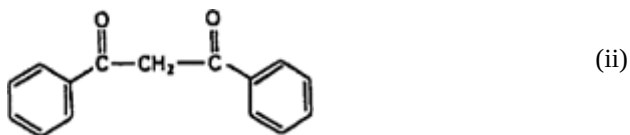
(i)

Parker and Barnes [48] carried out some experiments with spectrofluorometers and filter

fluorometers using the reaction of boron with benzoin. They showed that oxygen should be removed from this system and, although the maximum excitation is at 365nm, they recommended 405nm in order to decrease the decomposition of the reagent. In a later paper [46], these authors applied the method to the determination of boron in silicon (limit of detection about 0.03ppm) in seawater (with a precision of better than 2%).

White and Hoffman [74] showed that it is desirable to use a glycine buffer of pH 12.8 because the intensity readings are more stable than those obtained when using the original procedure in which sodium hydroxide was used. Elliot and Radley [76] also studied the deactivating effects of oxygen in this system and investigated other solvents in the hope of increasing the sensitivity of the reaction. They showed that the intensity of fluorescence when formamide is used is stronger than that when ethanol is used. They discussed the possible relationship between the dielectric constant of the solvent and the fluorescence intensity of the system. Other workers have applied this method to the determination of boron in raw material with iron [77] and in soils [78].

Boric acid forms a highly sensitive luminescent complex with dibenzoylmethane (ii) in concentrated sulphuric acid [51,79], which is proposed for the trace determination of boric acid. The limit of detection is 0.5ng mL⁻¹.



Neelakantam and Rao [80] proposed the determination of boric acid with resacetophenone (see below (iii)). In concentrated sulphuric acid a brilliant blue fluorescence is obtained with trace amounts of boric acid under ultraviolet radiation. A disadvantage of the method is the necessity of working under filtered ultraviolet radiation. In a later paper [81], various substituted resacetophenones were investigated in an attempt to find a material that would emit fluorescence in the visible range. No shift from the ultraviolet to the visible region were found, i.e. an increase in relative molecular mass did not bring about any shift of the fluorescence into the visible region. In the same paper, methods of overcoming interferences were discussed. The replacement of concentrated sulphuric acid by syrupy phosphoric acid rendered the method more sensitive [82], and also obviated the interference of some ions such as bromide, iodide and nitrate.

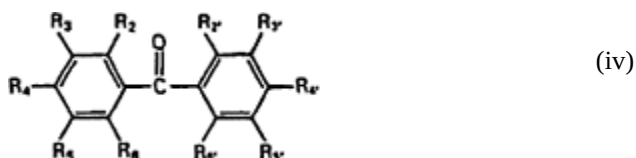


2,4-dihydroxybenzophenone forms a fluorescent complex with boric acid in sulphuric acid medium [83], with a stoichiometry of 1:1. Maximum fluorescence intensity is obtained after 10h. Under these conditions the blanks give a relatively high fluorescence because the reagent suffers partial oxidation and is converted into fluorescent products.

This is avoided by working at 70°C, where equilibrium is obtained in less than 20min. An essential factor is the purity of the acid utilised because if the sulphuric acid has only average purity, an increase in the photodecomposition of the blanks is observed and the spectral characteristics of the complex are modified.

Kristalev and Shevchenko [84] carried out a comparative study of methods for the determination of boron with 2,4-dihydroxybenzo-phenone and resacetophenone. They deduced that the former method is more sensitive but the fluorescence development is slow, the intensity depending on the ultraviolet irradiation time and the intensity decreasing in the presence of phosphate. The second complex forms almost instantaneously and is resistant to ultraviolet irradiation.

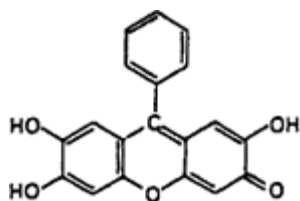
Marcantonatos *et al.* [85] studied the reactions of boric acid with nine substituted 2-hydroxybenzophenones (see below (iv)) in concentrated sulphuric acid: 2-hydroxy-4-methoxy-4'-chlorobenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4-n-octyloxybenzophenone, 2-hydroxy-5-chlorobenzophenone, 2-hydroxy-5-methylbenzophenone and 2,4,4'-trihydroxybenzophenone. All of these reagents form fluorescent complexes with boric acid. Their excitation spectra indicate that these complexes are similar in structure, and the fluorescence spectra show that the composition and intensity of fluorescent light depend on the electronic nature of the various substituents of the complexing agents. All of these reagents can be used for the determination of submicrogram amounts of boron, but 2-hydroxy-4-methoxy-4'-chlorobenzophenone is the most sensitive.



These workers also thoroughly studied the influence of some properties of the medium on the fluorescence of the boric acid—2-hydroxy-4-methoxy-4'-chlorobenzophenone complex [86]. When concentrated sulphuric acid is replaced by glacial acetic—concentrated sulphuric acid, the intensity of fluorescence increases considerably. The method has been applied to the determination of trace amounts of boron in analytical reagent grade sodium hydroxide [86], steels [87], plants [88], waters [89] and blood [44, 90]. Afghan *et al.* [91] developed an automated method based on this reaction for the determination of boron in non saline waters.

Other reagents

Shcherbov and Korzheva [92, 93] suggested a method for the determination of boron with phenylfluorone (see below (v)) in aqueous alkaline medium where the complex formed has a dark blue fluorescence [94]. On standing, the fluorescence intensity in solutions containing the reagent changes; in the blank solution it decreases, but in the solution containing boron it becomes higher; after a 24h period, 1µg of boron can

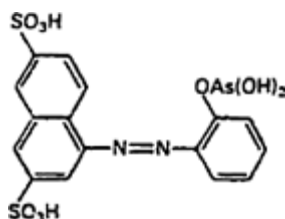


(v)

be detected in 1ml. This fluorescence persists for 2–3 days. Many cations interfere in the reaction by quenching of the fluorescence.

Nazarenko and Vinkovetskaya [95] studied sixteen 2,3,7-trihydroxy-6-fluorones with substituents in the 9-position as fluorescent reagents for boron. These reagents give fluorescence reactions of low sensitivity in neutral and weakly alkaline media with boron. The most sensitive reagent is phenylfluorone. Boron forms 1:1 complexes with trihydroxyfluorones by replacing the proton in the reagent molecule.

A method for the determination of boron with Thoron I [2-(2-hydroxy-3,6-disulpho-1-naphthylazo)benzenearsonic acid (see below (vi))] has been proposed [96]. It is slightly less sensitive than the method with benzoin, but is simpler and more precise and does not need special precautions. This method has been used to determine boron in high-purity silicon tetrachloride [97].



(vi)

Boric acid forms a fluorescent complex with salicylic acid [98]. Podchainova *et al.* [99] verified that decreasing the temperature from 20 to –196°C causes the fluorescence intensity to increase more than 10-fold. They also studied the reaction of boron with acetylsalicylic acid [100].

Chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulphonic acid) [36] has been proposed as a fluorometric reagent for boron. This method has a coefficient of variation of 2.9% for 0.5mM boric acid and 5.7% for 0.0mM boric acid. The addition of masking agents improves the selectivity of the method.

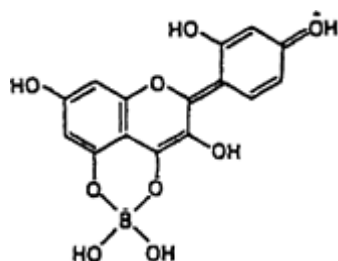
Formation of ternary complexes

Hydroxyflavones–oxalic acid

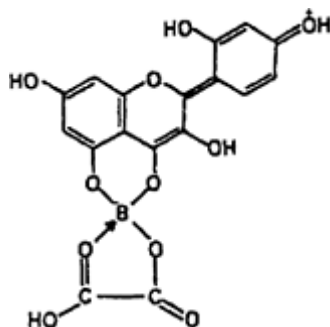
Pszonicki and co-workers [47,101–104] have studied extensively the determination of boron with morin, quercetin and kaempferol (see below (vii–xi)) in the presence of oxalic acid, by formation of ternary complexes.

The fluorescence of the boric acid-morin-oxalic acid complex is strongly quenched by alkali metals. This is probably caused by a reaction of the alkali metals with the 4'-

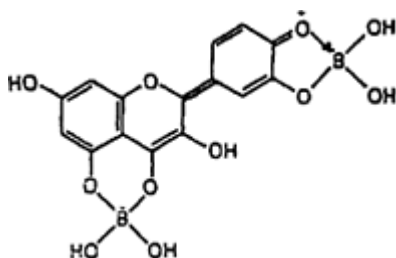
carbonyl group of morin and the resulting formation of compounds of the phenolate type. This reaction eliminates the conjugated double bonds that provide the fluorescence emission from the complex molecule. Alkali metals can be separated from boron with an ion exchange resin. In another paper [53] they described the formation and properties of two types of complex, a binary flavone-boric acid complex and a ternary flavone-boric acid-oxalic acid complex, in anhydrous acetic acid. The flavones studied were morin and quercetin and the proposed structural formulae are:



(vii)

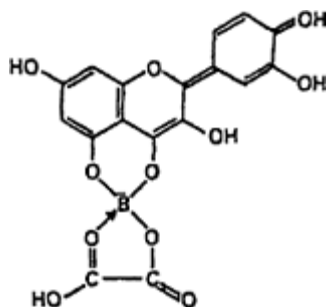


(viii)



(ix)

(x)



where (vii) and (viii) are the binary and ternary complexes of morin, respectively, and (ix) and (x) are the binary and ternary complexes of quercetin, respectively. All of these compounds have a flavone-boric acid stoichiometry of 1:1, except for the binary quercetin-boric acid complex, which has a ratio of 2:1. The ternary complexes in acetic acid decomposed to the binary complexes. The presence of about 1% of oxalic acid in the solution prevents degradation of the ternary complexes and improves their solubility considerably. Degraded ternary complexes can be reformed by addition of an excess of oxalic acid. The fluorescence spectrum of the binary complex coincides exactly with that of the ternary complex but the intensity is about 10 times lower. The fluorescence maximum for all of the complexes occurs at 505nm. The preparation of these compounds is based on the procedures of Hörhammer and Hänsel [105], and Hänsel and Strasser [106].

2.9.3 Flow injection analysis

Lussier *et al.* [45] determined borate in light and heavy water by flow injection analysis with indirect ultraviolet-visible spectrophotometric detection.

2.9.4 Atomic absorption spectrometry and emission spectrometry

Atomic emission spectrometry has been shown to be capable of determining down to 2µg boron in non saline waters [107–109]. Castillo *et al.* [110] exploited the extractions reaction between boric acid and methanol in a concentrated sulphuric acid medium to determine boron as methyl borate by flame atomic emission spectroscopy. The methyl borate formed was vaporised and introduced directly into the flame, so that no collection system or carrier gas were required. The possible interferences by competing ions were investigated and the results are tabulated, most ions caused no interference. Recoveries were in the range 90–100% for samples containing 0.25µg L⁻¹ boron.

Graphite furnace flameless atomic absorption spectrometry has been used [111] to determine 20–250µg L⁻¹ boron in water. The natural concentration of boron in river water is about 100µg L⁻¹. Samples are acidified to pH 2.0 and a magnesium/calcium solution is added before determination at 249.7nm, using a graphite furnace spectrometer.

Szydłowski [112] has described a method for determining down to less than 100µg L⁻¹ boron in natural and well waters. The recoveries were excellent at low concentrations, but

less satisfactory at higher concentrations. This may be the result of greater carbon-boron interactions at higher concentrations; this suggestion is supported by the broader peaks obtained. Dilution of samples may therefore be necessary, to ensure that they are run in the optimum range, when higher concentrations of boron are expected.

2.9.5 Ion selective electrodes

These are available commercially for the determination of borate in water.

2.9.6 Ion chromatography

Erkelens *et al.* [38] attributed three extraneous peaks (system peaks) produced from single-column ion chromatography of inorganic anions to complex formation of borate esters or polyhydroxy compounds (formed in the eluant at high pH) with polyvalent cations such as calcium. The behaviour of three system peaks obtained using high pH borategluconate buffer and a conductivity detector was studied in detail. All negative system peaks were avoided by treating samples with a cation exchanger in the sodium form prior to injection.

Hill and Lash [113] have also discussed the determination of borate in non saline water.

The application of this technique is also discussed under multianion analysis in section 12.2.5.

2.9.7 High performance liquid chromatography

Zun *et al.* [114] achieved a good separation of the anionic complex formed between boric acid and chromotropic acid using an ion exchange complex (TSKgelic-Anion-PW). This method showed few interferences from foreign ions, molybdenum(VI) and vanadium(V) causing positive errors at levels above 10 μ M.

2.9.8 Preconcentration

The application of preconcentration techniques is discussed in section 15.1.2.

2.10 Borofluoride

2.10.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.10.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.11 Bromate

2.11.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.11.2 High performance liquid chromatography

Salov *et al.* [115] determined bromate (also chloride, iodide, bromide, chlorate and iodate) in non saline waters by high performance liquid chromatography with an inductively coupled argon plasma mass spectrometric detector.

The application of this technique is also discussed under multianion analysis in section 13.1.1.7.

2.12 Bromide

2.12.1 Titration methods

The National Water Council (UK) [116] had described a classical titration procedure for the determination of bromide in river and seawaters in which bromide is oxidised to bromate by sodium hypochlorite at about 100°C in a medium buffered to pH 6.2 with phosphate. After reduction of the excess oxidant with formate, the bromate is determined iodometrically. The method is applicable up to 140 mg L⁻¹ bromide but is not designed for trace amounts, for which an alternative method is available. Iodine and certain oxidising or reducing agents interfere.

The potentiometric titration procedure described by Kuttel [117] for the determination of chloride in non saline water has also been applied to the determination of bromide.

2.12.2 Spectrophotometric methods

Yonehara *et al.* [118] have described a method for the determination of traces of bromide based on its catalysis of the pyrocatechol violet/ hydrogen peroxide reaction. The method was rapid, simple and sensitive and did not involve an extraction step. Most ions commonly occurring in non saline waters did not interfere except for iodide. Kinetic studies showed that the effect of bromide on the oxidation reaction was enhanced in the presence of large amounts of chloride (hydrochloric acid). Relative standard deviations were 6.4 and 13% respectively for 0.034 and 0.01mg bromide per litre.

In a further method [119], the sample is treated with hydrochloric acid and with chromotrope 2B (CI Acid Red) and 5 mmol L⁻¹ potassium bromide. The time taken for the colour to change from red to yellow as evaluated spectrophotometrically is measured and compared with calibration data obtained to known bromide standards.

The indirect Spectrophotometric method of Fishman and Skougstad [120] and Skougstad *et al.* [121] is based on the catalytic effect of bromide on the oxidation of

iodine to iodate by potassium permanganate in sulphuric acid solution. When an aqueous solution of iodine and permanganate is mixed with carbon tetrachloride, the iodine is extracted into the carbon tetrachloride. If bromide is present with the aqueous

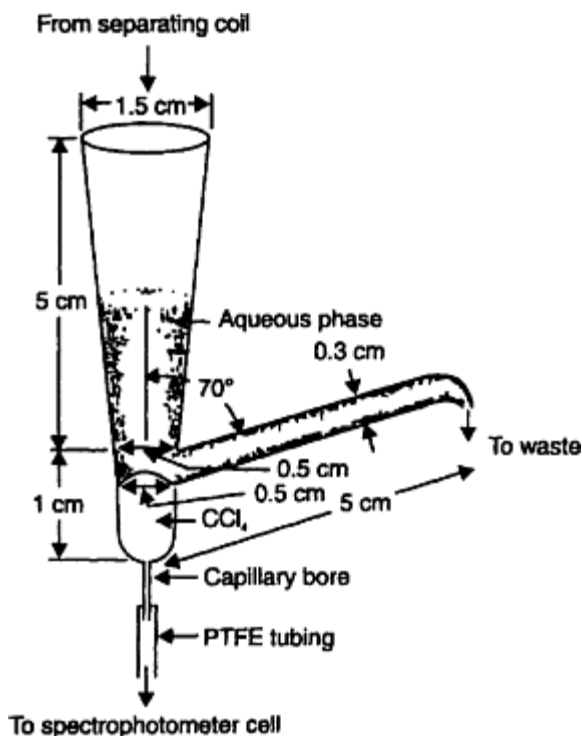


Fig. 2.5 Separator

Source: Reproduced with permission from the Royal Society of Chemistry [122]

iodine and permanganate for a certain time at a particular temperature prior to mixing with carbon tetrachloride, the amount of iodine remaining unreacted to iodate will decrease linearly with increasing bromide concentration. Iodine in a carbon tetrachloride extract can, therefore, serve as a sensitive measure of the bromide concentration in the aqueous solution. A skilled operator is required, as the reaction temperature and the time for each reaction step are very critical.

Pyen *et al.* [122] have described an automated version of the above manual kinetic method. This method is accurate and precise and quicker than the manual technique (20 samples per h). The detection limit is 0.01 mg L^{-1} bromide.

Apparatus

The automated equipment consists of a Technicon sampler, proportioning pump, manifold, spectrophotometer, voltage stabiliser and recorder. The spectrophotometer is fitted with specially designed matched 50mm flow cells and 529nm filters. The sampler

is used with a 20 h^{-1} (2/7) cam made by cutting off four sampling lobes from a 60 h^{-1} (2/1) cam. This results in

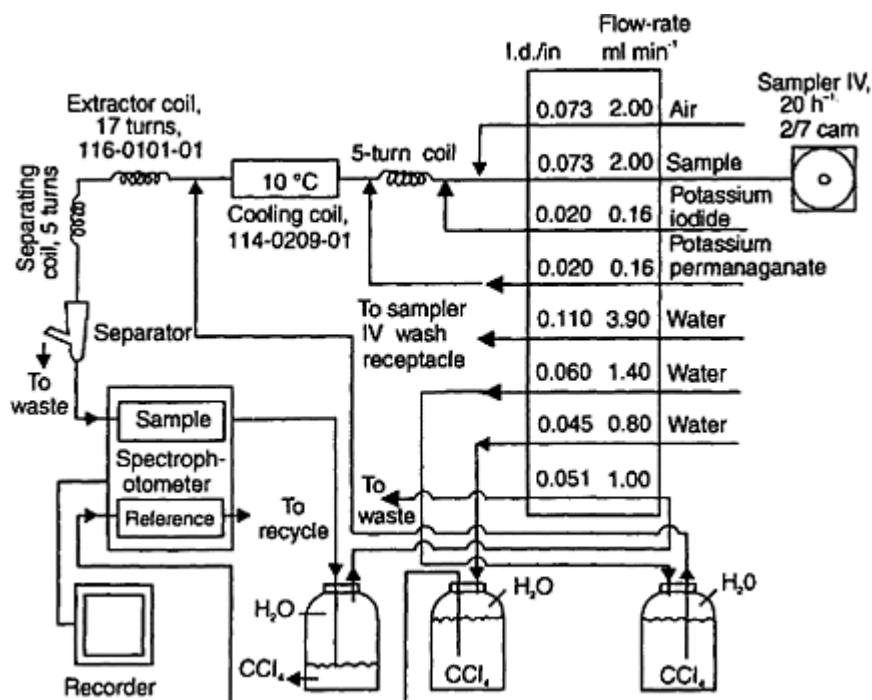


Fig. 2.6 Bromide manifold

Source: Reproduced with permission from the Royal Society of Chemistry [122]

a cycle time of 40s for sampling and 140s for rinsing. A 17-turn coil containing glass beads is used as the extractor. To separate the two phases, a five-turn mixing coil is placed perpendicular to the manifold; PTFE tubing is inserted inside the separating coil to facilitate rapid separation. All connections are made with glass tubing or silicone rubber sleeving. The final separator (Fig. 2.5) has a top portion that is enlarged to facilitate the clean separation of solvent from the aqueous phase. Three 11 flasks are used for the displacement of carbon tetrachloride. Connections are made with 1.0mm PTFE tubing. A circulating System-225 cold bath (GCA/Precision Scientific) maintains the reaction temperature of the condenser coil at 10°C .

Procedure

The manifold system (Fig. 2.6) is set up in a well ventilated hood to avoid contact with carbon tetrachloride vapour. The potassium iodide and potassium permanganate solution are placed in an ice bath. Demineralised water is fed into all reagent and sample lines, allowing sufficient time for good separation of carbon tetrachloride from the aqueous phase. The spectrophotometer is peaked optically and then the reversing switch is set

under the spectrophotometer cover to position I (inverse). The CAL control is set to position 2.0 and locked, and the Display Rotary Wwitch to Damp I. The reagents are fed through the system. Reaction will occur, and iodine will be extracted into the carbon tetrachloride, resulting in deflection of the recorder from full scale to the base line. The base line is adjusted to read approximately 5 chart divisions and allowed to stabilise (approximately 20min). A complete set of standards covering a concentration range from 0.01 to 0.20 mg L⁻¹ is placed in the first positions of the sample tray followed by a blank. Individual standards of different concentrations are placed in several positions of the remainder of the tray. The oxalic acid solution (SO₄H₂C₂O₄·2H₂OL⁻¹) is placed in the 38th position, followed by two blanks. The remainder of the tray is filled with unknown samples and the analysis begun.

A calibration graph is prepared by plotting the height of each standard peak against its respective bromide concentration. With the CAL control in position 2,0, the peak height reading for 0.20mg L⁻¹ of bromide using a Technicon recorder was about 30 chart units. Calculate the bromide concentration of each sample by comparing its peak height with the calibration graph. Any baseline drift that may occur must be taken into account when calculating the height of a sample or standard peak.

Spiking experiments carried out by this method gave recoveries in the range 94–110%.

A method based on the use of methyl orange [123] involves conversion of bromide to bromate, catalysed decomposition of bromate in acetic acid solution and spectrophotometric determination of the reduction in the optical density of methyl orange by the bromide.

Various other spectrophotometric methods have been described for the determination of low concentrations of bromide in non saline waters. These include methods based on the formation of coloured products with Chromotrope 2B (CI Acid Red), acid [119] roseaniline [124] (0.4mg L⁻¹), phenol red [125,126] (200µg L⁻¹) and o-toluidine [127] (detection limits in parentheses). A further method is based on oxidation of bromide to bromate by hypochlorite and subsequent decoloration of methyl orange by bromine formed by interaction of the bromate with bromide [128]. This method will detect 8µg L⁻¹ bromide in non saline water.

Yonehara *et al.* [129] developed a kinetic-spectrophotometric method for determining bromide (0.004–0.3mg L⁻¹ in non saline water) based on its catalysis of the oxidation of pyrocatechol violet by hydrogen peroxide in hydrochloric acid/sulphuric acid. They state that the effect of bromide is greatly increased in the presence of large amounts of chloride, but that most ions commonly occurring in non saline waters do not interfere except for iodide. The relative standard deviations (*n*=10) were 6.4% for 0.034mg of bromide L⁻¹ and 13% for 0.010mg of bromide L⁻¹. These workers have also reported a flow injection spectrophotometric determination of bromide, based on the same reaction. In this method the sampling rate employed was 45 samples/h with 500µL injection, the detection limit was 10µg L⁻¹ and relative standard deviations were 2.5% and 1.4% for 20µg L⁻¹ of bromide L⁻¹ and 105µg of bromide L⁻¹ respectively.

2.12.3 Spectrofluorometric method

Bromide has been determined by a method based on the quenching by bromine of the

fluorescence of fluorescein [130]. It has been applied to measurement of bromine aerosols and airborne particulates.

2.12.4 Flow injection analysis

Anfalt and Twengstrom [131] give details of equipment and a procedure for the determination of low concentrations of bromides in non saline waters by modifying the phenol red method for use in a flow injection system. The effect of various potential interfering substances was investigated. Ammonia, cyanide, and humic substances caused interference; ways of minimising the effects are indicated.

Freeman *et al.* [132] determined bromide in environmental waters by flow injection analysis.

The application of this technique is also discussed under multianion analysis in section 14.4.1.2.

2.12.5 Inductively coupled plasma atomic emission spectrometry

Michlewicz and Carnahan [133] give details of a method for the determination of bromide based on pneumatic nebulisation of the sample into a helium microwave induced plasma. The detection limit was 0.4mg L^{-1} . Potassium, magnesium, sodium and lithium interfered moderately with pneumatic nebulisation and significantly with ultrasonic nebulisation.

2.12.6 Cathodic stripping voltammetry

The application of this technique is discussed under multianion analysis in section 14.9.1.1.

2.12.7 Ion selective electrodes

Ion selective electrodes have been used for the determination of bromide in water [134].

2.12.8 X-ray spectrometry

Direct X-ray spectrometry, utilising the bromine $K\alpha$ line has been used to determine mg L^{-1} quantities of bromide in non saline waters. In one method the bromide was retained on an anion exchange column [135] and in another the liquid sample was contained in a lucite cup [136].

2.12.9 Helium microwave induced plasma method

Michlewicz and Carnahan [137] give details of a method for the determination of bromide, iodide and chloride based on pneumatic nebulisation and ultrasonic nebulisation of the sample into a helium microwave induced plasma.

Detection limits in mg for chloride, bromide and iodide were 0.4, 3.0 and 0.8 respectively. Interference effects from added potassium, sodium and lithium were

moderate with pneumatic nebulisation but significant with ultrasonic sample nebulisation.

2.12.10 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.1, 12.2.4 and 12.2.5.

2.12.11 High performance liquid chromatography

Stetzenbach and Thompson [138] employed high performance liquid chromatography on anion exchange columns to determine bromide in admixture with chloride, iodide, nitrate and thiocyanate in non saline waters.

Moss and Stephen [139] determined bromide, chloride and iodide in non saline waters by conversion to alkyl halide and measurement by high performance liquid chromatography.

The application of this technique is also discussed under multianion analysis in sections 13.1.1.2, 13.1.1.4 and 13.1.1.7.

2.12.12 Ion exchange chromatography

Akaiwa *et al.* [140] have used ion exchange chromatography on hydrous zirconium oxide, combined with detection based on direct potentiometry with an ion selective electrode, for the simultaneous determination of chloride and bromide in non saline waters.

Salov *et al.* [141] have described a procedure for determining bromide (and chloride, iodide, chlorate, bromate and iodate) in water employing high performance liquid chromatography with an indirectly coupled argon plasma mass spectrometric detector.

2.12.13 Micelle chromatography

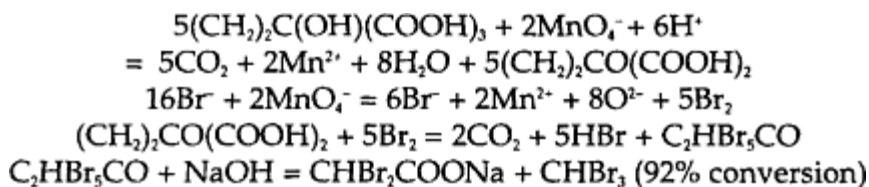
Okada [142] has used micelle exclusion chromatography to determine bromide in the presence of anions (iodide, iodate, nitrite and nitrate) in water. The method is based on partition of the anions to a cationic micelle phase and shows different selectivity from ion exchange chromatography.

Okada [142] also used micelle chromatography to analyse mixtures of bromide, iodide, nitrite, nitrate and iodate.

The application of this technique is also discussed under multianion analysis in section 13.5.1.2.

2.12.14 Gas chromatography

Narasaki *et al.* [143] determined bromide in non saline waters by head space gas chromatography. The solution containing bromide ($>0.3\mu\text{g}$) was evaporated to dryness, and the residue was oxidised with a citric acid solution, potassium permanganate solution, and an manganese dioxide suspension in sulphuric acid to form $\text{CHBr}_2\text{COBr}_3$ which was then decomposed with sodium hydroxide to form bromoform

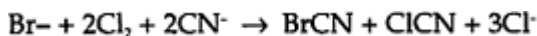


The bromoform was determined by head space gas chromatography. The calibration graph was linear for amounts of bromide in the range of 0.3–5.0 µg and the detection limit was 0.1 µg. The relative standard deviation was 4.3% for 2.0 µg of bromide. Chloride ion (<1000 µg) did not interfere. Aluminium, iron, zinc and humic acid had a positive interference, and iodide, glutamic acid and glucose had a negative interference.

Ando and Sayato [144] have described a gas chromatographic method for the determination of bromide ions in water. These workers found that the use of an ion exchange gas chromatograph using strong anion exchange resins enabled them to separate and concentrate chloride and bromide. The bromide was eluted with 0.1 mol L⁻¹ sodium nitrate through a 70mm column, until 70 ml of eluate was obtained (total 130ml). After elution of chloride with dilute sodium nitrate, the solution of bromide could be eluted with 0.5 mol L⁻¹ sodium nitrate. Interfering effects of phenols and humic acids could also be overcome by these procedures.

Bromide concentrations down to 1–2 µg L⁻¹ can be determined by this procedure. Calibration curves are linear up to 1.5 mg L⁻¹ bromide.

Nota *et al.* [145] have devised a simple and sensitive method for the determination of amounts of bromide down to 0.05 mg L⁻¹ in water. The procedure is in two stages. Cyanogen bromide is formed by the reaction between bromide, chlorine and cyanide. Cyanogen bromide is then separated by gas chromatography and selectively detected with an electron capture detector.



It should be noted in this method that the internal standard (nitromethane) must always be introduced after the addition of cyanide in order to prevent rapid darkening of the solutions, which causes nonreproducible results. No interferences are caused by oxidising or reducing substances or by mercury or cadmium at concentrations below 200 mg L⁻¹. Mercury and cadmium are, among the metals, the strongest complex-forming agents with bromide.

Even small amounts of aromatic compounds are likely to produce some interferences owing to their tendency to bind bromide, which is formed by reaction with chlorine water.

The application of gas chromatography is also discussed under multianion analysis in section 14.1.1.2.

2.12.15 Preconcentration

The application of preconcentration techniques is discussed in section 15.1.3.

2.13 Butyrate

2.13.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.4 and 12.2.5.

2.13.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.14 Carbonate and alkalinity

2.14.1 Carbonate

2.14.1.1 Flow injection analysis

Workers at Tecator Ltd [146] in an application note point out that carbonate is present in aqueous solutions as H_2CO_3 , HCO_3^- and CO_3^{2-} . The concentration of each species depends on pH. In strongly alkaline solutions CO_3^{2-} predominates. In acidic solutions gaseous carbon dioxide is formed

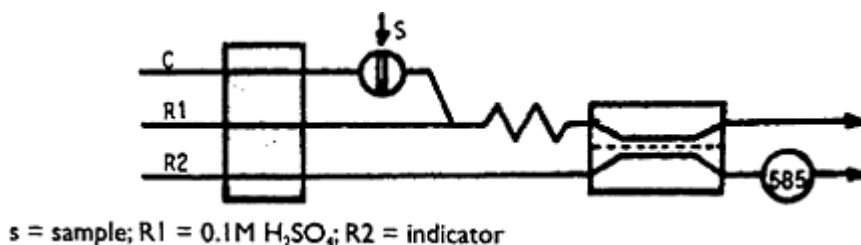
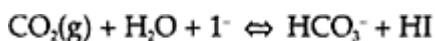


Fig. 2.7 Flow injection manifold, determination of carbonate

Source: Reproduced with permission from Tecator Ltd [146–148]

The principle of this application is that the aqueous sample containing carbonate is

injected into a carrier stream which is merged with a stream of sulphuric acid. Gaseous carbon dioxide is then formed which diffuses through a gas permeable membrane into an indicator stream. The indicator stream comprises a mixture of acid-base indicators and the reaction can be written.



By this reaction the anion concentration will decrease and the colour shift is measured photometrically. Coloured samples and samples containing small particles can be analysed as long as clogging can be prevented.

In a further flow injection analysis method for the determination of 20–180 mg L⁻¹ [147] or 100–1 000 mg L⁻¹ [148] total carbonate, the aqueous sample is injected into a carrier stream and mixed with 0.1 M sulphuric acid (Fig. 2.7). The joint stream passes along a PTFE membrane in a gas diffusion cell. The carbon dioxide formed diffuses through the membrane into an indicator stream. The resulting colour change of the indicator is measured at 585–590 nm.

The application of this technique to the determination of carbonate is also discussed in section 14.4.1.4.

2.14.1.2 Ion chromatography

This technique has been applied to the codetermination of carbonate and bicarbonate in natural and potable waters [149].

The application of this technique is also discussed under multianion analysis in section 12.2.5.

2.14.2 Total alkalinity

2.14.2.1 Titration methods

Alkalinity of water is its acid-neutralising capacity. It is the sum of all the titratable bases, and it is determined by titration with a standard solution of a strong mineral acid. In non saline waters, alkalinity is primarily a function of carbonate, bicarbonate and hydroxide content though borates, phosphates, silicates and other bases may contribute. If the only anions present in a solution are hydroxide and carbonate there will be two endpoints in the titration with acid; the first endpoint occurs at about pH 8.3 and corresponds to the hydroxide and half the carbonate; the second endpoint occurs at about pH 4.5 and corresponds to the rest of the carbonate [150].

In the classical determination of alkalinity by titration with an acid, phenolphthalein is used to indicate the pH 8.3 endpoint and methyl orange to indicate the pH 4.5 endpoint. Alkalinity determined with reference to these two endpoints is often called ‘P and M alkalinity’. The terminology is still in use, even though it is more usual today to use a calibrated pH electrode as an endpoint indicator. The ‘total alkalinity’ is based on the amount of acid required to neutralise the sample to the pH 4.5 endpoint; in many

determinations of alkalinity, especially in neutral waters where there is no hydroxide present, the only result required is 'total alkalinity'. Both types of alkalinity are usually expressed in units of ppm (or mg L^{-1}) calcium carbonate.

Sulphuric or hydrochloric acids are the usual acids used as titrants. Sulphuric is often preferred because chloride can be titrated with silver nitrate in the same sample solution after the alkalinity has been determined.

Several approaches to carrying out alkalinity titrations are possible.

(i) Preset endpoint

To measure 'total alkalinity' titrate to pH 4.5. If the sample pH at the start of analysis is greater than pH 8.3, two methods can be used if desired. In the first method, titrate to pH 8.3. The result from the second titration is added to the first result to give the 'total alkalinity'. The two methods can be linked together in a 'sequence'.

Nearly all standard methods for alkalinity titration are based on preset endpoint techniques. The greatest advantage of the preset technique occurs when the samples are complex, and buffered; in such samples it can be difficult to obtain clearly defined inflexion points. The pH electrode is calibrated in buffer solutions before using the preset endpoint technique.

(ii) First derivative, second derivative

First or second derivative techniques can be used for alkalinity titration if clearly defined, reproducible inflexion points can be obtained. Evaluate the sample before finalising a method. A good method of evaluation is to programme a maximum volume of 25ml of titrant, and 10mV constant increment, terminate the titration when the pH value of the sample solution has fallen to below pH 3.5. If two endpoints have been found, they probably correspond to 'P and M alkalinity' as defined above. Confirm this by checking the calculated pH values of each endpoint. If only one endpoint has been found, and the pH of the solution at the start of the titration was below pH 8.3, the endpoint probably corresponds to the total alkalinity.

(iii) Gran function

This is a powerful technique for measurement of alkalinity, but it has only recently become possible to perform automatic titrations based on Gran functions. The weak carbonate base is titrated with a strong acid. The result of the titration should indicate two endpoints; the first corresponds to the disappearance of hydroxide plus the first half of the carbonate as they are titrated with acid, and it represents the P alkalinity. The second corresponds to the appearance of strong acid after all the alkalinity has been titrated, and it represents the total alkalinity. The Gran technique is especially useful for resolving the two endpoints when carbonate levels are low compared with hydroxide, and for titrating low levels of total alkalinity. Non-continuous stirring is recommended if readings are required in a quiescent solution; this tends to maximise stability of electrode reading.

Hillbom *et al.* [151] describe a probe which allows potentiometric titration of total alkalinity to be automatically carried out *in situ* in non saline waters.

Automated methods of measuring alkalinity are typically based on the change of pH of a buffer containing methyl orange. The methyl orange is buffered at a pH at the acid end of the transition range of methyl orange. Additions of alkalinity cause the colour of the

methyl orange to change gradually from orange to yellow as the pH increases within the transition range.

Two instruments that are used to automate the measurement of alkalinity are the Technicon AutoAnalyzer and the Coulter Kem-O-Lab Industrial Model, made by Coulter Electronics. Coulter Electronics has published methods that are useful for concentrations of alkalinity from 10 to 500mg L⁻¹ as CaCO₃, whereas published methods for the Technicon AutoAnalyzer are useful only in the range of 100–500mg L⁻¹. Willis and Mullings [152] modified this apparatus to make it suitable for the measurement of concentrations of less than 50mg L⁻¹, a concentration commonly encountered in non saline water samples.

Reagents

As follows.

Table 2.3 Reagents and instruments used for different alkalinity determination

Reagent ^a	Instrument	ml of buffer	ml of methyl orange	ml of Brij-35	Range, mg L ⁻¹	
					Linear	Usable
A	TAA ^b	10	85	2	10–90	4–140
B	TTA ^b	60	85	2	50–250	10–600
C	TAA ^b	125	50	2	200–650	10–900
D	IKL ^c	43.5	32.6	0	10–90	4–150
E	IKL ^c	392	32.6	0	160–900	50–1000

^aEach reagent also contains enough water to make a total volume of 500 ml.

^bTAA–Technicon AutoAnalyzer.

^cIKL–Coulter Kem–O–Lab Industrial Model IKL.

Source: Reproduced with permission from the American Chemical Society [152]

Methyl orange stock solution, methyl orange 0.05% in water.

pH 3.1 buffer. Dilute 5.1 g of potassium acid phthalate with 87.5ml of 0.1N hydrochloric acid to 500ml with distilled water and adjust the pH to 3.1 with IN hydrochloric acid.

Methyl orange reagent. Mix varying amounts of methyl orange stock solution and buffer (Table 2.3) and dilute with distilled water. Prepare this reagent fresh daily. If the reagent is to be used with the Technicon AutoAnalyzer then also add 2 ml of Brij-35 (obtained from Technicon Instrument).

Alkalinity Standards. Prepare alkalinity standards of approximately 1000mg L⁻¹ as CaCO₃ by dissolving 1.060g of sodium carbonate in 1000ml of distilled water. Determine the exact concentration by titrating with 0.02N hydrochloric acid.

Apparatus

The Technicon AutoAnalyzer II, Industrial Model, was used with the same manifold as

described by Technicon for the measurement of alkalinity. A 15×2.0mm flow cell and a 550nm filter were used. The electronic gain on the colorimeters can be varied from 0 to 100. For the purpose of comparison the gain was set at 10.0. The Coulter Kem-O-Lab (IKL) was used following manufacturers' recommended procedure for measuring alkalinity. The IKL automatically takes a standard volume of sample and mixes it with 0.5ml of distilled water and 1.0ml of methyl orange reagent. Measure the absorbance with a 2cm flow cell and a wavelength of 540nm 12min after the reagent is added.

The titration was performed with a Brinkman pH meter, to monitor the pH and a Dosimat E535 (Brinkman) to deliver the titrant. Titrate a 25ml

Table 2.4 Comparison of results of alkalinity tests by titration

Sample	Titration	<i>Kem-O-Lab</i>		<i>Coulter</i>		<i>Technicon AutoAnalyser</i>	
		<i>mg L⁻¹</i>		<i>mg L⁻¹</i>		<i>mg L⁻¹</i>	
	<i>Mean</i>	<i>std dev</i>	<i>Mean</i>	<i>Std dev^a</i>	<i>Mean</i>	<i>Std dev^a</i>	
1103	26.1	0.9	26.5	0.5	25.4		0.2
1111	44.6	0.3	44.1	0.5	44.3		0.1
1112	14.9	0.7	15.2	0.9	13.9		1.2
1113	13.4	0.7	13.8	1.3	13.4		2.3
1114	20.3	0.7	10.6	0.6	18.7		1.5
1116	56.6	0.3	57.3	0.3	57.8		0.9
1118	147	0.3	144	3.5	141		1.4
1119	104	0.3	102	3.6	104		2.9
1120	226	1.6	259	2.4	264		1.2
Av		0.6		1.4			1.3

^aBased on five measurements for each determination of mean or standard deviation

Source: Reproduced with permission from the American Chemical Society [152]

sample to a preliminary endpoint of pH 5.6 with 0.02N sulphuric acid. With this volume of titrant as a measure of the approximate alkalinity, the sample was further titrated to a final endpoint based on the relationship of equivalence point pH to total alkalinity as described by Thomas and Lynch [153].

Willis and Mullings [152] concluded that five reagents would be sufficient to measure alkalinity at concentrations ranging from 5 to 700mg L⁻¹ CaCO₃ on the Technicon AutoAnalyzer. Solutions with concentration from 5 to 550mg L⁻¹ CaCO₃ will be within the linear range of at least one reagent. The reagents used are listed in Table 2.3 along with the range of linear and usable concentrations. The reagents that were used with the Coulter Instrument are the same as those described in their manual and are included in Table 2.3 for completeness. The calibration curves have a linear portion in the middle and a curved portion on each end. The usable range includes the linear portion as well as

some of the curved portion at each end.

In Table 2.4 are shown results obtained in alkalinity determinations on non saline water samples by the manual titration method and the two automated methods discussed above.

The titration method has greater reproducibility than automated methods, but it is much slower. About 8h are required for a set of 80 samples, whereas for both the automated methods analysis takes less than 2h for a set of 80. Also, once the standardisation is completed, the automated instruments require almost no attention. Both instruments were equally reproducible, i.e. the coefficient of variation was 2% for four or more samples analysed on separate days. Special precautions were needed in the automated methods to avoid carry over effects between one sample and the next.

2.14.2.2 Segmented flow analysis

The National Water Council (UK) [154] has described three methods for determining alkalinity in river water. These comprise the determination of alkalinities in the range 20–100mg L⁻¹ as calcium carbonate, the determination of alkalinity at low levels, ie below 20µg L⁻¹ as calcium carbonate, and the use of a continuous flow air-segmented system for automated determinations in the range 20–300mg L⁻¹ as calcium carbonate in polluted waters and certain types of trade waste waters. Each of the methods described is empirical in nature but correct adherence to the stated procedure will enable reproducible results to be obtained. In the preamble, a number of alternative systems commonly used to express alkalinity values are compared and some examples of the amounts of alkalinity contributed by the sodium salts of weak acids are tabulated.

2.14.2.3 Flow injection analysis

Canate *et al.* [155] have described a flow injection analysis system for the simultaneous determination of the alkalinity, pH and total ionic concentration of potable water. The pH measurements are performed by means of a glass calomel microelectrode inserted into the water stream. The alkalinity and total ionic concentration are determined by flow injection analysis titrations, acid base reactions and spectrophotometric detection. In addition, the determination of the total ionic concentration requires the incorporation of an ion exchange minicolumn. The results obtained are in agreement with those obtained by conventional methods for the determination of these parameters and are obtained with higher degrees of automation, which results in a smaller reagent consumption, greater convenience and higher reproducibility and sampling frequency. A microcomputer is installed for on-line data collection and the treatment and display of results.

The apparatus consists of a Pye Unicam SP6–500 spectrophotometer connected to a Radiometer REC–80 recorder, a FIA tron 721 flow cell with a glass calomel microelectrode connected to a Beckman 3500 pH meter for continuous monitoring of the pH, a 150×3mm Omnifit minicolumn packed with Dowex 50–X8 cationic resin in proton form, a Gilson Minipuls–2 peristaltic pump, a Hellman 178.10QS flow cell, two Tecator L100–1 injection valves, a Rheodyne 5301 three-way valve and a Hewlett

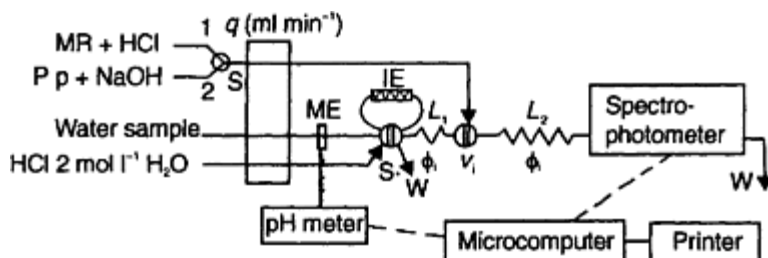


Fig 2.8 Manifold for the simultaneous determination of pH, alkalinity and total ionic concentration, MR=methylred, pp=phenol phthalein (for details see text)

Source: Reproduced with permission from the Royal Society of Chemistry [155]

Packard HP-85 microcomputer with HP 3478A analogue to digital converter and an HP-1B 82937 interface.

Manifold

Fig. 2.8 shows the reversed FIA configuration used. It involves the use of two detectors; a potentiometric detector ME (a glass microelectrode) located before the confluence of the sample with any reagent for the continuous monitoring of pH, and a spectrophotometric detector for the monitoring of the acid base reactions. Two serial injection valves are placed along the water stream. The first of these, S' , is aimed at incorporating the ion exchange microcolumn (IE) into the stream in order to determine the total ionic concentration. This valve is synchronised with the selecting valve S and in the filling position of valve S' , selects channel 1 (methyl red in an acidic medium) which fills the loop of V_i (ordinary injection valve 1126 μL). The alkalinity of the water sample is determined in this position. In the emptying position, S' incorporates the mini-column IE, S selects channel 2 (phenolphthalein in a basic medium) and the determination of the total ionic concentration is carried out. The flow rate adopted was 0.75 ml min^{-1} and the reactor lengths $L_1=2.40 \text{ cm}$ and $L_2=110 \text{ cm}$.

The microcomputer collects the data from both detectors and, by means of the computer program described below, processes the data and gives the pH, alkalinity and total ionic concentration for each sample.

Computer program

The microcomputer collects the pH and absorbance values (measurement frequency, 0.2s) which are introduced into a BASIC program. The data acquisition process starts at a time from the reagent injection equal to the travel time, so that as little memory as possible is used. Data treatment is

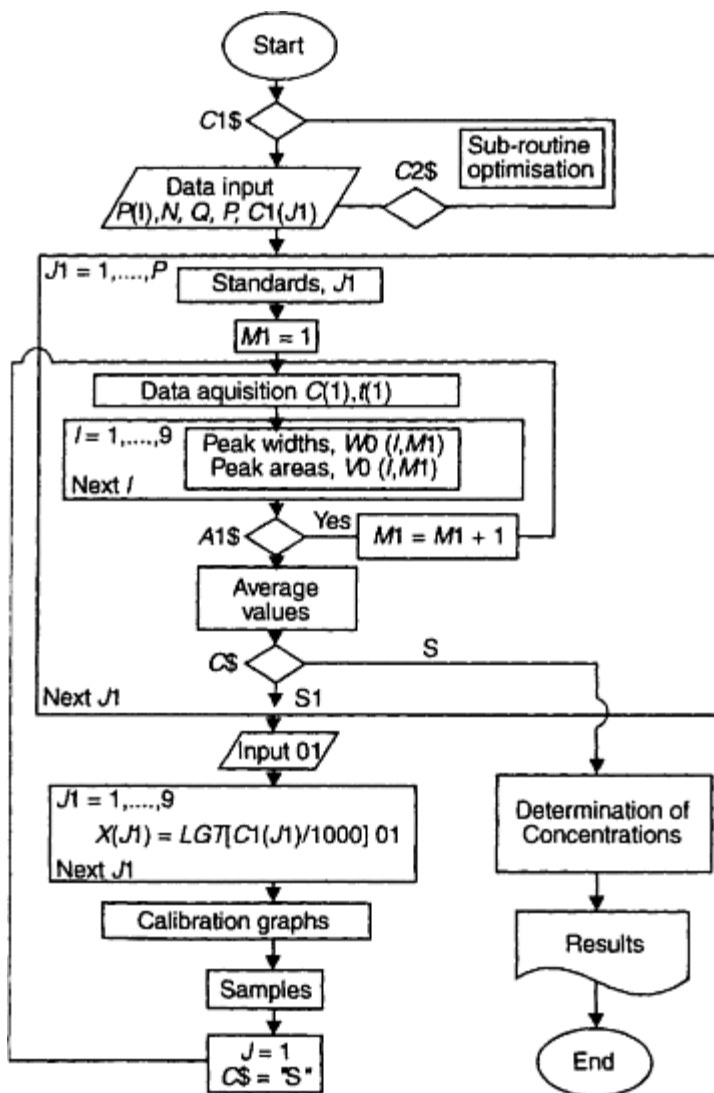


Fig. 2.9 Flow diagram of the computer program, C1%=inquiries to the program; P(1)= measurement height; N=number of absorbance-time data points; A=interval between two consecutive data points; P=number of standards; C1(j1)=concentration of standards; C(1)=concentration of analyte; t(1)=time; WO=peak width; VO=peak area; 01=molecular mass; S=sample; SI=standard; and J1, M1 and I=counters

Source: Reproduced with permission from the Royal Society of Chemistry [155]

carried out according to the scheme in Fig 2.9. The width of each peak (in seconds) at

heights pre-fixed by the user for the sample, standards and blanks, is collected. The program features a subroutine for the optimisation of each system. The program also allows data to be discarded from anomalous peaks or standards that would give a low correlation coefficient for the linear range of the calibration graph. This corresponds to the change in the width (Δt) at a height h as a function of $\log C$ (C = analyte concentration).

Alkalinity is measured by titration with hydrochloric acid to the methyl red endpoint.

Similar to a conventional titration, the reaction is monitored after the equivalence point so that the blank signal (distilled water) shows a higher peak width. The greater the alkalinity, the smaller is the peak width. The analytical signal was $\Delta t_{\text{blank}} - \Delta t_{\text{sample}}$ so that the slopes of the calibration graphs were positive. To determine total ionic concentration the salts present in the water sample are transformed into their corresponding acids on passing through the cationic resin in the H^+ form. The acids are then titrated with sodium hydroxide and phenolphthalein. In this method the minicolumn is placed in the loop of valve S' (Fig. 2.8) which is inserted into the circulating stream in the emptying position.

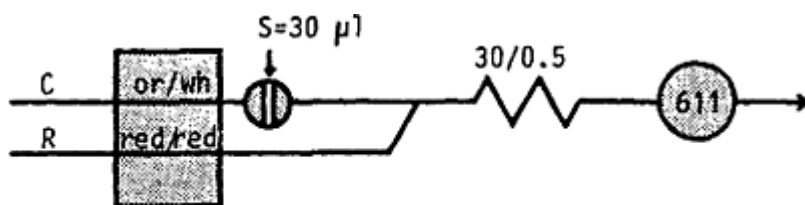
In the filling position, the minicolumn is regenerated with a sodium hydroxide stream and washed with distilled water, thus allowing continuous use for 4–5h.

The reaction is monitored at 552nm (after the equivalence point in the conventional titration) so that, as in the above system, the peak width is wider for the blank than for the samples.

As the insertion of a glass calomel microelectrode into the flow injection analysis configuration introduced no species that disturb the system, pH monitoring can be readily carried out by inserting the sensor prior to the reagent injection (Fig. 2.8) and calibrating it with standard buffer solutions at the working flow rate.

Table 2.5 summarises the features of the simultaneous determination of alkalinity, pH and total ionic concentration.

Workers at Tecator Ltd have published flow injection analysis methods for the determination of total alkalinity [156] in non saline waters. In this method the sample zone is merged with an acidic bromocresol green reagent (Fig. 2.10). Depending on the amount of acid consumed, the indicator changes its colour from yellow to blue.



C = water; S = sample; R = bromo cresol green in 0.8M acetic acid (pH 3.5)

Fig. 2.10 Flow injection manifold, determination of total alkalinity

Source: Reproduced with permission from Tecator Ltd [156]

Table 2.5 Features of the simultaneous determination of pH, alkalinity and total ionic

concentration

Parameter	Detection method	Range of determination ^a	Equation of calibration graph ^b	Regression coefficient	RSd, % concentration
pH	Potentiometric (continuous control)	3–11			
Alkalinity	Spectrophotometric	Δt : 5.0–600 $\mu\text{g mL}^{-1}$ CaCO_3 ΔS : 10.0–600 $\mu\text{m mL}^{-1}$ CaCO_3	$\Delta t = 31.28 \log C + 151.5$ $\Delta S = 3.48 \log C + 17.3$	0.9952 0.9965	$\pm 1.5 (11.9 \mu\text{g mL}^{-1})$ $\pm 1.7 (11.9 \mu\text{g mL}^{-1})$
Concentration	Spectrophotometric	0.7–2.8 mequiv L^{-1} Cl^- 2.8–2.7 mequiv L^{-1} Cl^-	$\Delta t = 3.09 \log C + 9.4$ $\Delta t = 34.43 \log C + 109.3$ $\Delta^s = 2.53 \log C + 7.4$	0.9998 0.9994 0.9790	$\pm 3.4 (7.04 \text{ mequiv L}^{-1})$ $\pm 2.1 (7.04 \text{ mequiv L}^{-1})$ $\pm 3.5 (7.04 \text{ mequiv L}^{-1})$

^a Δt =peak width/s ΔS =peak area covered by the base line and the measured height^b C =analyte concentration

Source: Reproduced with permission from the Royal Society of Chemistry [155]

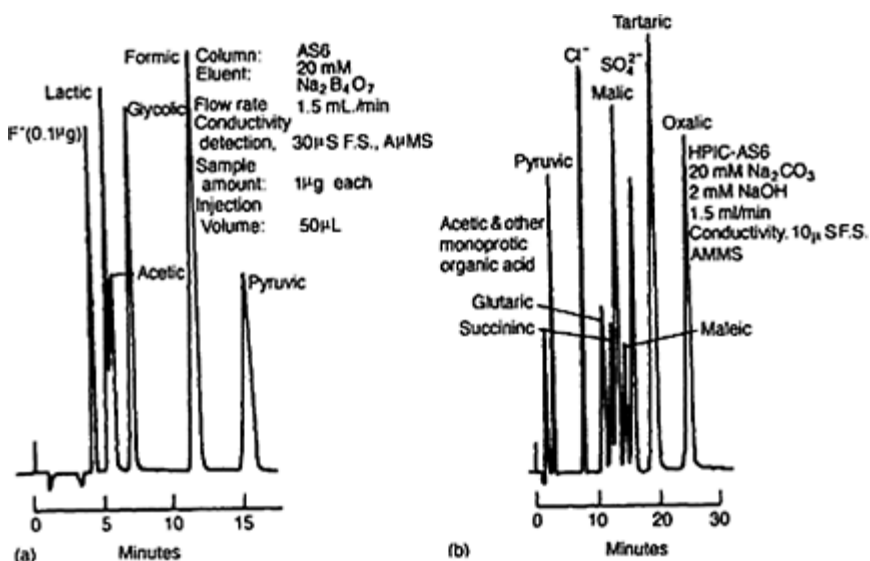


Fig. 2.11 Ion chromatograms obtained with Dionex instrument using (anodic)

AMMS and CMMS micromembrane suppression; (a) monoprotic organic acids
by anion exchange; (b) diprotic organic acids by anion exchange

Source: Own files

2.14.2.4 Miscellaneous

Pearson [157] has proposed a method for determining alkalinity (and acidity) employing fixed endpoints and involving less manipulation of samples than existing methods of analysis. It involves calculation of alkalinity and acidity values to equivalence endpoints from results of titrations to pH 4.5 and pH 8.3. The validity of the technique was confirmed experimentally within a limited range of conditions, although some anomalous results may be obtained in some waters such as those of high ionic strength.

The measurement of alkalinity in non saline water has been discussed by several other workers [20,151,152,158–160].

2.15 Carboxylates

2.15.1 Ion chromatography

Some typical separations of anions achieved within this system are shown in Fig. 2.11. Fig. 2.11(a),(b) illustrates ion chromatographic separations of mono and diprotic organic acids by ion exchange using anodic AMMS and CMMS micromembrane suppressors.

1. F^- (1.5 ppm)	13. Cl^- (3 ppm)	25. SeO_4^{2-}
2. α -Hydroxybutyrate	14. Galacturonate	26. α -Ketoglutarate
3. Acetate	15. NO_2^- (5 ppm)	27. Fumarate
4. Glycolate	16. Glucuronate	28. Phthalate
5. Butyrate	17. Dichloroacetate	29. Oxalacetate
6. Gluconate	18. Trifluoroacetate	30. PO_4^{3-}
7. α -Hydroxyvalerate	19. HPO_3^{2-}	31. AsO_4^{3-}
8. Formate (5 ppm)	20. SeO_3^{2-}	32. CrO_4^{2-}
9. Valerate	21. Br^-	33. Citrate
10. Pyruvate	22. NO_3^-	34. Isocitrate
11. Monochloroacetate	23. SO_4^{2-}	35. <i>cis</i> -Aconitate
12. BrO_3^-	24. Oxalate	36. <i>trans</i> -Aconitate

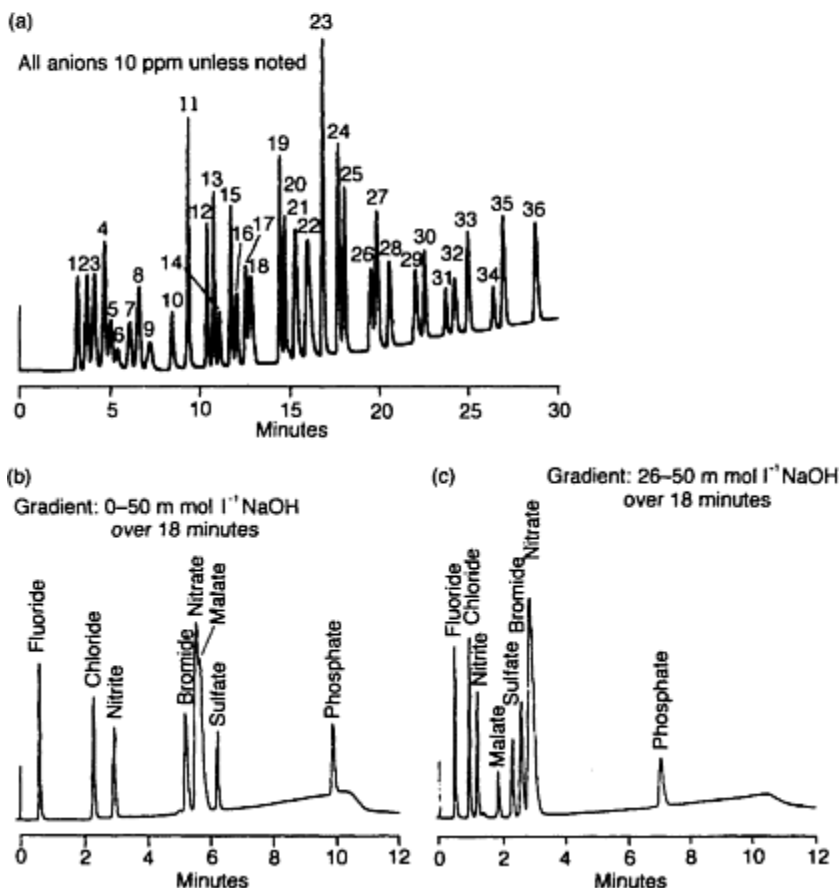


Fig. 2.12 Multi-component analysis by ion chromatography

Source: Own files

A further development is the Dionex HPIC AS5A–5 μ analytical anion separator column. This offers separation efficiency previously unattainable in ion chromatography. When combined with a gradient pump and an anion micro-membrane suppressor the

AS5A-5 μ provides an impressive profile of inorganic ions and organic acid anions from a single injection of sample (Fig 2.12). Note that phosphate and citrate, strongly retained trivalent ions, are efficiently eluted in the same run that also gives baseline resolution of the weakly retained monovalents fluoride, acetate, formate and pyruvate. Quantitation of all the analytes shown in Fig. 2.12 using conventional columns would require at least three injections under different eluent conditions.

Another benefit of using the AS5A-5 μ gradient pump combination is the ability to change easily the order of elution of ions with different valencies simply by changing the gradient profile. For example, if nitrate were present in high enough concentration to interfere with a malate peak, the malate peak could be moved ahead of the nitrate peak by using a slightly different gradient (Fig 2.12c).

2.15.2 Column chromatography

Liquid chromatography separation and indirect detection using iron(II), 1,10-phenanthroline as a mobile phase additive have been used for the separation of carboxylates (and sulphonic acids) [161]. Detection limits approach 20ng.

2.15.3 Ion exclusion chromatography

Okada [162] has described a redox suppression for the ion exclusion chromatography of carboxylic acids with conductimetric detection. The reaction between hydriodic acid (the eluant) and hydrogen peroxide (the precolumn reagent) is used as the redox suppressor for ion exclusion chromatography of carboxylic acids. The suppressor is useful with highly acidic eluents and reduces background conductance more effectively than a conventional ion exchange suppressor.

2.15.4 Gas chromatography

The application of this technique is discussed under multianion analysis in section 14.1.1.1.

2.15.5 Miscellaneous

The determination of carboxylic acids is also discussed in the following sections:

Ion chromatography (sections 2.1, 2.3, 2.13, 2.18, 2.20, 2.21, 2.26, 2.27, 2.33–2.36, 2.38–2.41, 2.44–2.46, 2.51–2.56, 2.60, 2.71, 2.74, 2.79, 2.80, 2.84, 2.86, 2.87, 2.92, 2.104, 2.108).

High performance liquid chromatography (sections 2.1, 2.13, 2.26, 2.40, 2.45, 2.51, 2.54, 2.72, 2.80, 2.82).

Micelle chromatography (section 2.51).

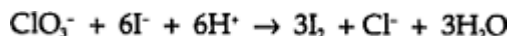
Ion exclusion chromatography (sections 2.21, 2.34, 2.40, 2.55, 2.56, 2.97).

Gas chromatography (sections 2.42, 2.56).

2.16 Chlorate

2.16.1 Titration methods

Chlorate ion concentration at the sub mg L⁻¹ level has been measured with high precision and accuracy by a iodometric method [163]. The chlorate is reduced by iodide ion in 6M hydrochloric acid:



Oxidation of iodide ion by air is prevented from removing the air with pure hexane and scrubbed nitrogen. Saturated disodium phosphate was used to neutralise the acid. The iodometric endpoint was detected either with thyodene as the indicator or the colour of iodine in the hexane layer. The precision of the method is better than 1%. For concentrations of chlorate below 3.5 mg L⁻¹ potentiometric titration is recommended.

2.16.2 Flow injection analysis

Miller *et al.* [164] have described two approaches to the determination of trace levels of chlorate ion based on the reaction of chlorate ion with iodide to produce iodine. High hydrochloric acid concentrations accelerated the reaction. Flow injection analysis, which excluded air from the flow stream, was used. The first method could detect chlorate ions at levels of 10µM and the second method, using a stopped flow condition, could detect levels of 1µM.

2.16.3 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.16.4 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.1.5 and 13.1.1.7.

2.17 Chloride

Titration methods for the determination of halides are convenient but limited in sensitivity or ability to automate. When these characteristics are required, then spectrophotometric or titration or ion selective electrode methods are recommended. Methods based on ion selective electrodes are also useful. When mixtures of anions are to be analysed and high sensitivity and speed are essential, then ion chromatography becomes the method of choice.

2.17.1 Titration methods

Three basic approaches have been made to the determination of chloride in water:

- Mohr titration;
- Mercuric nitrate and diphenyl carbazone titration;
- Technicon autoanalyser method (mercuric thiocyanate-ferric salt spectrophotometric method).

The precision and bias of these three standard approaches to the determination of chloride in river water has been evaluated [165,166] in trials carried out in a number of laboratories in the UK. The following targets were set in this exercise:

- maximum tolerable bias –10% of the chloride concentration or 0.5% mg L⁻¹ chloride, whichever is the greater;
- maximum tolerable standard deviation –5% of the chloride concentration, or 0.25% mg L⁻¹ chloride, whichever is the greater.

The results were analysed statistically to provide estimates of the standard deviation of individual analytical results in any batch of analyses. These estimates are summarised in Table 2.6 which shows that all laboratories and methods achieved the target standard deviation.

Portions of a standard chloride solution and two river water samples were analysed once on each of five days. The results, summarised in Tables 2.6 and 2.7, show that the confidence intervals of the mean results for a given solution do not all overlap, that is, some inter-laboratory bias is present. To assess whether or not the bias of any laboratory exceeded the target value, the following procedure was adopted. The mean result and its 90% confidence interval from laboratory i was denoted by $\bar{X}_i \pm L_i$ and the true value of the standard chloride solution or, for the two river waters, the overall mean of all laboratories, was denoted by $\bar{x}$. The value of the maximum possible bias (95% confidence level) was then calculated as:

$$\frac{100 (\bar{X}_i + L_i - \bar{x})}{\bar{x}} \quad \text{if } \bar{X}_i > \bar{x}$$

Table 2.6 Results of precision tests

Lab.	Standard solution 1			Standard solution 2			River water'			Spiked' river water		
Analytical method	Concn (mg CIL ⁻¹)	SD ^a (mg CIL ⁻¹)	Rel ^b (%)	Concn (mg CIL ⁻¹)	SD ^a (mg CIL ⁻¹)	Rel ^b (%)	Concn (mg CIL ⁻¹)	SD ^a (mg CIL ⁻¹)	Rel ^b (%)	Concn (mg CIL ⁻¹)	SD ^a (mg CIL ⁻¹)	Rel ^b (%)

$$^{-1})$$

1	Mohr titration	25	0.065	2.6	200	0.52	0.26	6.1	0.31	5.1/	106	0.38	0
2	Mohr titration	50	(0.0.)	(0.0)	250	0.49	0.20	54	0.68	1.3	99	0.58	0
3	Mercuric nitrate titration	20	0.29	1.5	180	0.42	0.23	47	0.55	1.2	139	0.70	0
4	Mercuric nitrate titration	8	0.12	1.5	80	0.14	0.18	16	0.091	0.57	65	0.073	0
5	AutoAnalyzer	20	0.71	3.6	180	1.6	0.89	42	0.94	2.2	124	2.4	
6	AutoAnalyzer	20	1.2	6.0	180	2.1	1.2	40	0.89	2.2	137	1.6	
7	AutoAnalyzer	30	1.1	3.7	270	2.7	1.0	18	0.97	5.4/	III	1.5	
8	AutoAnalyzer	5	0.19	3.8	45	0.15	0.33	26	0.24	0.92	45	0.19	0
9	AutoAnalyzer	5	0.17	3.4	45	0.42	0.93	23	0.71	3.1	36	1.0	
10	SMA AutoAnalyzer	20	0.84	4.2	180	1.6	0.89	53	1.52	2.9	144	1.38	0

^aThe estimate of the standard deviation of any one result in any one batch of analyses; the estimates have between 9 and 19 effective degrees of freedom.

^bThe standard deviation expressed as a percentage of the concentration of the solution.

*Not statistically significantly greater than 5.0% (0.05 probability level).

Source: Reproduced with permission from the Royal Society of Chemistry [165]

$$\frac{100 (\bar{X}_1 + L_1 - \bar{x})}{\bar{x}} \quad \text{if } \bar{X}_2 < \bar{x}$$

or

The values for the maximum bias shown in Table 2.6 are almost invariably less than 10% and often much less.

It is concluded that precision and bias are satisfactory in all three methods for the determination of chloride mentioned above.

Chloride can be automatically titrated with standard silver nitrate solution using a chloride selective electrode [167], and non-ionic detergent must be added to prevent fouling of the electrodes by precipitated silver chloride. A modification to the titrant-delivery tube on the commercial apparatus used is required to deliver the titrant against the indicating surface of the chloride-selective electrode. Reproducibility is good for all concentrations in the range 1 to 100mg L⁻¹ chloride; the standard deviation was ± 0.28 to 0.47mg.

Kuttel *et al.* [168] have described a potentiometric titration procedure for the simultaneous determination of chloride (and bromide and iodide) in non saline waters. Errors caused by adsorption of the common ion on to the surface of the precipitate in the potentiometric titration of mixtures of halides with use of a silver electrode or a AgI, AgBr or AgCl membrane electrode can be overcome by the addition of sodium nitrate at a concentration exceeding 1N. Because of the small difference in the solubilities of silver

bromide and silver chloride, the determination of bromide in the presence of chloride is not as accurate as the determination of other pairs of halides.

Hara and Okazaki [169] have described a method for the two point Gran titration of chloride in non saline water using a silver sulphide ion selective electrode. The analysis was performed without sample pretreatment and results correlated well with those obtained by potentiometry and spectrophotometry or ion chromatography. Interferences and the detection limit were examined, and the effects of temperature and number of titration points. The Monte Carlo simulation method was used to determine the precision of the method; two titration points were sufficient to obtain maximal precision of 0.2% provided that the potential difference between them exceeded 20mV. The two point Gran titration procedure was used to analyse stream and lake water with an error of less than 2% and compared with the usual seven point Gran titration method.

Levy [170] has described a titrimetric procedure for the determination of chloride ions in the presence of free chlorine. Previous workers have attempted to remove free chlorine by boiling the sample. This however leads to partial decomposition of hypochlorous acid to hydrochloric acid and oxygen:

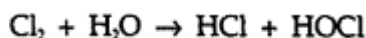


Table 2.7 Results of inter-laboratory bias tests

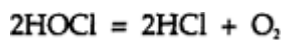
Lab	Analytical method	Std soln 46.0mg Cl L ⁻¹			River Water A			River Water B	
		Mean concn found ^a (mg Cl L ⁻¹)	Deviation from true value (%)	Max possible bias (%)	Mean concn found ^a (mg Cl L ⁻¹)	Deviation from mean value (%)	Max possible bias (%)	Mean concn found ^a (mg Cl L ⁻¹)	Deviation from mean value (%)
1	Mohr titration	46.0 ±0.09	0.0	±0.2	97.9 ±0.17	+1.4	+1.6	8.52 ±0.17	–
2	Mohr titration	45.0 ±0.26	–2.2	–2.7	97.4 ±0.49	+0.9	+1.4	8.28 ±0.13	–
3	Mercuric nitrate titration	46.0 ±0.41	0.0	±0.9	97.0 ±0.25	+0.5	+0.8	8.80 ±0.23	+
4	Mercuric nitrate titration	45.9 ±0.13	–0.2	–0.5	96.7 ±0.19	+0.2	+0.4	8.39 ±0.11	–
5	AutoAnalyzer	48.0 ±0.89	+4.3	+6.3	94.6 ±1.03	–2.0	–3.0	8.90 ±0.40	+

6	AutoAnalyzer	46.0 ±1.24	0.0	±2.7	95.7 ±1.47	-0.9	-2.4	8.24 ±0.60	-
7	AutoAnalyzer	45.8 ±1.57	-0.4	-3.8	97.2 ±1.57	+0.7	+2.4	8.60 ±0.52	+
8	AutoAnalyzer	45.0 ±0.20	-2.2	-2.6	95.2 ±0.27	-1.4	-1.6	9.02 ±0.43	+
9	AutoAnalyzer	46.1 ±0.43	+0.2	+1.2	97.1 ±0.17	+0.6	+0.8	8.48 ±0.38	-
10	SMA AutoAnalyzer	46.2 ±0.43	+0.4	+1.4	b	b	b	8.6 ±0.52	+
Average of all laboratories		46.0	0.0	-	96.5	-	-	8.58	
Concentration found by WRC			-	-	96.2	-	-	8.48	

^aThe figures after ± sign are the 90% confidence limits of the means.

^bThis laboratory originally conducted the analytical quality control work on another AutoAnalyzer work on changing to the present system. Insufficient river water A sample remained for work on the first of the regular 'follow-up' checks showed the bias target to be met

Source: Reproduced with permission from the Royal Society of Chemistry [165]



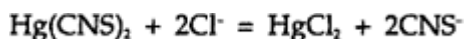
Levy [170] overcomes this problem by carrying out the reaction at a temperature close to 0°C and sweeping unhydrolysed chlorine out of solutions with a purge of nitrogen before commencing the determination of chloride ions.

Coulometric titration with dead stop end-point detection has been used for the determination of down to 0.3mg L⁻¹ chloride in acetic acid and nitric acid media [24] and in methanol-nitric acid medium [171].

Interstitial chloride in very low volumes of pore waters from oil shales rocks has been determined by coulometric titration [172].

2.17.2 Spectrophotometric methods

Dojlido and Bierwagen [173] have described an automated procedure utilising an autoanalyser for the determination of chloride in non saline water. The method is based on the displacement by chloride ions of thiocyanate ions from mercuric thiocyanate and subsequent Spectrophotometric determination of thiocyanate as ferric thiocyanate. The standard deviations are ±0.36 and ±0.75mg L⁻¹ for 8.9 and 34.5mg L⁻¹ chloride ion concentration.

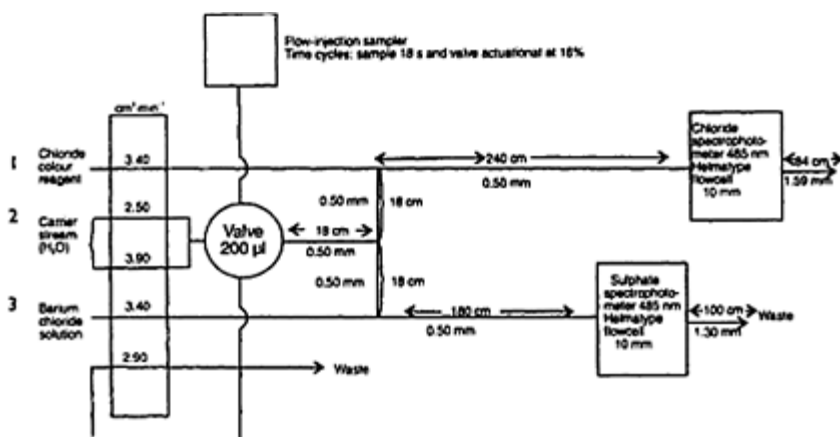


A further method [174] is based on the oxidation of chloride to free chlorine by potassium permanganate solution. Chlorine is then swept out of the solution by a nitrogen purge and determined by the o-toluidine Spectrophotometric method at a wavelength of 450nm.

Rossner and Schwedt [175] have described a Spectrophotometric method for the determination of chloride in non saline water which is based on the FeII-Hg tripyridyl-s-triazine system. This method is applicable in the $10\mu\text{g L}^{-1}$ to 10mg L^{-1} concentration range. A modification of the technique based on continuous flow analysis has a detection limit of $5\mu\text{g L}^{-1}$.

McCurdy *et al.* [176] give details of a procedure developed for routine determination of chloride in environmental groundwater samples using a Cobas Fara centrifugal analysis; the procedure was based on the Spectrophotometric hexacyanoferrate method. Ferric nitrate was a more sensitive donor of trivalent iron than ammonium ferric sulphate. The method was tested on several reference mineral samples and the results were compared with those obtained using a Technicon AAI continuous-flow analyser. The procedure gave results that were both accurate and precise.

Yoshida *et al.* [177] stirred a chloride-containing sample with thiocyanate-loaded anion exchange resin for 10min. The displaced thiocyanide reacted with iron(III) that was added to the system to produce a red colour; measurement of the absorbance at 455nm provided



1 Chloride colour reagent.

- (a) Solution I. Dissolve 6.34g mercuric thiocyanate with stirring in 950ml distilled water at a temperature of 50–70°C. After cooling, add 2ml concentrated nitric acid (specific gravity 1.42) and 8.08g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Stir until dissolved. The reagent is stable for several months at room temperature if stored in a dark bottle.
- (b) Solution II. Dissolve 6.85g mercuric nitrate in 100ml distilled water. Add 0.50ml of solution II to 100ml of solution I to give the chloride colour reagent. Leave solution overnight to stabilise.

2 Barium chloride solution (2.5%).

Dissolve 0.05g thymol crystals with stirring in 500ml distilled water at a temperature of about 80°C. Cool to 40°C and add 1500ml distilled water. Add 4g gelatin and swirl until dissolved. When dissolved, add 50g barium chloride and dissolve. Filter if necessary.

Fig. 2.13 Flow system for the simultaneous determination of chloride and sulphate. Sampling rate 200 samples h⁻¹. Tube length and i.d. are given in cm and mm respectively

Source: Reproduced with permission from Elsevier Science [179]

a measure of the chloride concentration in the initial sample. Not surprisingly, many anions interfere with this method when present in concentrations comparable to that of the chloride.

2.17.3 Flow injection analysis

Van Staden [178] has described an automated prevalve dilution inflow injection analysis method for the determination of chloride in ground water. This method can analyse samples containing up to 800mg L⁻¹ chloride. By adjusting the ratio of sample flow rate to dilution water flow rate, the concentration could be reduced to a level at which linearity of the calibration was preserved (about 160mg L⁻¹ maximum). The method was based on reaction with mercury thiocyanate in the presence of ferric ions, giving the deeply coloured ferric thiocyanate. Absorption was measured at 480nm.

Table 2.8 Precision of the proposed FIA method for chloride in surface, ground and domestic waters

<i>Sample</i>	<i>Number of tests</i>	<i>Automated segmented method [Cl⁻] (mg L⁻¹)</i>	<i>FIA method [Cl⁻] (mg l⁻¹)</i>	<i>Coefficient of variation (%)</i>
1	15	8	11	1.21
2	15	66	74	0.87
3	15	7	10	1.05
4	15	239	251	0.21
5	15	26	26	0.99
6	15	107	110	0.74
7	15	149	150	0.66
8	15	6	4	1.30
9	15	239	245	0.15
10	15	7	5	1.14
11	15	26	30	0.91
12	15	302	291	0.17

Student's *t*-test at 5% probability level: calculated *t*-value=1.298; critical *t*-value=2.060

Source: Reproduced with permission from Elsevier Science [179]

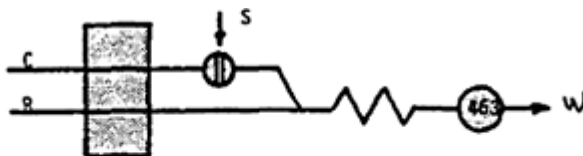
Basson and Van Staden [179] have described an automatic method for the simultaneous determination of chloride and sulphate in non saline water based on an adaptation of the flow injection concept. About 200 samples per hour can be analysed by this procedure with a coefficient of variation for chloride of less than 1.3%. This FIA method compares favourably with the standard segmented automated methods for chloride. Application of Student's *t*-test reveals differences insignificant at a 5% probability level.

A schematic diagram of the system employed is shown in Fig. 2.13. The manifold consists of Tygon tubing with tube lengths and inside diameters as indicated in the figure.

The sample is automatically injected into the system from a Breda Scientific flow injection sampler containing a valve with a capacity of 200 μ L. Using a sampling time of 18s gives a capacity of 200 samples per hour. The valve system is actuated on a time basis which is correlated with the sampler unit. The sampling valve actuates ever 16s after movement to the next sample.

The performance of this flow injection analysis procedure is shown in Table 2.8 for chloride. The coefficient of variation for chloride is less than 1.3%.

Workers at Tecator Ltd have described a flow injection analysis procedure [180,181] for the determination of 1–11mg L⁻¹ of chloride in

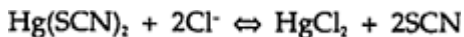


S = sample; **C** = distilled water; **R** = 0.31g mercury thiocyanate dissolved in 75ml methanol. Mix for 5min. Fill up with 350ml distilled water and 2.35g concentrated nitric acid. Dissolve 15.5g iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in the solution. Fill up to 500ml with distilled water and mix thoroughly. Filter and degas. This solution is stable for at least four weeks

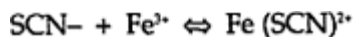
Fig. 2.14 Flow injection manifold, determination of chloride

Source: Reproduced with permission from Tecator Ltd [180]

non saline waters. In this procedure chloride reacts with mercury(II) thiocyanate to form a soluble nonionic compound



The thiocyanate ions released reacts with iron(III)-nitrate to form the red iron(III) thiocyanate complex



The aqueous sample containing chloride is injected into a carrier stream of distilled water and mixed with a reagent consisting of mercury(II) thiocyanate and iron(III) nitrate. Released thiocyanate ions react in the acid solution with iron(III) to give a red coloured iron(III) thiocyanate complex. The resulting colour is measured photometrically at

463nm (Fig. 2.14).

Sagara *et al.* [182] determined chloride in environmental waters by flow injection analysis.

The application of this technique is also discussed under multianion analysis in section 14.4.1.4.

2.17.4 Atomic absorption spectrometry

Belcher *et al.* [183] have described a procedure in which chloride is reacted with phenyl mercuric nitrate. The phenyl mercuric chloride produced is extracted with chloroform, and mercury (equivalent to original chloride content of sample) is determined by atomic absorption spectrometry in amounts down to $0\text{--}15\mu\text{g L}^{-1}$.

In a further atomic absorption method [184] the chloride in the sample is contacted with metallic copper in the flame of an atomic absorption spectrometer. Concentrations of copper (equivalent to chloride ions) in the flame are evaluated at 324.75nm. Between 2 and 5mg L^{-1} of chloride can be determined in samples by this method.

Martinez Jimenez *et al.* [185] developed an indirect flow-injection atomic absorption spectrophotometric method for determining chloride in non saline water by continuous precipitation of silver chloride. Two unsegmented flow configurations involving normal and reversed flow injection were used. By normal flow injection, chloride was determined in the range of $3\text{--}100\mu\text{g mL}^{-1}$, with a sampling rate of 50 samples/h, and a relative standard deviation of 2%. In reversed flow injection, chloride was determined in the range of $0.3\text{--}10\mu\text{g mL}^{-1}$ with a sampling frequency of 200 samples/h, and a relative standard deviation of 3.5%.

2.17.5 Inductively coupled plasma atomic emission spectrometry

Michlewicz and Carnahan [186] have described a method for determination of chloride in a continuous flowing cell. Hydrogen chloride is then determined in amounts equivalent to $0\text{--}2\text{ mg L}^{-1}$ in the sample by microwave techniques. These workers [187] have also described a procedure for determining chloride down to 7 mg L^{-1} based on direct nebulisation of aqueous sample into an atmospheric pressure helium microwave plasma.

Michlewicz and Carnahan [188] give details of a method for the determination of chloride (and bromide and iodide) based on pneumatic nebulisation and ultrasonic nebulisation of the sample into a helium microwave induced plasma.

Detection limits in mg L^{-1} for chloride, bromide and iodide were 0.4, 3.0 and 0.8 respectively. Interference effects from added magnesium, potassium, sodium and lithium were moderate with pneumatic nebulisation but significant with ultrasonic sample nebulisation.

2.17.6 Cathodic stripping voltammetry

The application of this technique is discussed under multianion analysis in section 14.9.1.1.

2.17.7 Column coupling capillary isotachophoresis

This technique offers very similar advantages to ion chromatography in the determination of anions in water, namely multiple analysis, little or no sample pretreatment, speed, sensitivity and automation. Very similar advantages are offered by capillary isotachophoresis. Bocek *et al.* [189] determined chloride (and sulphate) in mineral waters by this technique and Zelinski *et al.* [190] applied the technique to the determination of 0.02–0.1 mg L⁻¹ quantities of chloride, fluoride, nitrate, sulphate, nitrite and phosphate in river water.

The application of this technique is also discussed under multianion analysis in section 14.6.1.1.

Table 2.9 Results of determinations in potable water with the flow-through system in comparison with reference methods (mg L⁻¹)

Sample	Chloride		%	Fluoride		
	Flow-through system	Titration with Ag		Flow-through system	Potentiometric with TISAB	
1	115.7	112.8	+2.6	0.178	0.174	+2.2
2	108.6	109.0	-0.4	0.166	0.166	0
3	119.2	118.6	+0.5	0.198	0.199	-0.5
4	119.8	119.5	+0.2	0.197	0.209	-5.9
5	66.1	72.4	-8.7	0.169	0.174	-2.9

Source: Reproduced with permission from the American Chemical Society [192]

2.17.8 Ion selective electrodes

Zeinalova and Senyavin [191] examined conditions for the potentiometric determination of chloride in non saline water using an ion selective electrode. A pH range of 1–12 is suitable for the determination of chloride. Macro- and microcomponents of non saline water did not interfere with determining chlorides.

Trojanowicz and Lewardowski [192] have described a multiple potentiometric system for the continuous determination of chloride, fluoride, nitrate and ammonia in non saline waters. They describe a flowthrough system for the simultaneous determination of chloride (30–150mg L⁻¹), fluoride (0.08–0.4mg L⁻¹), nitrate (5–20mg L⁻¹) and ammonia (0.05–0.5mg L⁻¹). Solid state chloride and fluoride electrodes, a PVC membrane nitrate electrode and a gas-sensing Orion 95–10 ammonia electrode were employed, the air-segmented sample stream being mixed with appropriate buffering solutions before entering the measuring cell. During continuous operation, calibration twice daily was necessary to eliminate the effects of potential drift; best results were obtained when the chloride-nitrate ratio in the calibrating solution was similar to that in the non saline water

being analysed.

Chloride and fluoride determinations obtained in non saline water by this procedure are compared with those obtained by conventional methods in Table 2.9. Generally, results agreed within $\pm 5\%$ with those obtained by the reference method.

Trojanowicz and Matuszewski [193] investigated the usefulness of potentiometric detection in the flow injection analysis of chloride in river waters. A direct, as opposed to a logarithmic relation, exists between electrode potential and chloride concentration.

Hara *et al.* [194] found that preliminary treatment of river or stream water samples with silver chloride was effective in removing interferences caused by bromide, iodide and sulphide prior to potentiometric chloride determination using a chloride ion selective electrode. The effects of pH on interference by bromide were also studied. Complete removal of bromide interference was not possible by acidification of the sample alone.

Interference by humic substances in non saline waters in the ion selective electrode determination of chloride was studied by Sikora and Stevenson [195]. The interference was negligible in solutions containing less than 0.1g/L of humic substances but was serious in samples with low concentrations of chloride ($<10^{-4.5}\text{M}$) and high concentrations of organic matter (0.1g L^{-1}).

2.17.9 Vapour molecular absorption spectrometry

Zhang *et al.* [196] determined chloride in tap and lake water by vapour molecular absorption spectrometry. Chloride was oxidised to chlorine by a strong oxidiser (eg KMnO_4) in an acidic solution and the chlorine was introduced into a special cell of an atomic absorption spectrometer, and the absorbance was measured at the wavelength of the copper hollow cathode emission line of 324.7nm. The detection limit was 2.0mg L^{-1} .

2.17.10 Microwave induced helium plasma

Michlewicz and Carnahan have studied the application of this technique to the determination of chloride in non saline water. In one method [186] the chloride is converted to hydrogen chloride in a continuous flowing cell. The hydrogen chloride is volatilised into a microwave induced helium plasma and is determined by a microwave technique which involves matrix matching.

In a further method [187] the aqueous sample is directly nebulised into an atmospheric pressure helium microwave plasma.

2.17.11 Isotope dilution analysis

Henman *et al.* [197,198] employed mass spectrometric isotope dilution analysis to the determination of chloride ion in rainfall and snow. Detection limits of $1\mu\text{g L}^{-1}$ or lower can be achieved by this technique. For the isotope ratio measurement of chlorine and bromide, a single focusing mass spectrometer (Varian MAT, type CH5TH) with a double filament ion source and a Faraday cup as a detector was used. The filaments consist of rhenium. The best precision of the isotope ratio measurement is achieved when a solution of $(\text{Ag}(\text{NH}_3)_2) \text{X}$ ($\text{X}^- = \text{Cl}^-$, Br^-) is deposited on the evaporation filament and dried under

a heat lamp. In the ion source the temperature of the ionisation filament is increased stepwise up to a temperature of 1850°C.

Using sample amounts of 1µmol halide with natural isotope composition, ion intensities are achieved on the Faraday cup in the range of 10^{-11} to 10^{-10} for $^{35}\text{Cl}^-$ and in the range of 10^{-11} to 5×10^{-11} for $^{79}\text{Br}^-$.

Samples of 100–250g rain and snow were collected in polyethylene funnels of diameter 35cm connected by means of polyethylene tubes and Y-brackets with a 1L polyethylene flask. Approximately 100g of one sample was accurately weighed in a 250ml polyethylene beaker and approximately 1g ^{37}Cl spike solution was added. The spike solution contained 1.014×10^{19} chloride ions g^{-1} . Henman employed isotope dilution analysis coupled with mass spectrometry to determine down to $13\mu\text{g L}^{-1}$ chloride in water [197].

The spike solution had an isotope distribution of $^{35}\text{Cl}=24.63\%$ and $^{37}\text{Cl}=75.375\%$. After the solutions of the spike and the sample had been stirred up and thoroughly mixed, 0.5ml of saturated silver nitrate solution was added and the mixture left to stand for about 30min so that the silver chloride could precipitate. After this, the solution was filtered through a cellulose nitrate filter (Sartorius, Type 11301) and then, to purify it, the silver chloride was dissolved again in some drops of a semiconcentrated ammonia solution. The silver chloride was then precipitated again with concentrated nitric acid. After being filtered, the precipitate was dried at 60°C and kept in a non-transparent flask until mass spectrometry began. The silver chloride was kept away from light until measurement because the chlorine isotopes fractionate slightly when silver chloride is decomposed by light of a natural wavelength distribution. Shortly before the mass spectrometric measurement was taken, 1 to 2 drops of a 15% ammonia solution were added to the sample and placed on the evaporator filament of the thermal ion source of the mass spectrometer using a micro-liter injector.

Henman *et al.* [197] determined chloride and bromide in snow and rain and also measured their concentrations at different distances away from a highway (Table 2.10). Unlike the concentrations of bromide, the chloride concentration in snow continually decreases the further the snow is from the highway, a considerable proportion of the bromide originating from traffic exhausts.

2.17.12 Radiochemical methods

Johannesson [199] treated the sample with H^{35}Cl and evaporated it to dryness prior to counting. He found that 1mg L^{-1} chloride could be determined.

In a radiometric determination of chloride in non saline water, excess mercuric ions are added to the sample to form mercuric chloride complexes, followed by addition of a chloroform solution of ^{60}Co -labelled Co-pyrrolidinedithiocarbamate complex [200]. The excess mercuric ions displace an equivalent amount of cobalt from the dithiocarbamate complex

Table 2.10 Cl^- and Br^- content in snow depending on its distance away from a highway

Distance from highway (m)	Cl^- content ($\mu\text{g g}^{-1}$)		Br^- content ($\mu\text{g g}^{-1}$)	
	MS- IDA	Ion selective electrode	MS- IDA	Ion selective electrode
2	71	68	124	580
10	40	45	79	380
20	32	40	196	430
30	26	31	40	300
40	18	23	31	320
50	13	17	66	220
300	6	11		130

Source: Reproduced with permission from Gordon AC Breach [197]

which is then determined radiometrically to give a measure of the original chloride concentration. The detection limit can reach 0.05ppm chloride.

2.17.13 Ion chromatography

Various workers have discussed the codetermination of chloride with other anions [201–203]. This is discussed further under multianion analysis in sections 12.2.1, 12.2.4, 12.2.5 and 12.2.6.

2.17.14 High performance liquid chromatography

Stetzenbach and Thompson [138] employed high performance liquid chromatography on anion exchange columns to determine chloride in admixture with bromide, iodide, nitrate and thiocyanate in non saline waters. This method is discussed further under multianion analysis.

Moss and Stephen [139] have described the determination of chloride (and bromide, iodide and phosphate) in non saline waters by high performance liquid chromatography.

Salov *et al.* [115] determined chloride (and bromide, iodide, iodate, bromate and chlorate) by high performance liquid chromatography using inductively coupled argon plasma mass spectrometry as a detector.

The application of this technique is also discussed under multianion analysis in sections 13.1.1.1, 13.1.1.2, 13.1.1.5 and 13.1.1.7.

2.17.15 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section

13.2.1.3.

2.17.16 Ion exchange chromatography

Akaiwa *et al.* [140] have used ion exchange chromatography on hydrous zirconium oxide combined with a detection based on direct potentiometry with an ion selective electrode for the simultaneous determination of chloride and bromide in non saline waters.

2.17.17 Gas chromatography

Belcher *et al.* [204] determined chloride by a method based on reaction with phenyl mercuric nitrate to produce phenyl mercury chloride, followed by carbon tetrachloride extraction of the latter and gas chromatography. Down to 0.4 mg L^{-1} chloride in the sample could be determined.

2.18 Chlorobenzoate**2.18.1 Ion chromatography**

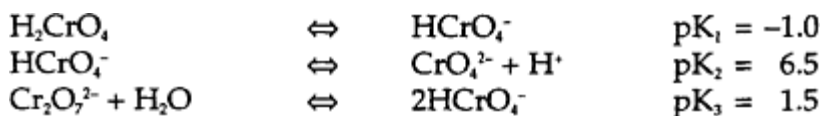
The application of this technique is discussed under multianion analysis in section 12.2.5.

2.19 Chromate and dichromate

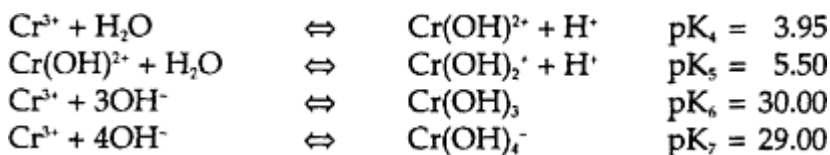
Differentiating between the two most frequent oxidation states of chromium is fundamental in speciation studies of this element on account of the toxicity of hexavalent chromium. In fact, most of the works on this element published so far deal solely with this aspect [205]. Flow injection analysis has been used several times for determining this element in one [206,207] or in its two most common oxidation states [208–214].

Nevertheless, it is known that there is a large variety of chemical forms of Cr(III) and Cr(VI), which show different properties depending on the groups or elements to which they are bound. Their relative abundance is a function of the type of medium. Since the pH is a major parameter in any type of solution (especially in aqueous ones), and taking into account that its value dictates the predominance of a particular species of Cr(III) and Cr(VI) (hydroxylated, dimer etc), the following species of chromium must be considered to be present in waters. Chromium (III): $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_4^-$. Chromium(VI): H_2CrO_4 , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} . Among these species, $\text{Cr}(\text{OH})_3$ is very insoluble, its concentration in water being negligible, and H_2CrO_4 is a relatively strong acid ($\text{pK}_a = -1.0$), which is unlikely to occur in water. Consequently the following equilibria, with their respective constants, must be considered:

Chromium(VI)



Chromium(III)



The pH range over which each species predominates can be conveniently inferred from plots of log/concentration/versus pH [215].

2.19.1 Spectrophotometric methods

Aoyama *et al.* [216, 217] have described a rapid method for the determination of down to $3\mu\text{g L}^{-1}$ of chromate in which hexavalent chromium is complexed with diphenylcarbazide, and this complex is floated with a sodium lauryl sulphate anionic surfactant. After dilution the subsidised foam is measured spectrophotometrically. The continuous flotation procedure is as follows.

Place the water (1 L), previously acidified to 0.1mol L^{-1} with sulphuric acid, in the separation tube, pass nitrogen into the tube at about 105ml min^{-1} , and pump in the 1% sodium lauryl sulphate solution at 0.39 ml min^{-1} . Continuously supply the sample pH and the 1% diphenylcarbazide solution to the separation tube at a rate of 2L h^{-1} and 0.230ml min^{-1} respectively. A steady state flotation was achieved 1 h after flotation had started. Mix the sample and diphenylcarbazide solutions in the mixing chambers before entering the tube. Collect the foam subsided in the collector and intermittently transfer to flasks and dilute to 50ml with water, and measure absorbances as described above.

The effect of diverse ions on the flotation of chromium(VI) were investigated. Only copper(II) and iron(III) in 10-fold amounts, and vanadium(V) in 20-fold amounts caused fading of the colour. Even in those cases, however, chromium(VI) could be measured by a standard addition method.

Diphenylcarbazone and diphenylcarbazide have been widely used for the Spectrophotometric determination of chromium [218]. Only relatively recently, however, has the nature of the complexation reactions been elucidated. Cr(III) reacts with diphenylcarbazone where Cr(VI) reacts (probably via a redox reaction combined with complexation) with diphenylcarbazide [219]. Although speciation would seem a likely prospect with such reactions, commercial diphenylcarbazone is a complex mixture of several components, including diphenylcarbaizide, diphenylcarbazone, phenylsemicarbazide and diphenylcarbidi azone with no stoichiometric relationship between the diphenylcarbazone and diphenylcarbazide [220]. Total chromium can be determined with diphenylcarbazone following reduction of all chromium to Cr(III).

2.19.2 Flow injection analysis

Ruz *et al.* [221] speciated different oxidation states of chromium. They were able to obtain a concentration profile for the chromium(III) and chromium(VI) species, namely HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} . Ruz *et al.* [222] also used reverse flow injection analysis for the simultaneous and sequential determination of chromate and chromium(III) by unsegmented flow methods. A photometric detector was employed.

Ruz *et al.* [221] used the flow injection analysis technique together with computerised numerical calculation methods to study the distribution of the type of water analysed and the above-mentioned pK values. By adding a microprocessor to the flow injection analysis system, and creating a suitable calculation program, the different equations established can be conveniently solved. The occurrence in the medium of complexing species for chromium, and/or the presence of a colloid resulting in adsorption phenomena for chromium ions, have not been taken into account. Including these would require information about the type of ligand and/or colloid, their concentration and corresponding equilibrium constants; additionally, the calculation program would need to be modified.

The value of the ionic strength of the sample must be taken into account because it affects the values of the constants. Constants with an ionic strength of 0.1M were used by Ruz *et al.* [221]. The reversed flow injection analysis, reverse flow injection analysis and asymmetric merging zones [211] were also utilised, together with the indicator reaction reported by several authors [207–212] involving Cr(VI) and 1,5-diphenylcarbazide.

Tandon *et al.* [213] have carried out a theoretical study on the effect of the pH on the Cr(VI) species present in solution. Cr(III) species were not considered.

In this procedure [221] the pH of the water sample, which travels through the system, is continuously monitored (glass-calomel microelectrode-ME- in Fig. 2.15) prior to its confluence with a sulphuric acid stream, whereupon the stream is split into two channels with an injection valve each. The oxidant (Ce[IV]) is injected into channel 1, while 1,5-diphenylcarbazide is injected into channel 2. The reactor lengths and

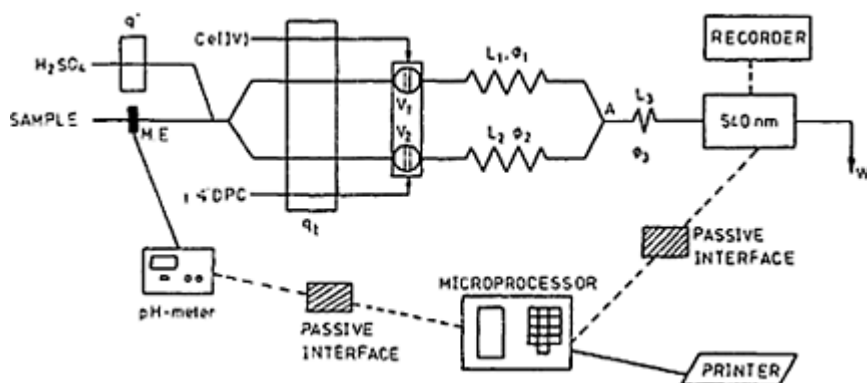


Fig. 2.15 Diagram of the system used for chromium speciation studies.

Optimum working conditions: diphenyl carbazide 0.17% (w/V)/Ce (IV)/0.5g L⁻¹/H₂SO₄/1M, q, 3.28ml min⁻¹, q₁ 0.30ml min⁻¹, V₁

130 μ L, V_2 475 μ L, L_1 650cm, L_2 360cm, L_3 60cm, $\theta_1=\theta_2=\theta_3=0.5$ mm, Me
=glass-calomel electrode

Source: Reproduced with permission from Taylor and Francis, UK
[221]

injection volumes are optimised in such a manner that the confluence of the injected plugs at point A is asymmetric, the plug travelling along channel 1 and merging with the tail of the plug circulating through channel 2. A plug with two reaction zones is formed in reactor L_3 . The first of such zones corresponds to the reaction between 1,5-diphenylcarbazide and Cr(VI) from the sample, while the second one is due to the overall chromium content (Cr(III)) being previously oxidised to Cr(VI) by injected Ce(IV)). The detection of this plug provides two peaks per simultaneous injection, which are related to the Cr(VI) concentration and the total chromium present in the samples, respectively. The presence of two passive interfaces between the two detectors and the microprocessor means that the pH and absorbance data can be acquired and processed. A printer provides the results, which are expressed as the concentration of each species.

Three calibration curves were run:

- (1) Curve for Cr(VI) from the absorbance of the first peak, A_1 , which allows the direct determination of this species in the sample.
- (2) Curve for the contribution, A_2 , of Cr(VI) from the sample to the absorbance of the second peak.
- (3) Curve for the contribution, A_2' , of Cr(III) from the sample to the absorbance of the second peak.

The equations of these straight lines, regression coefficients and determination ranges found are as follows:

$$A_1 = 0.553 |Cr^{6+}| + 0.003 \quad (r = 0.9999) \quad 0.20 \leq |Cr^{6+}| \leq 1.20 \text{ (}\mu\text{g.mL}^{-1}\text{)}$$

$$A_2 = 0.450 |Cr^{6+}| - 0.022 \quad (r = 0.9959)$$

$$A_2 = 0.450 |Cr^{6+}| - 0.022 \quad (r = 0.9959)$$

$$A_2 = 0.247 |Cr^{3+}| + 0.018 \quad (r = 0.9979) \quad 0.50 \leq |Cr^{3+}| < 3.00 \text{ (}\mu\text{g.mL}^{-1}\text{)}$$

The calculation program allows, from a series of Cr(III) and Cr(VI) standards, the above-mentioned calibration curves to be established; and, hence, the concentrations of both oxidation states of chromium can be calculated. These data, together with the pH for each sample, permits the determination of the concentration of the different species on the basis of the following equations:

Chromium(VI)

$$|\text{HCrO}_4^-| = \frac{-B_2 \pm \sqrt{(B_2)^2 + 8K_3 |\text{Cr}^{6+}|_{\text{overall}}}}{4K_3} \quad (1)$$

$$B_2 \text{ being equal to: } 1 + \frac{|\text{H}^+|}{K_1} + \frac{K_2}{|\text{H}^+|}$$

$$|\text{H}_2\text{CrO}_4| = \frac{|\text{HCrO}_4^-| |\text{H}^+|}{K_1} \quad (2)$$

$$|\text{CrO}_4^{2-}| = \frac{K_2 |\text{HCrO}_4^-|}{|\text{H}^+|} \quad (3)$$

$$|\text{Cr}_2\text{O}_7^{2-}| = 2K_3 |\text{HCrO}_4^-|^2 \quad (4)$$

Chromium(III)

$$\text{pH} = 14 - \frac{1}{2} (\log P_s - \log |\text{Cr}^{3+}|) \quad (5)$$

$$S = \frac{P_s}{|\text{OH}^-|^3} + K' |\text{OH}^-| \quad (6)$$

$$K' = K_7 P_s \quad (7)$$

$$|\text{Cr}(\text{OH})_4^-| = K' |\text{OH}^-| \quad (8)$$

The fraction, F of precipitated Cr(III) being:

$$F = |\text{Cr}^{3+}| - S \quad (9)$$

$$|\text{Cr}(\text{OH})_3| = M/B_1 \quad (10)$$

B_1 and M being:

$$B_1 = 1 + \frac{[H^+]}{K_4} + \frac{K_5}{[H^+]} \quad (11)$$

$$M = S - [Cr(OH)_4^-] \text{ (where } S = \text{solubility)}$$

$$[Cr^{3+}] = \frac{M}{B_1} \frac{[H^+]}{K_4}$$

$$[Cr(OH)^{2+}] = \frac{M}{B} \frac{K_5}{[H^+]} \quad (12)$$

Equations (1) to (12) are used in the calculation program, MECROM. Table 2.11 shows the values corresponding to several synthetic water samples containing different chromium concentrations. Owing to the moderately acidic pHs of these samples, the H_2CrO_4 , $Cr(OH)_3$ and $Cr(OH)_4^-$ contents are almost nil. The predominant species at such pHs are $Cr(OH)^{2+}$ and $HCrO_4^-$ for Cr(III) and Cr(VI), respectively.

This work demonstrates that it is possible to automate studies with a non-segmented flow system and a microprocessor. The system described provides a concentration profile of the different chemical forms in which an element can occur in natural or artificial samples. The most important advantage of this new technique for speciation studies are: rapidity, easy operation and economy. The suggested system can be applied to the speciation of other elements.

Marshall *et al.* [214] has also evaluated methods for determining the conic forms of chromium in water while Yoshimura used ion exchanger phase absorbtometry coupled to flow injection analysis to determine trace levels of dichromate in water [215].

2.19.3 Atomic absorption spectrometry

In the method observed by Fukamachi *et al.* [223] and Yanagisawa [224] hexavalent chromium (ie chromate and dichromate) is reduced by diethyldithiocarbamate to trivalent chromium with which it forms an isobutyl methyl ketone soluble complex. Preconcentrated chromate is then determined in the solvent extract by atomic absorption spectrometry at 357.9nm.

Parkow *et al.* [225] have described a procedure for the differential analysis of traces of chromium(VI) (chromate) and chromium(III) in non saline waters. The sample is filtered, acidified and divided into three portions, one of which is left untreated while the others are passed through a cation exchange resin and an anion exchange resin, respectively. The three aliquots are then treated with nitric acid, evaporated and

Table 2.11 Chromium speciation with the suggested configuration and using the MECROM program

Added (μg mL ⁻¹)			Found (μg L ⁻¹)								
			Species of Cr(III)					Species of Cr(VI)			
Cr (III)	Cr (VI)	pH	Cr (H ₂ O) ₆ ³⁺	Cr (OH) ₂ ²⁺	Cr P* (OH) ₂ ²⁺	Cr (OH) ₄ ⁺	H ₂ CrO ₄	HCrO ₄ ⁻	Cr ₂ O ₇ ²⁻	CrO ₄ ²⁻	
3.000	0.200	4.51	0.573	2.032	0.203	—	—	—	0.200	—	—
2.500	0.400	4.58	0.497	1.763	0.176	—	—	—	0.411	—	0.004
2.000	0.600	4.65	0.287	1.440	0.203	—	—	—	0.600	—	0.008
1.500	0.800	4.78	0.158	1.072	0.204	—	—	—	0.792	0.002	0.015
1.000	1.000	4.95	0.069	0.696	0.196	—	—	—	0.960	0.002	0.027
0.500	1.200	5.24	0.015	0.290	0.160	—	—	—	1.138	0.003	0.064
0.500	0.500	5.26	0.015	0.309	0.178	—	—	—	0.486	0.001	0.028
2.000	1.200	4.65	0.280	1.405	0.198	—	—	—	1.178	0.004	0.017
1.500	0.300	4.75	0.180	1.115	0.193	—	—	—	0.314	—	0.005

P* = fraction precipitated as hydroxide

Source: Reproduced with permission from Taylor and Francis, UK [221]

analysed by atomic absorption using the chromium 357.9 line to give the concentrations of cationic, anionic and non-ionic chromium. The concentration of chromium(III) is probably closely related to the sum of the cationic and non-ionic fractions and the concentration of chromium(VI) corresponds to the anion portion.

The concentrations of total, anionic, cationic and non-ionic chromium in the original 3L sample are obtained by difference. The precisions of the analyses for total, anionic, cationic and non-ionic chromium were respectively ± 14 , ± 20 , ± 20 , and $\pm 25\%$ relative.

Subramanian [226] studied the factors affecting the determination of trivalent and hexavalent chromium (chromate) by direct complexation with ammonium pyrrolidinedithiocarbamate, extraction of the complex into methyl isobutyl ketone, and determination by graphite furnace atomic absorption spectrometry. Factors studied included the pH of the solution, concentration of reagents, period required for complete extraction, and the solubility of the chelate in the organic phase. Based on the results, procedures were developed for selective determination of trivalent and hexavalent chromium without the need to convert the trivalent to the hexavalent state. For both states the detection limit was $0.2\mu\text{g L}^{-1}$.

2.19.4 Polarography

Differential pulse voltammetry has been used to determine chromate and chromium [227,228].

Crosmun and Mueller [228] achieved a detection limit of $10\mu\text{g L}^{-1}$ chromate in non saline waters.

2.19.5 Enzymic method

Guilbault *et al.* [229] showed that dichromate can be determined by its inhibitory action on the enzymic activity of the hyaluronidase enzymic system.

2.19.6 Ion chromatography

The application of this technique to the determination of chromate is discussed under multianion analysis in section 12.2.5.

2.19.7 High performance liquid chromatography

Reverse phase high performance liquid chromatography has been used to carry out the simultaneous determination of Cr(III) and Cr(VI) in water [230]. The sample is buffered to pH 5.8 and allowed to react overnight at

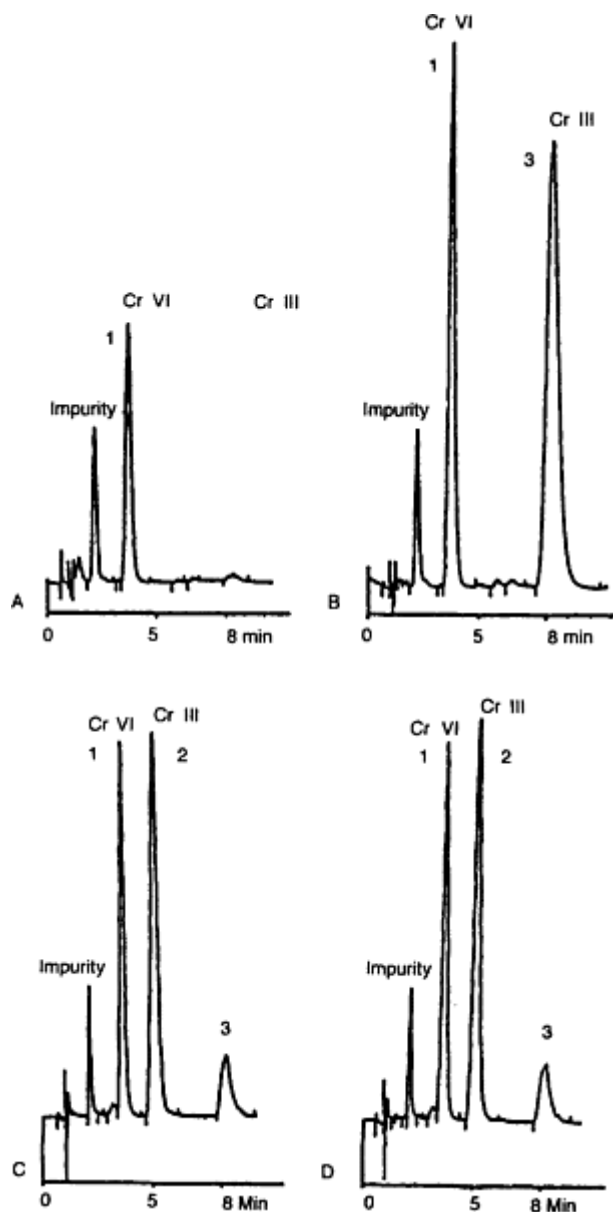


Fig. 2.16 Chromatograms of reaction mixtures of Cr(III) and Cr(VI) Conditions for high performance liquid chromatography: column RP-8, mobile phase; methanol-water (65:35); flow rate, $3\text{cm}^3\text{ min}^{-1}$ detection at 254nm: (A) $10.0\mu\text{g}$ Cr(III), pH 4.0; (B) $10\mu\text{g}$ Cr(III), pH 5.8; (C) $10.0\mu\text{g}$ Cr(IV), pH 4.0; (D) $10.0\mu\text{g}$ Cr(VI)+ $10\mu\text{g}$ Cr(III) pH 4.0.1, unidentified disulphide; 2, $\text{Cr}(\text{S}_2\text{CH}(\text{C}_2\text{H}_5)_2)_2$ ($\text{OS}_2\text{CN}(\text{C}_2\text{H}_5)_2$),

(Cr(VI)); $3 \text{Cr}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_3$ (Cr(III))

Source: Reproduced with permission from Frederick Wieweg and Son, Wiesbaden [230]

room temperature with 5% sodium diethyldithiocarbamate. It is then extracted with chloroform and analysed by reversed phase high performance liquid chromatography, after the residue from evaporation of the chloroform has been dissolved in acetonitrile, using methanol:water (65:35) as mobile phase. Detection was by ultraviolet at 254nm. Corrections were made for interference between chromium(III) and chromium(VI) and concentrations of $2\text{--}10\text{mg L}^{-1}$ of each ion were determined with accuracies of the order of $\pm 5\%$.

In this method chromium(II) chelates at pH 5.8 but not at pH 4.0.

Evaluation of the peaks shown in Fig. 2.16 produced with chromium(III) and chromium(VI) standard solutions enables the concentration of these two species in unknown water samples to be deduced.

The application of this technique is also discussed under multianion analysis in section 13.1.1.5.

2.19.8 Preservation of chromate containing samples

Stollenwerk and Grove [231] investigated the effect on the concentration of hexavalent chromium of sample preservation techniques. Acidification of samples could reduce hexavalent chromium to the trivalent form. The rate of such reduction was increased by impurities such as nitric oxide present in nitric acid. Organic matter could also accelerate reduction of hexavalent chromium in acidified samples, and could also reduce the chromium even in unacidified samples. The best method for preserving hexavalent chromium involved filtration and cooling of the sample. Storing the sample at 4°C might preserve the concentration of hexavalent chromium for some time, depending on the reactivity of other constituents in the sample, but should not be relied on. Measurement of total chromium is recommended as a method of checking on chromium reduction.

2.19.9 Preconcentration

The preconcentration of chromium is discussed in sections 15.1.4 and 15.1.13.

2.19.10 Miscellaneous

Differential pulse voltammetry has been used to determine chromate and chromium(III) [227,228].

Crosmun and Mueller [228] achieved a detection limit of $10\mu\text{g L}^{-1}$ chromate in non saline waters. Rajendrababu and Nanda Kumar [232] have described a simple paper chromatographic method for the rapid detection of chromate in non saline water in amounts down to $2\mu\text{g}$. Chemiluminescence with luminol peroxide [233] and with lophine [234] have been used to determine low concentrations of chromate in water. The former technique achieved a detection limit of 0.05mg L^{-1} and the latter $0.3\mu\text{g L}^{-1}$ without preconcentration and $0.015\mu\text{g L}^{-1}$ with preconcentration.

Cranston and Murray [235] have reviewed methods for the determination of chromium species in non saline waters.

2.20 Cis aconitate

2.20.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.21 Citrate

2.21.1 Spectrofluorometric method

Bishop [236] has proposed spectrofluorometric tests for the presence of citrate in water.

2.21.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.21.3 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.4.

2.22 Condensed phosphates

Condensed phosphate is a generic title for all phosphates which are formed by the removal of one or more water molecules from orthophosphoric acid, which may be represented as $3\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$. These include metaphosphoric acid ($\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$ ie HPO_3), pyrophosphoric acid ($2\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$ ie $\text{H}_4\text{P}_2\text{O}_7$), ultraphosphoric acid (general formula $m\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$ where $0 \leq m \leq 1$), and polyphosphoric acid (general formula $m\text{H}_3\text{PO}_4 - (m-1)\text{H}_2\text{O}$ where $1 \leq m \leq \infty$). The most common condensed phosphates are pyrophosphate and tripolyphosphate which have dissociable protons and behave as typical polyprotic acids. Both exist in three forms.

Pyrophosphoric acid is represented as $\text{H}_4\text{P}_2\text{O}_7$ ($2\text{H}_2\text{OP}_2\text{O}_5$). The three forms of pyrophosphate are:

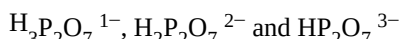
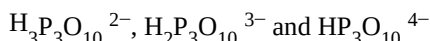


Table 2.12 Major environmental factors affecting the hydrolytic degradation of condensed phosphates

<i>Factor</i>	<i>Approximate effect on rate</i>
Temperature	10^5 – 10^6 faster from freezing to boiling
pH	10^3 – 10^4 slower from strong acid to base
Enzymes	As much as 10^5 – 10^6 faster
Colloidal gels	As much as 10^4 – 10^5 faster
Complexing cations	Very many-fold faster in most cases
Concentration	Roughly proportional
Ionic environment in the solution	Several-fold change

Source: Own files

Tripolyphosphoric acid is represented as $H_5P_3O_{10}$ ($3H_3PO_4-2H_2O$). The three forms of tripolyphosphate are:



A number of factors affect the rate at which condensed and organic phosphates undergo hydrolytic degradation in aqueous solution. The major environmental factors in decreasing order of effectiveness are listed in Table 2.12. Consideration of Table 2.12 indicates that pH is one of the factors which exerts a considerable influence on the rate of hydrolysis.

In domestic waste waters, all these factors may influence the hydrolysis of condensed phosphate to orthophosphate. Thus if the sample is not analysed immediately, changes in the concentrations of condensed and orthophosphates will occur. If the forms of phosphate are to be determined rather than total phosphate, hydrolysis must be prevented.

2.22.1 High performance liquid chromatography

High performance liquid chromatography has also been used [237] to determine orthophosphate, pyrophosphate and tripolyphosphate.

Speciation and quantitative analysis of orthophosphate, pyrophosphate and tripolyphosphate are performed by using high performance liquid chromatography with inductively coupled argon plasma emission spectrometric detection. High performance liquid chromatography is used to separate mixtures of phosphates on an anion exchange column using tartrate magnesium buffer. The ICP is used as a selective detector by observing P II emissions at 214.9nm. The detection limit is 0.5, 1 and 3 μ g respectively for ortho-, pyro- and tripolyphosphate respectively.

In this procedure a Waters Associates liquid chromatograph was connected to anion

exchange columns. Column packings used were

Table 2.13 ICP response factor for various phosphorus compounds

Compounds		Response factor	Purity
KH_2PO_4	Orthophosphate	1.00	1.00
$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	Pyrophosphate	1.01	1.02
$\text{Na}_5\text{P}_3\text{O}_{10}$	Tripolyphosphate	1.00	1.00
(NaPO_3)	Metaphosphate	1.02	0.93
$\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_7\text{PNa} \cdot 6\text{H}_2\text{O}$	—	0.98	1.14
$\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_{10}\text{P}_2$	—	1.03	0.98
$\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_{13}\text{P}_3\text{Na}_3 \cdot 3\text{H}_2\text{O}$	—	1.02	0.97

Source: Reproduced with permission from the American Chemical Society [237]

Table 2.14 HPLC variables

Column	μ -Bondapak-NH ₂ 1/8in×1ft Nucleosil N(CH ₃) ₃ 1/8in×1ft
Eluant	Tartaric acid (0.1 mol L ⁻¹)+MgSO ₄ (0.01 mol ⁻¹)+NaOH (0.1 mol ⁻¹)
Buffers	Oxalic acid (0.1 mol ⁻¹)+MgSO ₄ (0.01 mol ⁻¹)+NaOH (0.1 mol ⁻¹) Ammonium formate (0.1mol ⁻¹)+MgSO ₄ (0.01 mol ⁻¹)+HCl (0.1 mol ⁻¹) Acetic acid (0.2 mol ⁻¹)+NaOH (0.1 mol ⁻¹) Tris(hydroxymethyl)amine (0.3mol ⁻¹)+H ₂ SO ₄ (0.075mol ⁻¹)

Source: Reproduced with permission from the American Chemical Society [237]

μ -Bondapak-NH₂ and Nagel SA. The outlet of the liquid chromatograph was connected to the crossflow nebuliser of the ICP spectrometer (Jarrell-Ash-Atom-Comp 750) with Teflon tubing (1/16in×5in). Eluant flow rate was set at 1ml min⁻¹.

Phosphorus was monitored at 214.9nm (second order). The analog signal was taken out through the profile mode of a computer program. In order to filter noise, a 50k Ω resistor and 20 μ F condenser were installed before the recording, giving an approximate time constant of 1s.

The ICP operational parameters were RF power 1.3kw, coolant gas 18L min⁻¹, sample gas 0.5L min⁻¹, plasma gas 0.1min⁻¹ and observation height in plasma 15mm.

The results in Table 2.13 indicate that under these conditions the detection response is substantially independent of the chemical form of the phosphorus compounds.

Optimum chromatographic conditions are summarised in Table 2.14.

Among the eluants examined, oxalate plus magnesium gave the best resolution, tartrate plus magnesium gave the second best but formate plus magnesium and acetate plus

magnesium gave poor resolutions.

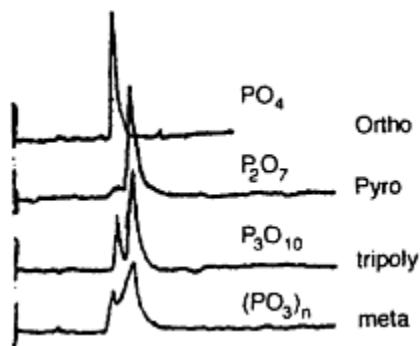


Fig. 2.17 Chromatogram of orthophosphate, pyrophosphate, triphosphate and trimetaphosphate. Eluant was Tri-sulphate buffer (pH 8.2)

Source: Reproduced with permission from the American Chemical Society [237]

Oxalate plus magnesium buffer should be freshly prepared as it is subject to decomposition. The column should be rinsed after usage.

Calibration curves prepared by injecting an aliquot of different concentrations showed a linear relationship with a dynamic range of 10^{-4} – 10^{-2} mol L⁻¹. The practical detection limit was estimated for the chromatogram taking the peak height to noise level ratio at 2. It was 0.5 µg of P, 1 µg of P and 3 µg of P for mono-, di- and triphosphate.

With the use of a basic eluant such as ammonium or Tris buffer, it was noticed that triphosphate was rapidly decomposed to orthophosphate and pyrophosphate during chromatography. Fig. 2.17 shows the chromatogram of orthophosphate, pyrophosphate, triphosphate and metaphosphate using Tris buffer as an eluant. It may reasonably be expected that the triphosphate peak would appear later than pyrophosphate. However, no peak appeared in such a later retention time range and, instead, two peaks which had the same retention time as orthophosphate and diphosphate appeared. The areas of the first and second peaks had the ratio of 1:2 indicating the mole ratio of 1:1. This suggests that the third P-O bond of triphosphate is readily cleaved at the column head giving 1mol of phosphate and 1mol of diphosphate. Diphosphate is stable enough to give a single peak during chromatography. When triphosphate aqueous solution was kept at room temperature for 1 week, significant deterioration was observed. Basic condition and the presence of µ-Bondapak-NH might accelerate decomposition rate.

When the ionic strength of the water sample is not high, phosphate can be trapped at the column top and be eluted with eluant buffer. By use of this concentration technique, dilute solutions can be analysed. Orthophosphate aqueous solution (10^{-4} , 10^{-5} and 10^{-6} mol L⁻¹) was pumped into the column at the rate of 1.5, 1.5 and 2.0 ml min⁻¹ respectively. Since too much time is required to load the water sample, a faster loading rate is

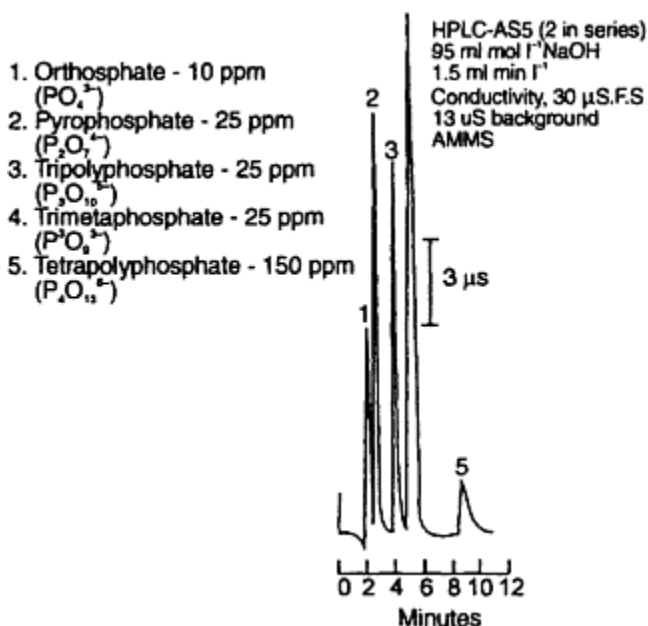


Fig. 2.18 Chromatogram of orthophosphate, pyrophosphate tripolyphosphate, trimetaphosphate and tetrapolyphosphate Column is μ -Bondapak. NH_2 and the eluant was oxalate-Mg buffer at the flow rate of 1.0ml min^{-1} , 50 μL of mixed solution containing $10^{-3} \text{ mol L}^{-1}$ of each phosphate

Source: Reproduced with permission from the American Chemical Society [237]

Table 2.15 A Elution recovery of orthophosphate from high performance liquid chromatography column at different sample concentrations

Concn, mol L^{-1}	Emission intens integrated	Recovery (%)
10^{-3}	114	100
10^{-4}	125	109
10^{-5}	108	95
10^{-6}	100	87

Source: Reproduced with permission from the American Chemical Society [237]

chosen for the most dilute sample ($10^{-6} \text{ mol L}^{-1}$). Recovery from the column is listed in Table 2.15.

In Fig. 2.18 a typical chromatogram obtained by this technique for a mixture of

orthophosphate, pyrophosphate and tripolyphosphate ($\text{P}_3\text{O}_{10}^{5-}$) is shown.

Yaza *et al.* [238] used high performance liquid chromatography with a photodiode array detector to analyse mixtures of polyphosphates, orthophosphates and monofluorophosphates.

2.22.2 Ion exclusion chromatography

Ion exclusion chromatography provides a convenient way to separate molecular acids from highly ionised substances. The separation column is packed with a cation exchange resin in the H^+ form so that salts are converted to the corresponding acid. Ionised acids pass rapidly through the column while molecular acids are held up to varying degrees. A conductivity detector is commonly used.

Tanaka *et al.* [239–241] have reported that the separation of phosphate from chloride, sulphate and several condensated phosphates $\text{P}_2\text{O}_7^{4-}$ (pyrophosphate) and $\text{P}_3\text{O}_{10}^{2-}$ and $\text{P}_3\text{O}_{10}^{3-}$ (tripolyphosphates) could be achieved by ion exclusion chromatography on a cation exchange resin in the H^+ form by elution with an acetone:water and dioxan:water mixture. As the separation mechanism of the ion exclusion chromatography by elution with water alone for numerous anions or their respective acids is based on the Donnan membrane equilibrium principle (ion exclusion effect), it is a highly useful technique for the separation of non-electrolytes such as carbonic acid from electrolytes such as hydrochloric acid and sulphuric acid [242]. Ion exclusion chromatography has also been coupled to ion chromatography to determine simultaneously both weak and strong acids [243]. The ion exclusion chromatography separation of orthophosphate from the strong acid anions by elution with organic solvent-water described above is based on this ion exclusion effect and/or the partition effect between the cation exchange resin phase (water rich) and the mobile phase (organic solvent rich) owing to the hydration of the resin [239] and phosphate has been monitored as the corresponding acid (H_3PO_4) with a flow coulometric detector for the detection of H^+ ion and a conductometric detector.

The application of this technique is also discussed under multianion analysis in section 13.2.1.3.

2.23 Cyanide (free)

2.23.1 Spectrophotometric method

Williams [244] and others [245] have described an autoanalyser method for the determination of $1\text{--}250\mu\text{g L}^{-1}$ cyanide in non saline waters. In this method cyanide is determined spectrophotometrically by means of the pyridine-pyrazolone method. The extinction of the formed complex is measured at 620nm and is in relation to the concentration of the cyanide. The cyanide is oxidised with chloramine-T. The formed cyanogen chloride reacts with the pyridine-pyrazolone mixture to form a blue coloured complex. The apparatus used is illustrated in Fig. 2.19.

Broderius [246] determined free cyanide and hydrocyanide in non saline waters and industrial waters directly by bubbling compressed air

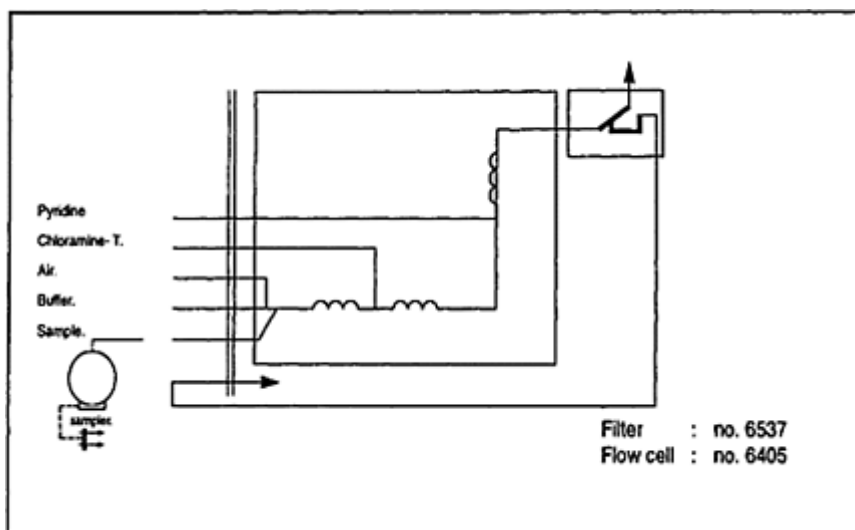


Fig. 2.19 Autoanalyser method for determination of cyanide

Source: Reproduced with permission from Butterworth Press, UK [244]

through the solution to displace cyanide, and collecting it in a glass bead concentration column. In a second method, hydrogen cyanide was allowed to diffuse from an enclosed solution into dilute sodium hydroxide in a dish suspended above the solution. The separated and concentrated cyanide was determined spectrophotometrically by the chloramine-T method. The diffusion procedure was recommended for determining low concentrations of hydrogen cyanide.

Reagents

Sodium hydroxide, 1N

Sodium hydroxide, 0.02N

Acetic acid, 2.25N

Phosphate buffer, chloramine-T [247]

Chloramine-T, $1\text{ g } 1100\text{ ml}^{-1}$

Standard cyanide solution: prepare concentrated sodium cyanide solutions, dilute to the required concentrations and adjust to pH 5.5 with hydrochloric acid to convert to free cyanide.

The apparatus used to isolate and concentrate hydrogen cyanide by the diffusion principle is shown in Fig. 2.20 [248].

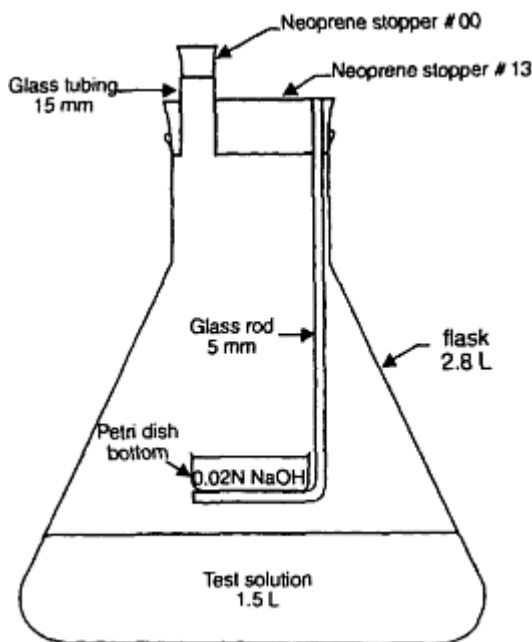


Fig. 2.20 Apparatus used to isolate and concentrate molecular hydrogen cyanide by the diffusion procedure

Source: Reproduced with permission from the American Chemical Society [246]

Air purge method

The method for determining hydrogen cyanide uses a gas regulator and flow meter, a temperature regulated sparging chamber and a glass bubbler through which finely dispersed air is bubbled at $25\text{--}300\text{ ml min}^{-1}$ into 20L of test solution. A glass bead concentration column coated with about 0.4ml of 1.0N sodium hydroxide is used to collect the displaced hydrogen cyanide and a water displacement bottle measures the volume of air dispersed in the sample and passed through the column. At the end of the collection period the cyanide absorbed in the concentration column is washed off with three 5ml washings of deionised water into a 25ml volumetric flask for colorimetric analysis.

The hydrogen cyanide concentration in a solution is calculated from the quantity of hydrogen cyanide collected in a column and by reference to a calibration curve relating the micrograms of hydrogen cyanide displaced per litre of air dispersed with the known hydrogen cyanide concentration in standard solutions of the same temperature.

Diffusion method

The apparatus used to determine hydrogen cyanide by the diffusion method consists of a 2.8L Fernbach flask (Corning 4420) fitted with an airtight No 13 neoprene rubber stopper and the bottom section of a petri dish (Corning 3160, 60×15 mm) attached by silicone

cement to a solid glass support rod (Fig. 2.20). The isolation and concentration of hydrogen cyanide from an aqueous solution is accomplished by adding 1.5L of sample to the flask and sealing with a stopper. After a short equilibration period either 8.5 or 20.5ml of 0.02N sodium hydroxide is pipetted through a small hole in the large stopper into the petri dish suspended in the air space above the sample. Seal the system and absorb the hydrogen cyanide diffusing from the surface of the test solution into the alkali solution. The air space between the sample and alkali serves to separate the nonvolatile and ionic species in solution from the collected hydrogen cyanide. A 2h collection period is generally sufficient to allow for an analytically measurable amount of hydrogen cyanide to be transferred from the sample to the sodium hydroxide. The small stopper in the lid is removed and an 8 or 20ml aliquot of alkali absorbent containing the dissolved hydrogen cyanide is transferred to a 10 or 25ml volumetric flask, respectively.

In the spectrometric finish, 25ml portions of solutions referred to above are acidified to about pH 5.6 with 3 or 6 drops of 2.25N acetic acid, respectively. Four drops of chloramine-T solution (1.0g 100mL⁻¹) are added and the solution left to stand for about 2min. A single solution containing a phosphate buffer and chloramine-T [247] can be used to lower the pH of the 0.02N sodium hydroxide and to halogenate the cyanide [247]. Then 1.0 or 2.5ml respectively of the pyridine-barbituric acid reagent [24] are added and the solution made up to the mark with deionised water. After about 10min the intensity of colour produced at 582nm is measured against a blank. The cyanide content expressed as hydrogen cyanide is determined from a suitable calibration curve.

The detection limit achieved in the diffusion method was approximately 1.3µg cyanide L⁻¹. The amount of hydrogen cyanide collected by the diffusion procedure is temperature dependent. This effect is minimal, however, in the temperature range of 15°C to about 22°C. At higher temperatures the rate of hydrogen cyanide displacement increases rapidly.

In the diffusion method, ammonia (50mg L⁻¹), sulphide (1mg L⁻¹) and phenol (50mg L⁻¹) resulted in only about an 8%, 13% and 0% reduction in the coloured development by the pyridine-barbituric acid method for solutions containing 40µg cyanide L⁻¹. The displacement of hydrogen cyanide by diffusion from 1.5L test solutions containing 25µg cyanide L⁻¹ chemicals: 130 mg L⁻¹ chloride, 7.4mg L⁻¹ SO₄²⁻, 3.0mg L⁻¹ NO₃⁻, 100mg was virtually unaffected by the individual presence of the following L⁻¹ SCN⁻, 50mg L⁻¹ NH₃⁻, 0.1mg L⁻¹ Na₂S-S, 50mg L⁻¹ phenol, 50mg L⁻¹ o-cresol, 5mg L⁻¹ Zn²⁺, 5mg L⁻¹ Cd²⁺, 5mg L⁻¹ Pd²⁺, 1.0mg L⁻¹ Fe(CN)₆⁴⁻ or Fe(CN)₆³⁻.

Table 2.16 Determination of HCN by the diffusion procedure for sodium cyanide spiked water samples at 20°C

<i>Amount of total cyanide added (as HCN)</i>			<i>HCN conc (µgL⁻¹)</i>	
<i>Sample</i>	<i>pH value</i>	<i>Natural waters</i>	<i>(µgL⁻¹) Expecteda</i>	<i>Determined</i>
Well	7.92	27.2	26.2	18.8

Spring	7.38	27.2	26.9	27.0
Creek	6.53	27.2	27.1	26.2
Lake	7.85	27.2	26.3	23.4
Pond	8.57	27.2	23.1	20.6

^aExpected concentration is equal to that added as sodium cyanide plus that present in the effluent portion; all values adjusted for pH and temperature

Source: Reproduced with permission from the American Chemical Society [246]

Sulphide at concentrations of 1.0mg L^{-1} $\text{Na}_2\text{S-S}$ extensively interfered with the determination of hydrogen cyanide. Since it was observed that such a concentration will only have minimal effect on the direct colorimetric procedure for cyanide determination, the interference process must occur in the test solution itself. Possibly sulphide oxidation products, especially polysulphides, react with cyanide to produce thiocyanate. Therefore, sulphide should be removed from a sample as soon as possible after collection to prevent its potential interaction with cyanide. Recommended procedures for sulphide removal suggest the addition of either lead or cadmium salts.

In Table 2.16 are shown some results obtained in applying the diffusion procedure to several spiked non saline water samples.

Montgomery *et al.* [250] determined free hydrogen cyanide in river water by a method based on extraction of cyanide ion from water with 1:1:1 trichloroethane, then re-extraction of cyanide in aqueous pyrophosphate solution. After the extraction of hydrogen cyanide into sodium pyrophosphate solution it is treated with saturated aqueous bromine, sodium arsenite and p-phenylene diamine and determined spectrophotometrically at 508nm. Less than 0.01mg L^{-1} of hydrogen cyanide can be detected.

Aoki *et al.* [251] determined cyanide in non saline water, in the presence of heavy metals, based on its separation as hydrogen cyanide by passage through a microporous poly(tetrafluoroethylene) membrane and reaction with hypochlorite. Absorption was measured at the λ_{max} for hypochlorite (290nm). The relative standard deviation was 1.9% at the $1 \times 10^{-6}\text{M}$ cyanide level.

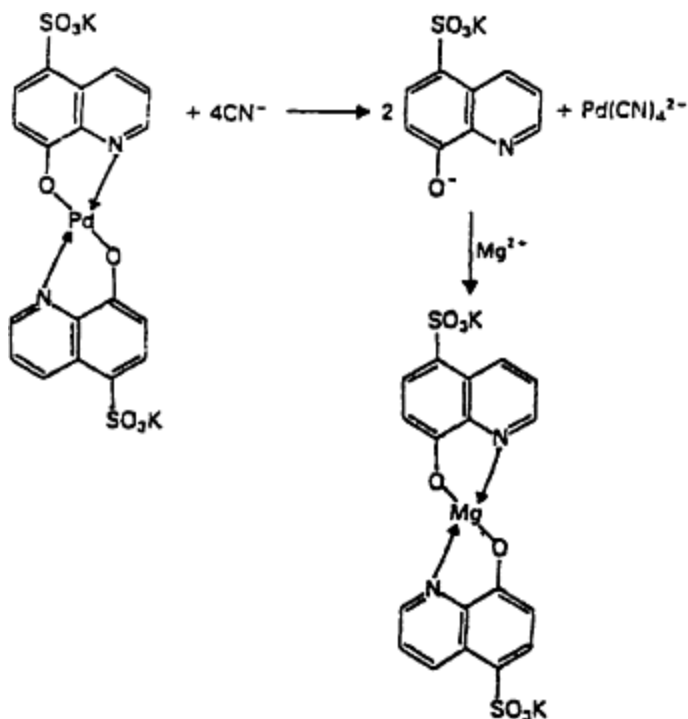
2.23.2 Spectrofluorometric method

1,10 Phenanthroline complexes

Yin and Ho [252] described a method for free cyanide in non saline water based on released fluorescence of a dissociated ternary complex. A cationic ternary silver complex formed by the reaction of tetrabromofluorescein (TBF) with silver 1,10-phenanthroline at pH 3–8, dissociated in the presence of cyanide to give the highly fluorescent anion, the intensity of which was directly proportional to cyanide concentration. Interference by magnesium, calcium and lead(II) ions found in water were masked by chelation with EDTA. Lead acetate was used to precipitate sulphide; other common anions, such as chloride, sulphate and nitrate, did not interfere. The detection limit was $0.02\mu\text{g L}^{-1}$ cyanide.

Palladium complexes

A rapid and sensitive method has been developed for the determination of microgram amounts of sulphide and cyanide [253]. This method depends on the demasking of quinolin-8-ol-5-sulphonic acid by cyanide or sulphide from the non-fluorescent potassium bis(5-sulphoxino)-palladium. The liberated quinolin-8-ol-5-sulphonic acid then coordinates with the magnesium ion present to form a fluorescent chelate, which is a measure of the amount of cyanide or sulphide present. The reactions are shown below.



Cyanide can be determined by a method [254] based on the liberation of piazselenol naphtho(2,3-c)(1,2,5)selenadiazole (L) from the $\text{Pd}_2\text{L}_2\text{Cl}_4$ complex [255]. The organic reagent is then extracted into hexane and its fluorescence is measured.

Pyridoxal and pyridoxal-5-phosphate complexes

Bonavita [256] studied the reaction of pyridoxal and pyridoxal-5-phosphate with cyanide. This anion produces a catalysed oxidation of pyridoxal to the lactone of 4-pyridoxic acid [257]. The rate of the reaction is measured by measuring the fluorescence intensity. The method consists in treating cyanide with pyridoxal at pH 7.5 and measuring the fluorescence intensity at pH 10.

Chloramine and nicotinic acid

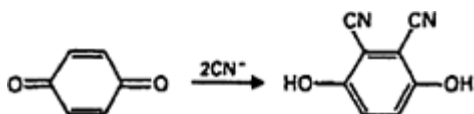
A method has been proposed for the determination of cyanide based on its reducing reaction with chloramine-T and nicotinamide [258]. Cyanide is converted into cyanogen

chloride with chloramine-T and this cleaves the pyridine ring of nicotinamide (Von Braun reaction), giving a product which has a strong blue fluorescence in alkaline medium.

Quinone monoxime benzenesulphonate ester

Cyanide has been determined by redox and substitution reactions. The reactions of cyanide with quinone monoxime benzenesulphonate ester [259,260] are highly selective. This reagent reacts specifically with cyanide. Other anions such as sulphide and thiocyanate, which interfere in most tests for cyanide, do not interfere in these determinations.

Guilbault and Kramer [261] have proposed a specific method for the determination of cyanide based on its reaction with quinone monoxime benzenesulphonate ester, giving a green fluorescent compound. In a later paper these authors reported the reaction of cyanide with several quinones and quinone derivatives: *p*-benzoquinone, *N*-chlorobenzoquinoneimine and substituted quinone monoxime benzenesulphonate esters and ethers. All of these compounds react specifically with cyanide to give fluorescent products. The proposed reaction of cyanide with *p*-benzoquinone is



In general, all of the products have approximately the same excitation and emission wavelengths, 440 and 500nm, respectively. Substitution on the quinone ring decreases the fluorescence of the product and the rate of reaction. The order of fluorescence intensity and the rate of reaction increase in the following order of solvents used: dioxane<ethyl formate <2-methoxyethanol<methanol<acetonitrile<dimethylformamide< dimethyl sulphoxide. This parallels the order of the dielectric constants of the solvents.

Quinoline-8-ol-5 sulphonic acid

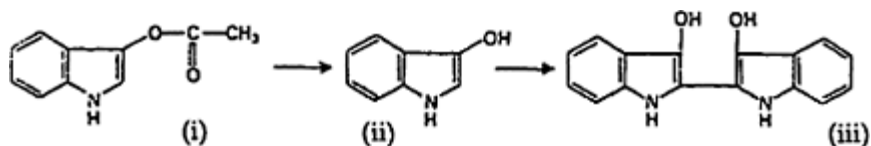
The better sensitivity of fluorometric methods *versus* colorimetric methods can be observed in the determination of cyanide with quinoline-8-ol-5-sulphonic acid [262]. The colorimetric method is sensitive to $1\mu\text{g mL}^{-1}$ of cyanide whereas the sensitivity of the fluorometric method is $0.02\mu\text{g mL}^{-1}$ of cyanide.

2', 7'-di(acetoxymercuri) fluorescein

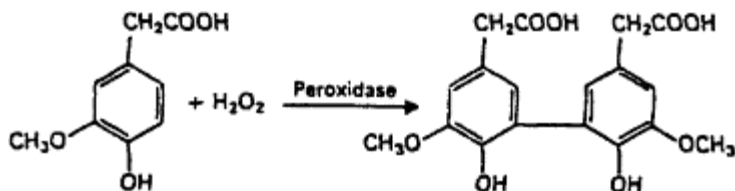
Using 2',7'-di(acetoxymercuri) fluorescein, two methods for the determination of cyanide have been proposed [263].

Enzymatic methods

Cyanide can be determined by the inhibitory action over the enzymatic activity of the hyaluronidase enzymatic system. One method involves the hydrolysis of the non-fluorescent indoxyl acetate (i) which measures the enzymic activity of hyaluronidase through the formation of the highly fluorescent indigo white (iii) [264].

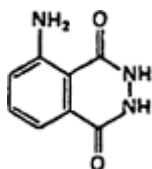


The other method [229], involves the use of peroxidase, in which non-fluorescent homovanillic acid is converted by hydrogen peroxide into the highly fluorescent 2,2'-dihydroxy-3,3'-dimethoxybiphenyl-5,5'-diacetic acid:



2.23.3 Chemiluminescence methods

One method is based on the inhibiting action of this anion on the chemiluminescence of luminol with hydrogen peroxide in the presence of copper(II) [265]. The induction period increases with increase in the concentration of cyanide and the logarithm of the induction period is proportional to the concentration of cyanide.



Ishii *et al.* [266] used flow injection analysis with chemiluminescence detection for determining very low levels of cyanide in non saline waters by means of the uranine-sodium hydroxide-didocecyldimethylammonium bromide system. The emission induced by cyanide is efficiently sensitised by uranine in organised surfactant aggregate bilayer vesicles solution. The method is selective for cyanide and has a detection limit of 3×10^{-10} M for continuous sample flow and of 2×10^{-9} M for 20 μ L sample injection. The relative standard deviation was 2.1% ($n=10$) for 0.05 ng of cyanide.

2.23.4 Atomic absorption spectrometry

Rosentreter and Skogerboe [267] and Razmilic [268] have described an atomic absorption spectrometric method for the determination of sub-ppm concentrations of cyanide in non saline waters.

Haj-Hussein *et al.* [269] have developed a flow injection method for the determination of cyanide ion by atomic absorption spectrometry. Aqueous cyanide samples (pH 11.0)

are injected into an on-line cupric sulphide packed column, and potassium hydroxide solution (pH 11.0) is used as the carrier. The eluent containing the analyte as cuprocyanide complexes is introduced into the nebuliser of the atomic absorption spectrometer. This novel flow injection analysis/atomic absorption spectrometric method has a sensitivity of 1mg L^{-1} cyanide for 0.0044A and a detection limit also of 1mg L^{-1} cyanide. The precision of the technique is better than 2% relative standard deviation at 26ppm cyanide with a sampling rate of 40–50 samples/h. The effects of flow rate, sample volume, and anionic interference on the flow injection analysis/atomic absorption spectrometric signals are discussed. Only citrates were found to interfere significantly (+5% at 20-fold concentration). The conversion method is potentially applicable to other anions.

2.23.5 Flow injection analysis

Fogg and Alonso [270] have described an oxidative amperometric flow injection method for the determination of cyanide at an electrochemically pretreated glass carbon electrode.

The application of this technique is also discussed under multianion analysis in section 14.4.1.4.

2.23.6 Potentiometric method

A method based on microdiffusion coupled with potentiometric measurement has been used to determine cyanide in non saline waters [271].

2.23.7 Ion selective electrodes

Ion selective potentiometry in alkaline solution provides a suitable finish for the determination of cyanide [272–277]. Sulphide ion is an interferent, and a cadmium nitrate treatment has been found to remove sulphide without influencing the response of the silver iodide-silver sulphide electrode. If both the precipitate and solution from this treatment are colourless (sulphide absent), filtration of the mixture before the potentiometric measurement is unnecessary. Since the electrode response of the electrode is pH dependent, standards and samples must be brought to the same pH. It is noteworthy that the silver-silver sulphide electrode (eg Orion 94–16) is more sensitive to cyanide than the silver iodide-silver sulphide one [272,274] but the response is affected by cadmium ion.

2.23.8 Infrared spectroscopy

Stuart *et al.* [278] used infrared spectroscopy in speciation studies of cyanide in non saline waters. These workers applied the method to the determination of $10\text{--}100\text{mg L}^{-1}$ cyanide in non saline waters.

2.23.9 Enzymatic method

Fenong [279] has described an enzymatic method for the spectrophotometric determination of micro amounts of cyanide.

2.23.10 Ion chromatography

Bond *et al.* [280] have discussed the determination of free cyanide together with sulphide in non saline waters by ion chromatography.

Peschet and Tinet [281] applied ion chromatography to the determination of free cyanide (and hypochlorite and sulphide) in ground waters.

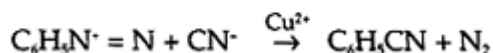
Various other workers [282–284] have recently applied ion chromatography to the determination of free cyanide (and metal cyanide complexes) in waste water (see section 2.57) which no doubt would be applicable to non saline waters.

2.23.11 Ion pair chromatography

The application of this technique is discussed under multianion analysis in section 13.5.1.3.

2.23.12 Gas chromatography

Funazo *et al.* [285] have described a method for the determination of cyanide in water in which the cyanide ion is converted into benzonitrile by reaction with aniline, sodium nitrite and cupric sulphate. The benzonitrile is extracted into chloroform and determined by gas chromatography with a flame ionisation detector. The detection limit for potassium cyanide is 3mg L^{-1} . Lead, zinc and sulphide ions interfere at 100mg L^{-1} but not at 10mg L^{-1} .



To carry out the derivatisation reaction, 0.25ml of sodium nitrite ($7.0 \times 10^{-2} \text{ mol L}^{-1}$ aqueous solution) and 1.0ml of potassium cyanide (known concentration) were added to 0.25ml of cupric sulphate ($1.0 \times 10^{-1} \text{ mol L}^{-1}$) in a 10ml glass reaction tube with a glass stopper. Then 1.0ml of chloroform solution was added and the tube was mechanically shaken for 30min in an incubator kept at 55°C . The chloroform solution contains aniline ($3.0 \times 10^{-1} \text{ mol L}^{-1}$) and p-dichlorobenzene ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) as an internal standard. At the end of the reaction period, 0.5ml of the organic layer was taken out of the tube and washed with 5.0mol of 1mol L^{-1} hydrochloric acid. The chloroform extract ($1\mu\text{L}$) was injected into the gas chromatograph. The resulting benzonitrile was determined by an internal standard method.

A Shimadzu GC-3BF gas chromatograph equipped with a dual flame ionisation detector was used. A glass column ($1.7\text{m} \times 3\text{mm}$ id) was packed with 10% PEG-20M on 60–80

mesh Shimalite W. The column and injection port temperatures were maintained at 140 and 250°C respectively. The nitrogen flow rate was 25ml min⁻¹. The peak areas were measured by a digital integrator.

Down to 3mg L⁻¹ free cyanide can be determined in waste waters by this procedure without interference from 100mg L⁻¹ of ammonium, cadmium(II), chromium(VI), fluoride, chloride, bromide, iodide, thiocyanate, nitrate, bicarbonate and phosphate. Lead (II), zinc(II) and sulphide interfere at 100mg L⁻¹ but do not interfere at 10mg L⁻¹.

2.23.13 Miscellaneous

Other techniques used for the determination of free cyanides in water samples include ultraviolet spectroscopy as the Ni(CN)₄²⁻ complex [286], squarewave polarograph [287] and conventional polarography. The sensitivity of the polarographic methods range between 0.1mg [286] and 1µg [287] cyanide .

2.24 Cyanide (total)

Total cyanide includes free cyanide ions plus complexed metal cyanides, eg ferrocyanides. The methods discussed in the previous section determine only free uncomplexed cyanide. To determine uncomplexed plus complexed cyanide, ie total cyanide, it is necessary prior to analysis to decompose the complexed cyanides to free cyanide [288].

2.24.1 Atomic absorption spectrometry

Rameyer and Janauer [289] have described a method using reactive ion exchange for the determination of complex iron cyanides in water in the mg L⁻¹ range. The cyanide complexes are preconcentrated on shallow beds of sulphonated cation-exchange resins in copper(II) form by precipitation as copper hexacyanoferrate(II) or copper hexacyanoferrate (III). Other cations, including contaminant iron species, are eluted with hydrochloric acid. Aqueous ammonia relatively releases and elutes the hexacyanoferrate by the formation of the copper ammine complex. Finally the complex cyanides are determined as iron by atomic absorption spectrometry.

2.24.2 Ion selective electrodes

A procedure has been developed for determination of cyanide [290] in concentrations down to 2mg L⁻¹ by manual or automated potentiometry using a cyanide ion selective electrode. Distinction is made between simple and complex cyanides by irradiation with ultraviolet light.

2.24.3 Ion chromatography

Rocklin and Johnson [291] have applied ion chromatography to the analysis of mixtures of the complex cyanides of cadmium, zinc, copper, nickel, gold, iron and cobalt.

2.24.4 Gas chromatography

Complex cyanides have been determined gas chromatographically in amounts down to $1\mu\text{g L}^{-1}$ [292]. The complex cyanides are broken down by ultraviolet radiation, reacted with bromine water and the cyanogen bromide formed is separated and determined selectively by means of an electron capture detector.

2.25 Decane sulphonate

2.25.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.26 Dichloroacetate

2.26.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.4 and 12.2.5.

2.26.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.27 Dimethyl benzoate

2.27.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.28 Dithionate

2.28.1 Spectrophotometric methods

Dithionate has been determined spectrophotometrically in the presence of sulphite and sulphate [293].

2.28.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.29 Dodecane sulphate

2.29.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.30 Dodecane sulphonate

2.30.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.31 Fluoride

2.31.1 Spectrophotometric methods

Anosova [294] determined fluoride in highly demineralised water by separating fluoride ion as hydrofluoric acid by stream distillation of the sample (concentrated by evaporation and treated with silver nitrate solution to precipitate fluoride ion) from sulphuric acid medium. The distillate is treated with Alizarin red S (CI Mordant Red 3) solution, buffered at pH 2.5–3.5, and then allowed to react with a known volume of standard thorium nitrate solution. After 30min, the colour is compared with those of a series of standards covering the range 0.0–0.1mg L⁻¹ fluoride.

Moraru and Suten [295] have reviewed Spectrophotometric methods for the determination of fluorides. The methods have been described based on the use of zirconium-xylenol orange [296], lanthanum-alizarin [297], and zirconium solochrome cyanine R [298]. These methods are all capable of determining fluoride in µg quantities in water samples. In an extractive Spectrophotometric determination of micro and submicro amounts (down to 50µg L⁻¹) of fluoride [299], buffered alizarin complex is added to the sample which is then extracted with triethylaminepentanol (1:19) prior to Spectrophotometric evaluation of the organic phase at 570nm.

A method for the determination of fluoride is based on the bleaching effect of fluoride on a column of the zirconium eriochrome organic R complex [300]. This method is applicable over the range 2–25µg fluoride. Sulphate does not interfere in the determination. Lanthanum-alizarin complexone has been used to determine fluoride [301]. The main interfering ions are removed from the sample with a strongly acidic cation exchanger. The reagent (a buffered pH 4.3 mixture of 3-aminomethylalizarin-NN-diacetic acid and lanthanum nitrate with added acetone) is added, and the red chelate is allowed to develop in the dark for about 20min and the extinction determined against a reagent blank at 620nm. If very high sulphate and chloride concentrations are present in the sample, the results must be corrected by reference to a calibration graph. Water samples containing aluminium (greater than 0.1mg L⁻¹) must be adjusted to pH 9 with

potassium hydroxide solution before analysis, to ensure quantitative ion exchange.

Ion exchange/spectrophotometry was used by Capitan-Vallvey *et al.* for determining low levels of fluoride in non saline waters [302]. Fluoride reacts with slightly polymerised zirconium and xylenol orange, and the reaction product is sorbed on Dowex 1-X8. The absorbance of the resin phase at 580 and 750nm is measured directly. The calibration graph is linear in the concentration range of 2–20 $\mu\text{g L}^{-1}$, and the relative standard deviation is 1.8%. The detection limit is 1.1 $\mu\text{g L}^{-1}$ for a 500mL sample.

Long and Huang [303] observed that fluoride causes a decrease in the absorbance due to a zirconium complex of salicylfluorone and cetyltrimethylammonium bromide. The calibration curve is linear for 5–50 μg of fluoride per 50ml. Relative standard deviations were 5.43% at 0.050% fluoride and 2.78% in 0.223% fluoride levels in non saline water.

2.31.2 Spectrofluorometric methods

Various spectrofluorometric systems have been proposed for the determination of fluorides in non saline waters.

Substitution reactions

Aluminium quinolin-8-ol(oxine) system

A method for determining fluoride has been proposed with the aluminium quinolin-8-ol (oxine) system [304]. This system was studied by Gentry and Sherrington [305] in chloroform solution. The presence of fluoride in the aqueous phase before extraction removes some of the aluminium as a complex ion, reducing the amount present as quinolin-8-olate and extractable with chloroform. The necessity for extraction adversely affects the precision of this method.

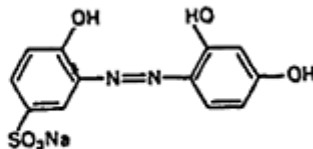
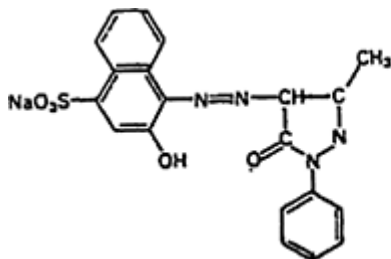
Morin system

The quantitative determination of fluorides with the aluminium-morin system has been widely studied [304,306,307]. Willard and Horton [304] used this system, among others. They obtained a curved calibration graph of fluorescence *versus* fluoride concentration because more than one fluoride complex is formed by aluminium ions. As the fluoride concentrations increase, AlF_2^{2+} , AlF_2^+ , AlF_3 , AlF_4^- and perhaps AlF_5^{2-} and AlF_6^{3-} complexes are formed consecutively. In this series, as more and more fluoride is required to complex a certain amount of aluminium, the rapidity of the decrease in fluorescence decreases, with a consequent loss in sensitivity and precision for large amounts of fluoride. Fortunately, the sensitivity is highest at the lowest levels of fluoride where other methods have lower accuracy. To avoid the numerous interferences, the authors advise the separation of the fluoride by Willard and Winter's method [304] for liquid samples or as hydrogen fluoride by pyrohydrolysis [309] for heavy metal fluorides. Bouman [307] used Willard and Horton's method to determine fluoride but he changed the conditions to increase the sensitivity. He determined fluorides in 0.25ml of water with an accuracy of 20mg L^{-1} .

Eriochrome Red 8 and Superchrome Garnet Y

Powell and Saylor [310] developed two methods for the determination of trace amounts

of fluorides based on the fact that the intensity of fluorescence in the compounds formed in the reaction of aluminium chloride with two dihydroxyazo dyes, Eriochrome Red B (sodium salt of 4-*p*-sulphonaphth-2-ol- α -azo-1-phenyl-3-methyl-5-hydroxypyrazole) (I) and Suprachrome Garnet Y (sodium salt of 5-sulpho-2-hydroxybenzene-azoresorcinol) (II) is decreased on the addition of fluoride. These methods were tested by analysing solutions of pure sodium fluoride both before and after a Willard-Winter distillation. The ions that are often present after distillation, such as sulphate and phosphate do not interfere seriously.



Quenching reactions—Morin system

Fluorescent aluminium chelates have been widely used to determine several anions indirectly, especially fluoride. The aluminium-morin complex is the most commonly utilised.

Bishop [236] studied the influence of anions on the morin test for aluminium, gallium, beryllium and zinc and proposed several tests for the detection of fluoride (oxalate, citrate, phosphate, tartrate and vanadate).

Calcein Blue zirconium system

Hems *et al.* [311] and others [312] studied the determination of zirconium with Calcein Blue (XV) and verified the positive interference that fluoride and sulphate ions produced on the fluorescence intensity of the complex. Based on this fact, Har and West [313] proposed two methods for the determination of both anions.

1-(2-pyridylazo)naphtho-2-ol system

Another fluorescent aluminium chelate used to determine fluoride is the aluminium 1-(2-pyridylazo)naphth-2-ol (PAN) system [314]. Two procedures have been described, one for high sensitivity and the other for a wider range but with poorer sensitivity.

Pontachrome Blue Black R

Bourstyn [315] suggested that the fluorescence quenching produced on the aluminium Pontachrome Blue Black R (2,2'-dihydroxy-1,1'-azonaphthalene-4-sulphonic acid) system could be used to characterise this anion.

Zirconium flavanol system

This system [313,316,317] is particularly sensitive and can be used to determine fluoride at the 2–100 $\mu\text{g L}^{-1}$ level.

Magnesium-quinolin-8-ol system

Fluoride ions cause fluorescence quenching on the magnesium-quinolin-8-ol system. This is used to measure air pollution with a fluoride analyser in which air is drawn past a moving 35mm tape freshly impregnated with magnesium-quinolin-8-ol [318,319]. Variations in the fluorescence are recorded continuously for the assay of fluoride. Ivie [320] and Thompson *et al.* [321] also designed a simplified fluoride analyser with the same system.

2.31.3 Flow injection analysis

Manzoori and Miyazaki [322] applied indirectly coupled plasma atomic emission spectrometry to the determination of $0.03\mu\text{g L}^{-1}$ of fluoride in solvent extracts of non saline water.

Gehlhausen and Carnahan [323] have described a method for the determination of aqueous fluoride by flow injection analysis with a helium microwave-induced plasma. This system operates at 500W and utilises a modified TM_{010} resonator cavity with a demountable plasma torch. Both direct nebulisation and flow injection analysis in conjunction with ultrasonic nebulisation were investigated. Flow injection analysis was found to be the most reliable method because extended nebulisation of aqueous fluoride was found to cause memory effects. Detection limits for aqueous fluoride of 35 and 4ppm were observed for flow injection analysis and direct ultrasonic nebulisation respectively. The interference effects of pH and selected elements were also studied.

2.31.4 Inductively coupled plasma atomic emission spectrometry

To preconcentrate fluoride, Miyazaki and Brancho [324] converted fluoride into the ternary lanthanum-alizarin complexone fluoride and extracted it into hexanol containing *N,N*-diethylaniline. The extract was analysed directly by inductively coupled plasma atomic emission spectrometry for the determination of fluoride. Measurement of the lanthanum(II) 333.75nm, emission line and comparison with a calibration graph enabled fluoride concentrations as low as $0.59\mu\text{g L}^{-1}$ to be determined in Japanese river water (polluted and unpolluted), coastal seawater, and potable water samples. The relative standard deviation was 2.6% for $40\mu\text{g L}^{-1}$ of fluoride. Alkali and alkaline earths do not interfere with this method.

2.31.5 Column coupling capillary isotachophoresis

This technique offers very similar advantages to ion chromatography in the determination of anions, namely multiple ion analysis, ie little or no sample pretreatment, speed, sensitivity and automation. Very similar advantages are offered by capillary isotachophoresis. Zelinski *et al.* [325] applied the technique to the determination of 0.02–0.1mg L^{-1} quantities of fluoride, chloride, nitrate, sulphate, nitrite and phosphate in river water.

The application of this technique is also discussed under multianion analysis in section 14.6.1.1.

2.31.6 Ion selective electrodes

Shiraishi *et al.* [326] showed that a fluoride ion selective electrode could be used to determine fluoride in well water in the presence of aluminium. These workers showed that the de-masking of fluorine from its aluminium complexes is enhanced by dilution of the sample. The permissible limits of aluminium concentration increase markedly with decreasing fluoride concentration, hence fluoride could be determined by a successive dilution method.

Zernalova and Senyavin [327] examined conditions for the potentiometric determination of fluoride in non saline water using an ion selective electrode. Some micro constituents of water did interfere when determining fluorides.

Ion selective electrodes have been extensively applied to the determination of fluoride at the mg L^{-1} and $\mu\text{g L}^{-1}$ levels in water [328–332]. Warner [328], Sekerka and Lechner [329] and Erdmann [330] have applied the technique to non saline waters. Sekerka and Lechner [329] achieved a detection limit of $0.2\mu\text{g L}^{-1}$ fluoride. Their methods employ a total ionic strength adjustment buffer usually comprising sodium hydroxide, 1,2-diaminocyclohexane-*N,N,N*-tetraacetic acid and acetic acid in fixed proportions. Aluminium, iron, calcium and magnesium do not interfere in these procedures within prescribed concentration limits. Pakalns and Farrar [331] have discussed the effect of surfactants on the determination of fluoride. Erdmann [330] has described an automated ion selective electrode method for determining fluoride in non saline waters. This method is capable of analysing 30 samples per hour and utilises an autoanalyser system.

Trojanowicz and Lewardowski [192] have described a multiple flow-through potentiometric system for the continuous determination of fluoride in admixture with chloride and nitrate in non saline waters. Classic ion selection electrode methods for fluoride suffer from the disadvantages of excessive electrode drift, long response time and inadequate precision.

Kissa [333] has described modifications to the determination of fluoride using the fluoride ion selective electrode to enable the determination of concentrations in the range $1\text{--}10\text{mg L}^{-1}$ fluoride with relative errors from 0.2 to 0.6%.

Kissa [333] overcame the aforementioned problems by

- (a) limiting the fluoride concentration to which the electrode is exposed to a $0.01\text{--}0.1\text{mg L}^{-1}$ fluoride or $0.05\text{--}1\text{mg L}^{-1}$ fluoride concentration range;
- (b) measuring the electrode potential in the analyte by approaching equilibrium in the same direction from a higher potential to a lower potential; and
- (c) keeping the temperature of the solutions constant within $\pm 0.2^\circ\text{C}$. The fluoride concentration in the analyte is adjusted to the concentration range of the ion selective electrode by dilution or fluoride addition.

It has been observed by previous workers [334] that the electrode response drifted while the fluoride solution was stirred, but when stirring was stopped, the electrode assumed a stable potential within 5–30min, depending on the fluoride concentration. Kissa [333] examined this procedure and concluded that the apparently stable potential resulted for a reduced transport of fluoride ions to the electrode and did not always represent an

equilibrium potential in the bulk of the solution. Under the conditions outlined in this modified method a stable electrode potential can be obtained in a short time in stirred solutions as dilute as $20\mu\text{g L}^{-1}$ fluoride.

Fucsko *et al.* [335] have described a flow injection ion selective electrode determination of fluoride in non saline waters. This has a sampling rate of 40 samples/h at concentrations $<10^{-6}\text{M}$ and a rate of 60 samples/h at concentrations $>10^{-5}\text{M}$.

2.31.7 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.1.

2.31.8 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.31.9 Ion exchange chromatography

Okabayashi *et al.* [336] collected fluoride ion selectively on an anion exchange resin loaded with alizarin fluorine blue sulphonate.

2.31.10 Gas chromatography—atmospheric pressure helium microwave induced plasma emission spectrophotometry

This technique has been applied to the determination of picogram quantities of fluoride in water [337]. The emission line of fluorine at 685.6nm was used for detection.

Miyazaki and Bransho [324] determined fluoride indirectly in non saline waters with lanthanum alizarin complexone and inductively coupled plasma emission spectrometry. The ternary lanthanum-alizarin complexone-fluoride (La-AC-F) complex was extracted into hexanol containing N,N-diethylaniline, and the extract analysed directly by ICPES for the determination of fluoride. Measurement of the lanthanum(II) 333.75nm emission line and comparison with a calibration graph enabled fluoride concentrations as low as $0.59\mu\text{g L}^{-1}$ to be determined in river water (polluted and unpolluted), coastal seawater and potable water.

2.31.11 Miscellaneous

Perez Ruiz [338] describes a catalytic-kinetic method for determining nanogram amounts of fluoride in non saline waters based on its inhibiting effect on the catalyst in the iron (III)-catalysed photooxidation of thionine. The rate measurements are made by monitoring the decreasing absorbance after illumination for a fixed time. Relative standard deviation was 2.58% for a concentration of $152\text{mg of fluoride mL}^{-1}$ ($n=10$).

2.32 Ethylene diamine tetraacetate

2.32.1 Column exchange chromatography

Nitriloacetate and ethylene diamine tetraacetate anions have been detected in the eluate of a liquid chromatographic column using a carbon paste amperometric detector [339]. With no sample preparation or preconcentration, 0.1mg L^{-1} nitriloacetate or 1.5mg L^{-1} ethylene diamine tetraacetate can be determined in natural and waste waters at a relative standard deviation of less than 7%.

2.33 Formate

2.33.1 Ion chromatography

Kieber *et al.* [340] determined formate in non saline waters (including seawater) by a coupled enzymatic/high performance liquid chromatographic technique. The precision is approximately $\pm 5\%$ relative standard deviation. Intercalibration with an anion chromatographic technique showed an agreement of 98%. Down to $0.5\mu\text{mol L}^{-1}$ absolute of formate could be determined. Kieber *et al.* [340] found $0.2\text{--}0.8\text{mol L}^{-1}$ formate in seawater and $0.4\text{--}10\mu\text{mol}$ in rainwater.

The procedure involves precolumn oxidation of formate with formate dehydrogenase which is accompanied by a corresponding reduction of β -nicotinamideadenine dinucleotide ($\beta(\text{NAD})^+$) to reduced β -nicotinamide dinucleotide (ie β NADH). The latter is quantified by high performance liquid chromatography.

The application of this technique is also discussed under multianion analysis in section 12.2.4.

2.33.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.6.

2.33.3 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.4.

2.34 Fumarate

2.34.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.34.2 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.4.

2.35 Galactonurate

2.35.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.36 Gallate

2.36.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.37 Germanate

2.37.1 Flow injection analysis

Fogg and Bselsn [5] have discussed the determination of germanate in non saline waters by flow injection analysis.

2.38 Gluconate

2.38.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.39 Gluconurate

2.39.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.40 Glycollate

2.40.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.4 and 12.2.5.

2.40.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.40.3 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.4.

2.41 Glyoxylate

2.41.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.42 Hexabenzene carboxylate

2.42.1 Gas chromatography

The application of this technique is discussed under multianion analysis in section 14.1.1.1.

2.43 Hexane sulphonate

2.43.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.44 Hydroxy benzoate

2.44.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.45 α Hydroxy butyrate

2.45.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.4 and 12.2.5.

2.45.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.46 α Hydroxy valerate

2.46.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.47 Hypochlorite and chlorite

2.47.1 Titration procedure

Gordon [341] had described a procedure for the determination of chlorite and hypochlorite in amounts down to 0.1mg L^{-1} by a modified iodometric technique.

2.47.2 Anodic stripping voltammetry

Potentiometric stripping analysis using copper has been employed for the determination of down to $5\mu\text{g L}^{-1}$ hypochlorite in non saline waters [342].

2.47.3 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.48 Hypophosphite

2.48.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.4 and 12.2.5.

2.49 Iodate

2.49.1 Spectrophotometric methods

Truesdale and Smith [343] described an automated method for the determination of iodate on iodide in river water. The method is based on catalytic spectrophotometry. Butler and Gershey [344] have described an automated method for the determination of iodate, iodide, iodine and bromide in river waters based on automated catalytic spectrophotometry. The method involves both the determination of total iodine in concentrations up to $5\mu\text{g L}^{-1}$ and the separate determination of iodide and iodate. The second method was a two-step procedure in which total inorganic iodide was determined using the first method, then iodide extracted with tetraphenyl ammonium hydroxide, after which the first determination was repeated, the iodide being obtained by difference.

Jones *et al.* [345] give details of a procedure for the determination of traces of iodate, iodide and total iodine in fresh waters, based on catalytic determination of iodide, using the reaction between ammonium cerium sulphate and arsenious acid; iodate is determined by the same method after extraction of iodide-iodine into chloroform as an ion pair with the tetraphenylarsonium cation. Iodate can be determined in amounts down to $1\mu\text{g L}^{-1}$ with a resolution of $\pm 0.1\mu\text{g L}^{-1}$ (95% confidence limits).

Apparatus

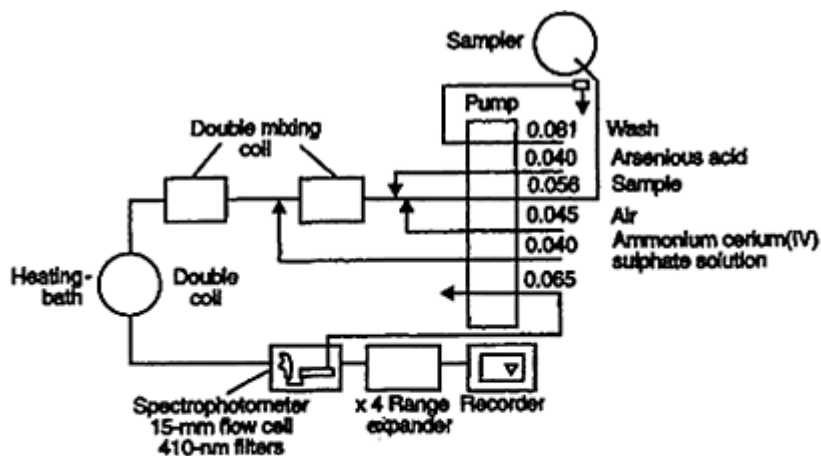
Automatic analysis was performed with a Technicon AutoAnalyzer 1 Instrument. Extractions with chloroform were conducted in 100 ml separating funnels fitted with stoppers and taps made of PTFE. An MSE Hi-Spin 21 centrifuge with glass centrifuge tubes was used to aid separation of the chloroform and aqueous phases. After extraction of iodide an aliquot of each aqueous phase was placed in a 2ml glass sample cup used with the AutoAnalyzer; the chloroform present in the aqueous phase dissolves the standard polystyrene cups.

The AutoAnalyzer manifold system used in these analyses is shown in Fig 2.21.

Determination of total iodide

Assemble the AutoAnalyzer manifold according to the design given in Fig 2.21. While aspirating only the arsenic reagent and deionised distilled water, set 0 and 100% transmission on the recorder. Introduce the cerium (IV) reagent and establish the base line between 31 and 35% transmission (absorbance 0.45–0.5) using a temperature of approximately 34°C. When the baseline has been settled within this transmission range,

expand the 30–50% transmission interval to full scale by using the X 4 range-



Ceric ammonium sulphate, 3.75 $(2(\text{NH}_4)_2\text{SO}_4 \cdot \text{Co}(\text{SO}_4)_2 \cdot 3(\frac{1}{2}\text{H}_2\text{O}))$ plus 200ml distilled water plus 52ml conc. sulphuric acid (18mole L^{-1}) diluted to 1L. Filtered through Whatman GF/C paper before use. Arsenious acid 19.6 As_2O_3 plus 14g sodium hydroxide in 20ml water, dilute to 600ml with water. Conc sulphuric acid (18mole L^{-1}) added until solution neutral to phenol phthalein and add further 56ml conc sulphuric acid and 50g sodium chloride. Make up to 1L. Filter through Whatman GF/C paper before use

Fig.2.21 Auto analyser manifold

Source: Reproduced with permission from the Royal Society of Chemistry [345]

expansion facility. Allow the baseline to settle at 5% apparent transmission and then introduce samples and standards at the rate of 50 per h. Read off the peak height, relative to the base line, of the standards and construct a calibration graph. Remove arsenic and cerium reagents and pump out the manifold with the deionised distilled water and wash for a few minutes. When reducing agents are suspected to be present in the samples, introduce the cerium reagent used for blank determinations and re-establish a base line at 5% apparent transmission as described above. Aspirate samples at the rate of 50 per h. Read off the peak heights of the sample blanks and subtract these from the peak heights returned for the samples. By using the calibration graph and the blank-corrected peak heights, determine the total iodine concentration of each sample.

Determination of iodine

Pipette a 20ml aliquot of sample into a clean glass separating funnel. Add 0.1ml of the tetraphenylarsonium hydroxide reagent from an Eppendorf pipette. (Tetraphenylarsonium hydroxide solution, 0.2mol L^{-1} . Dissolve 4.55g of solid AnalR-grade tetraphenylarsonium chloride hydrochloride (Koch-Light Laboratories) in 50ml of distilled water. Add 2.0g of silver oxide and stir overnight, using an automatic stirrer. Filter through a Whatman GF/C glass-fibre filter before use and store in a dark glass bottle.) Shake, add 4.0ml of chloroform and shake for 2min. Allow the two phases to

separate for 10min and then remove the organic phase. Add a further 4.0ml of chloroform, shake for 1min and repeat as above. Centrifuge the final aqueous phase at 4500g for 15min. Decant this aqueous phase into a 2.0 ml glass sample cup and aspirate, in duplicate, at the rate of 50 per h into the Auto Analyzer used for the total iodine method.

Prepare a calibration graph by feeding appropriate iodate-iodine standards directly to the AutoAnalyzer. Determine the reagent blank by treating a sample of deionised, distilled water according to the procedure above. Subtract this reagent blank from the peak height returned for each sample. Where reducing agents are present, or a new water type is under investigation, determine the 'catalytic method' blank as discussed above. Subtract this blank from the peak height of the sample, and finally read off the iodate-iodine concentration from the calibration graph.

The addition of 100mg L^{-1} of S(as SO_4^{2-}), HCO_3^- , P(as PO_4^{3-}), Ca^{2+} , Mg^{2+} , K^+ and Na^+ , 30mg L^{-1} of Cl^- and NO_3^- , 15mg L^{-1} of Si(as SiO_3) and Br^- and $100\mu\text{g L}^{-1}$ of Fe^{2+} , Fe^{3+} , Mn^{2+} and Ni^{2+} did not produce any significant interference in the procedure for the determination of iodate. In these experiments a mixture containing $3.0\mu\text{g L}^{-1}$ of iodide and $2.0\mu\text{g L}^{-1}$ of iodate-iodine together with the other chemicals was analysed and in each instance analysis gave $2.0 \pm 0.1\mu\text{g L}^{-1}$ of iodate-iodine. The addition of up to $10^{-2}\text{ mol L}^{-1}$ of either hydrogen or hydroxyl ion to the sample prior to its analysis also produced an insignificant interference.

2.49.2 Inductively coupled plasma atomic emission spectrometry

Miyazaki and Brancho [346] carried out a differential determination of iodate and iodide in non saline water by solvent extraction-inductively coupled plasma atomic emission spectrometry. Iodate was reduced to iodide, which was oxidised to iodine and extracted into xylene. Combined extracts were introduced into the spectrometer and iodine determined at 178.28nm. Iodine alone was detected as previously without reducing iodate. Detection limits at 178.28nm and at 206.16nm were 8.3 and $21\mu\text{g L}^{-1}$. Large concentrations of bromide interfered. The use of non-polar solvents would improve the detection limits.

2.49.3 Cathodic stripping voltammetry

The application of this technique is discussed under multianion analysis in section 14.9.1.2.

2.49.4 Polarography

The application of this technique is discussed under multianion analysis in section 14.10.1.1.

2.49.5 Ion selective electrodes

The determination of iodate and iodide has been carried out using an iodide selective

electrode in a solution at pH 9 [347,348]. No interference was caused by fluoride, chloride, bromide or thiosulphate. Only low concentrations of sulphide and cyanide can be tolerated.

Nakayama *et al.* [349] carried out automated determination of iodate in non saline waters using a flow-through electrode system. Following oxidation to iodine, quantitative concentration was obtained on a carbon wool electrode in a preconcentration cell. Residual chloride and bromide ions were then removed by rinsing the preconcentration cell with acetic acid. Iodine was eluted with reducing agent in a detection cell housing a polished silver electrode and iodate determined after being reduced to iodide. Current voltage curves obtained with the polished electrode are illustrated. The effect was studied of various salts on the peak current obtained in the analysis of filtered seawater. A detection limit of 5ng of iodine is claimed for this method.

2.49.6 High performance liquid chromatography

Salov *et al.* [115] determined iodate, chloride, iodide, chlorate and bromate in non saline waters by high performance liquid chromatography with an inductively coupled argon plasma mass spectrometric device.

The application of this technique is also discussed under multianion analysis in section 13.1.1.7.

2.49.7 Micelle exclusion ion chromatography

Okada [350] has used micelle exclusion chromatography to determine iodate in the presence of other anions (iodide, bromide, nitrite and nitrate) in water. The method is based on partition of the anions to a cationic micelle phase and shows different selectivity from ion exchange chromatography.

This technique has been applied to the determination of iodate, nitrite, nitrate, bromide and iodide in non saline waters [351].

2.49.8 Preconcentration

The preconcentration of iodate is discussed in section 15.1.5.

2.50 Iodide

2.50.1 Titration methods

The potentiometric titration procedure described by Kuttel *et al.* [117] for the determination of chloride in non saline waters has also been applied to the determination of iodide.

Bardin and Tolstousov [352] used a flow-type concentration cell with two silver-silver iodide electrodes for the potentiometric determination of down to $3\mu\text{g L}^{-1}$ of iodide in non saline waters. At iodide concentrations of up to $0.6\mu\text{M}$ the variation in emf of the cell is rectilinearly proportional to the concentration of iodide.

2.50.2 Spectrophotometric methods

Weil *et al.* [353] have described a rapid quantitative ultramicro method for the determination of iodide in concentrations of $1\text{--}100\mu\text{g L}^{-1}$ based on the catalytic acceleration of the reaction between chloramine-T and *N,N'*-tetramethyldiaminodiphenylmethane, and the photometric measurement of the extinction of the reaction product at 600nm. Iodate can also be determined after reduction with zinc.

Kinetic spectrophotometric methods based on the catalytic effect of $\mu\text{g L}^{-1}$ quantities of iodide ions in water on various chemical reactions have been described. These include reactions of cerium(IV) with arsenious acid [354], 3,3'-dimethyl naphthidine with hydrogen peroxide [355] and the oxidation of Cation IRE A by potassium persulphate [356]. The reaction of Malachite Green, Brilliant Green and Basic Turquoise Blue with iodide ions has been used as the basis of a method for the determination of microgram quantities of iodide [357].

Novak and Slama [358] determined iodide in the presence of bromide and chloride by adding to the sample potassium bromide to convert the iodide to iodine, followed by palladous chloride which is converted by iodine to palladous iodide. The latter was estimated spectrophotometrically at 465nm. Using this method from 2 to 8m mole iodide can be determined in the presence of 1000-fold excesses of chloride or bromide.

Koh *et al.* [359] reported on a spectrophotometric method involving solvent extraction with methylene blue for determining iodide at the nanomolar level in non saline waters. The method had a relative standard deviation of 0.87% at the $1.5\times 10^{-6}\text{M}$ level.

Chandrawanski and Patel [360] used Brilliant Green to complex $\text{I}_2\text{C1}^-$ in a method for the determination of $4\mu\text{g L}^{-1}$ iodide in non saline waters.

2.50.3 Spectrofluorometric methods

There are few fluorometric methods for the determination of iodide. None of them is specific for iodide but they have high sensitivity, especially the method using cerium(IV) [361] ($6.25\mu\text{g L}^{-1}$). Also 2,7-di(acetoxymercuri) fluorescein [263] is a sensitive fluorometric reagent for iodide ($35\text{--}400\mu\text{g L}^{-1}$) but the $\Delta\lambda$ of the Stokes shift is not favourable and the method cannot be used with filter fluorimeters.

A special substitution method for the determination of iodide is based on its inhibitory action on the fluorescence of uranyl acetate [362].

2.50.4 Chemiluminescence method

Liu *et al.* [363] have reported a method for determining iodide in non saline waters utilising the suppression of the chemiluminescence of the luminol hydrogen peroxide—gold system. This method is reported to have a detection limit of $5\times 10^{-11}\text{g}$ of iodide mL^{-1} and a relative standard deviation of 2.1% at $4\times 10^{-9}\text{g}$ of iodide mL^{-1} .

2.50.5 Flow injection analysis

The application of this technique is discussed under multianion analysis in section

14.4.1.2.

2.50.6 Inductively coupled plasma atomic emission spectrometry

Miyazaki and Brancho [346] preconcentrated iodide by conversion to iodine and extraction into xylene. The extract was determined at 172.28nm using inductively coupled plasma atomic emission spectrometry. Iodate was reduced to iodide which was then treated in the same way to give a total iodide plus iodate content. Detection limits were, respectively, 8.3 and 21 $\mu\text{g L}^{-1}$ for iodate and iodide. Large concentrations of bromide interfere.

Michlewicz and Carnahan [133] give details of a method for the determination of iodide based on pneumatic nebulisation and ultrasonic neutralisation of the sample into a helium microwave induced plasma. The detection limit was 3mg L⁻¹ bromide.

Potassium, magnesium, sodium and lithium interfered moderately with pneumatic nebulisation but significantly with ultrasonic nebulisation.

2.50.7 Cathodic stripping voltammetry

The application of this technique is discussed under multianion analysis in section 14.9.1.2.

2.50.8 Polarography

In the polarographic determination [364] of 0.2 μmol quantities of iodide in non saline waters, the iodide was oxidised to iodate with sodium hypochlorite and the excess oxidant destroyed with sodium sulphite.

Iodate was determined by differential pulse polarography and the concentration of iodide calculated as the difference between the concentrations of iodate in a sample before and after oxidation.

Luther *et al.* [365] carried out a direct determination of down to 12ng L⁻¹ of iodide in seawater using cathode stripping square wave voltammetry.

The application of this technique is also discussed under multianion analysis in section 14.10.1.1.

2.50.9 Potentiometric method

Bardin and Tolstousov [352] used a flow-type concentration cell with two silver-silver iodide electrodes for the potentiometric determination of down to 3 $\mu\text{g L}^{-1}$ of iodide in non saline waters. At iodide concentrations of up to 0.6 $\mu\text{mol L}^{-1}$ the variation in EMF of the cell is nearly proportional to the concentration of iodide.

Zernalova and Senyavin [327] examined conditions for the potentiometric determination of iodide in non saline water.

2.50.10 Ion selective electrodes

Yuan *et al.* [366] used schiff base complexes of cobalt(II) as neutral carriers for highly

selective iodide electrodes. This electrode demonstrates excellent selectivity to iodine. The selectivity sequence is $I > CNS > NO_2 > ClO_4 > Br > NO_3 > Cl > SO_4$.

Various other workers [134,344,367,368] have used an iodide-ion electrode for the determination of iodide in non saline waters. Butler and Gershey [344] used an iodide-selective electrode to measure down to $1nM$ iodide separated from other anions by ion exchange high performance liquid chromatography. Nakayama and Kimoto [368] used a flow-through electrode system. Weiss [134] determined both iodides and cyanides in micromole quantities using an iodide-selective electrode.

2.50.11 Neutron activation analysis

Malvano *et al.* [369] determined iodide in water by this technique and compared results obtained with those obtained by the autoanalysed spectrometric method.

2.50.12 Isotope dilution analysis

This technique combined with mass spectrometry has been used to determine down to $0.1\mu g L^{-1}$ iodide in non saline waters [370].

2.50.13 Ion chromatography

Dils and Smeenk [371] have discussed the determination of iodide and phosphate in non saline waters.

2.50.14 High performance liquid chromatography

Moss and Stephen [139] determined iodide, bromide and chloride in non saline waters by conversion to alkyl mercury(II) halide and measurement by high performance liquid chromatography.

Stetzenbach and Thompson [138] employed high performance liquid chromatography on anion exchange columns to determine iodide in admixture with chloride, bromide, nitrate and thiocyanate in non saline water.

Iodide in non saline waters has been determined [344] by ion exchange high performance liquid chromatography using an iodide ion selective electrode as a detector. On-line preconcentration of iodide on an anion guard cartridge allowed determinations down to $1n mol L^{-1}$.

Verma *et al.* [372] determined iodide in non saline waters by high performance liquid chromatography after precolumn derivatisation of iodide to 4-iodo-2,6-dimethylphenol. The derivative was detected by an ultraviolet detector. Down to $2\mu g L^{-1}$ iodide can be determined by this procedure.

The application of this technique is also discussed under multianion analysis in sections 13.1.1.2, 13.1.1.3, 13.1.1.4 and 13.1.1.7.

2.50.15 Micelle chromatography

Okada [350] has used micelle exclusion chromatography to determine iodide in the

presence of other anions (bromide, iodate, nitrite and nitrate) in water. The method is based on partition of the anions to a cationic micelle phase and shows different selectivity from ion exchange chromatography.

The application of this technique is also discussed under multianion analysis in section 13.5.1.2.

2.50.16 Gas chromatography

The application of this technique is discussed under multianion analysis in section 14.1.1.2.

2.50.17 Miscellaneous

Pilipenko *et al.* [373] have described a chemiluminescence method for determining trace iodide in non saline waters based on iodide oxidation to iodine by bromine water or by 1,3-dibromo-5,5-dimethylhydantoin, followed by iodine cyanide (ICN) generation and its determination using luminol. The detection limit was 5ng of iodide mL⁻¹ in the absence of interfering impurities. Interferences from calcium and magnesium were eliminated by sample dilution or by precipitation of calcium carbonate and magnesium hydroxide.

2.50.18 Preconcentration

The application of preconcentration techniques is discussed in section 15.1.5.

2.51 Isobutyrate

2.51.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.51.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.52 Isocitrate

2.52.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.53 α ketoglutarate

2.53.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.54 Lactate

2.54.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.54.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.1.5 and 13.1.1.6.

2.55 Maleate

2.55.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.55.2 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.4.

2.56 Malonate

2.56.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.4 and 12.2.5.

2.56.2 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.4.

2.56.3 Gas chromatography

The application of this technique is discussed under multianion analysis in section 14.1.1.1.

2.57 Metal cyanide complexes

2.57.1 Ion chromatography

The cyanide ion in inorganic cyanides can be present as both complexed and free cyanide. In order to study the chromatography of metal cyanides, Rocklin and Johnson [374] prepared and assayed solutions of cadmium, zinc, copper, nickel, gold, iron and cobalt cyanides. Table 2.17 lists the percentage of total cyanide detected.

The results suggest that the complex cyanides can be grouped into three categories depending on the cumulative formation constant and stability of the complex.

Table 2.17 Percentage of total cyanide in metal complexes determined as 'free' cyanide

<i>Metal complex</i>	$\log \beta_t$	%
$\text{Cd}(\text{CN})_4^{2-}$	18.8	102
$\text{Zn}(\text{CN})_4^{2-}$	16.7	102
$\text{Ni}(\text{CN})_4^{3-}$	31.3	81
$\text{Cu}(\text{CN})_4^{3-}$	30.3	52
$\text{Cu}(\text{CN})_3^{2-}$	28.6	42
$\text{Cu}(\text{CN})_2^-$	24.0	38
$\text{Au}(\text{CN})_2^-$	38.3	0
$\text{Fe}(\text{CN})_6^{3-}$	42	0
$\text{Co}(\text{CN})_4^{3-}$	64	0

Source: Reproduced with permission from the American Chemical Society [374]

Category 1 includes the weakly complexed and labile cyanides $\text{Cd}(\text{CN})_4^{2-}$ ($\log B_4=18.78$) and $\text{Zn}(\text{CN})_4^{2-}$ ($\log B_4=16.7$). These complexes completely dissociate under the chromatographic conditions used, the cyanide being indistinguishable from free cyanide.

Category 2 includes the moderately strong cyanide complexes $\text{Ni}(\text{CN})_4^{2-}$ ($\log B_4=31.3$) and $\text{Cu}(\text{CN})_4^{3-}$ ($\log B_4=30.3$). Although these complexes are labile, they are retained on the column and slowly dissociate during the chromatography. This slow dissociation produces tailing which lasts for several minutes as the free cyanide elutes and is detected. As the results presented in Table 2.17 demonstrate, the tailing and the

non-quantitative recovery of cyanide preclude the use of direct injection to determine total cyanide in samples containing copper and nickel. These samples may be analysed after acid distillation and caustic trapping. The cyanide in the caustic solution can then be determined by ion chromatography with electrochemical detection.

Category 3 includes those cyanides which are inert and therefore totally undissociated, such as $\text{Au}(\text{CN})_2^-$ ($\log B_2=38.3$), $\text{Fe}(\text{CN})_6^{3-}$ ($\log B_6=42$) and $\text{Co}(\text{CN})_6^{3-}$ ($\log B_6=64$). No free cyanide was detected for these complexes. Although these complexes do not elute under the chromatographic conditions used, they can be eluted and determined by using different chromatographic conditions and conductivity detection.

Samples containing both free cyanide (or weakly complexed cyanide) and strongly complexed cyanide can be analysed for free cyanide by direct injection. The determination of total cyanide (both free and strongly complexed) requires distillation of the sample with caustic trapping.

The application of this technique is also discussed under multianion analysis in section 12.2.3.

2.57.2 Preconcentration

The application of preconcentration techniques is discussed in section 15.1.6.

2.58 Mixed halides

2.58.1 Ion selective electrodes

Trojanowicz and Lewardowski [192] have described a multiple potentiometric system for the continuous determination of chloride, fluoride, nitrate and ammonia in non saline waters. They describe a flowthrough system for the simultaneous determination of chloride ($30\text{--}150\text{mg L}^{-1}$), fluoride ($0.08\text{--}0.4\text{mg L}^{-1}$), nitrate ($5\text{--}20\text{mg L}^{-1}$) and ammonia ($0.05\text{--}0.5\text{mg L}^{-1}$). Solid state chloride and fluoride electrodes, a PVC membrane nitrate electrode and a gas-sensing Orion 95–10 ammonia electrode were employed, the air-segmented sample stream being mixed with appropriate buffering solutions before entering the measuring cell. During continuous operation, calibration twice daily was necessary to eliminate the effects of potential drift. Best results were obtained when the chloride-nitrate ratio in the calibrating solution was similar to that in the non saline water being analysed (14:1).

Apparatus

Peristaltic multichannel pump type DP2–2 VEB MLW (GDR) with tubings from Ismatec (Switzerland). Ionalyzer Orion (USA) model 801A and digital printer model 751. Homemade electronic electrode switch for 5 channels, controlled by digital printer. Thermostat model U–1 from VEB MLW (GDR). The following electrodes were used as sensors—Chloride electrode from MERA–ELWRO (Poland), home made fluoride electrode, nitrate electrode with solid silver contact and PVC membrane containing bathophenanthroline–nickel(II) complex and 2-nitrophenyloctyl ether, ammonia electrode Orion (USA) model 95–10.

In the measurement of chloride, fluoride and nitrate a silver-silver chloride electrode was applied as reference electrode.

Measuring cells were manufactured from Perspex. Internal diameter of all channels was 2mm.

Reagents

The compositions of solutions used for adjusting appropriate conditions of determination and of standard solutions are listed in Table 2.18.

Table 2.18 Composition of solutions used in flow measurements for adjusting appropriate conditions and for standardising

Solution	Components	Concentrations mol L ⁻¹
Solution 1	CH ₃ COOH	0.1
	CH ₃ COONa	0.1
	H ₂ O ₂	0.03
	DCTA	0.01
Solution II	H ₃ PO ₄	1.0
Solution III	NaOH	0.2
	EDTA	0.01
Standard solution I	NaCl	0.01 (pCl 2.00)
Standard solution I	NaF	5×10 ⁻⁵ (pF 4.30)
	NaNO ₃	7×10 ⁻⁴ (pNO ₃ 3.15)
	(NH ₄) ₂ SO ₄	5×10 ⁻⁴ (pNH ₃ 3.00)
Standard solution II	As above	10-fold diluted standard solution I

Source: Reproduced with permission from Springer Verlag GmbH [192]

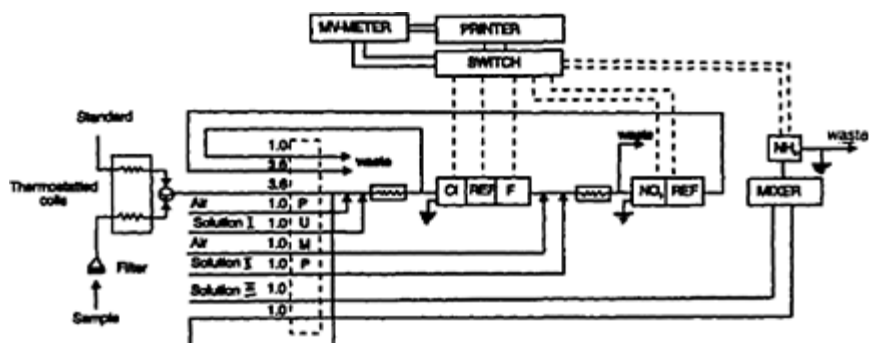


Fig. 2.22 Flow diagram of the four-parameter potentiometric system for the

determination of chloride, fluoride, nitrate and ammonia in non saline waters

Source: Reproduced with permission from Springer Verlag [192]

Procedure

A general scheme of the whole flow-through system is given in Fig. 2.22. By changing the position of the stopcock either standard solution or sample solution is introduced into the system. In the case of many days of continuous analysis of river water, it was indispensable to separate suspended matter on a glass frit. The standard solutions and sample streams pass through coils thermostated at $25 \pm 0.5^\circ\text{C}$. After passing the peristaltic pump the sample or standard solution stream is divided into two

Table 2.19 Results of determinations in water with the flow through system in comparison with reference methods (mg L^{-1})

Sample	Fluoride			Chloride		
	Flow through system	Potentiom with TISAB	%	Flow through system	Titration with Ag	%
1	0.178	0.174	+2.2	115.7	112.8	+2.6
2	0.166	0.166	0	108.6	109.0	-0.4
3	0.198	0.199	-0.5	119.2	118.6	+0.5
4	0.197	0.209	-5.9	119.8	119.5	+8.7
5	0.169	0.174	-2.9	66.1	72.4	-8.7

Source: Reproduced with permission from Springer Verlag GmbH [192]

parts. One of them flows directly to the mixing chamber preceding the ammonia sensor, while the second one, after mixing with solution K (acetate buffer containing hydrogen peroxide and DCTA) and debubbling approaches the measuring cell with chloride and fluoride electrodes and a common reference electrode. Leaving this cell, the stream is mixed with solution II (phosphoric acid) and, after debubbling, enters the nitrate electrode cell. The automatic electrode switch allows the potential values of all electrodes to be printed with the frequency controlled by the printer using the Orion 751 printer. The frequency of changes is in the range 6s—1h.

Chloride and fluoride determinations obtained in non saline water by this procedure are compared with those obtained by conventional methods in Table 2.19. Generally, results agreed within $\pm 5\%$ with those obtained by the reference method.

2.58.2 High performance liquid chromatography

Salov *et al.* [115] determined chloride, bromide, iodide, chlorate, bromate and iodate in non saline waters by high performance liquid chromatography with inductively coupled oxygen plasma mass spectrometry as a detector.

Moss and Stephen [139] determined chloride, bromide and iodide by converting them to alkylmercury(II) halides and measurement by high performance liquid chromatography.

Akaiwa *et al.* [140] have used ion exchange chromatography on hydrous zirconium oxide combined with a detection based on direct potentiometry with an ion selective electrode for the simultaneous determination of chloride and bromide in non saline waters.

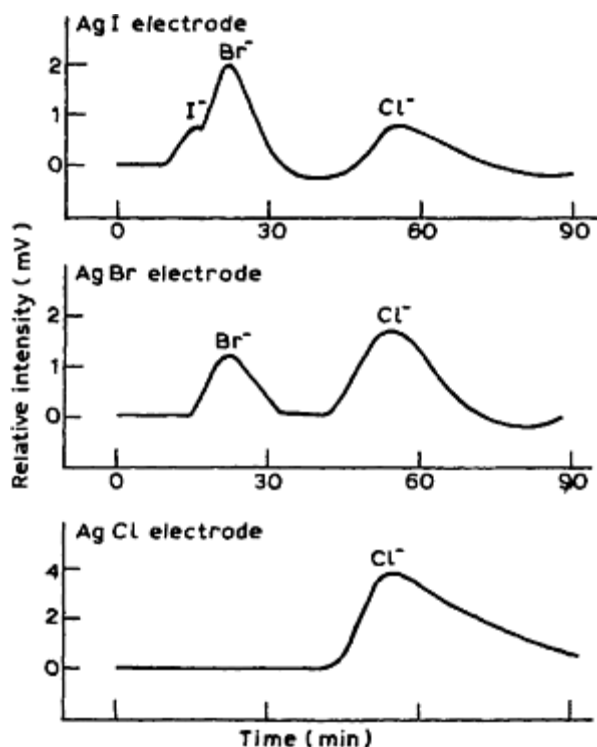


Fig. 2.23 Chromatograms of halide standards: iodide 5.0ng mL^{-1} ; bromide 50ng mL^{-1} ; chloride $2.0\mu\text{g mL}^{-1}$

Source: Reproduced with permission from Elsevier Science [140]

The response of the three silver halide electrodes in the chromatography of a mixture of iodide, bromide and chloride is shown in Fig. 2.23. The silver chloride electrode gave poor response to iodide and bromide, and so did the silver bromide electrode to iodide. Although the silver iodide electrode responded to all three halides, the peaks are not sufficiently resolved and they are asymmetric. Further, there was a drift of the base line after detection of a halide ion which was not a component of the electrode and this drift caused disturbance in the following peak. This difficulty is eliminated by using hydrous zirconium oxide instead of the anion exchange resin for the chromatography since it reverses the elution order for halide ions. The silver bromide electrode is then the most

suitable as the detector for both bromide.

2.58.3 Micelle exclusion chromatography

Okada [375] carried out micelle exclusion chromatography on mixtures of iodide, bromide, nitrite, nitrate and iodate.

2.59 Molybdate

2.59.1 Atomic absorption spectrometry

Vazquez-Gonzalez *et al.* [376] have described a method for preconcentrating and determining molybdenum by electrothermal atomisation atomic absorption spectrometry after preconcentration by means of anion exchange using Amberlite IRA-400 in resin citrate form. The optimal analytical parameters were established by drying, carbonisation, charring, atomisation and cleaning in a graphite furnace. The precision and accuracy of the method were investigated. Less than $0.2\mu\text{g L}^{-1}$ molybdenum could be determined by this procedure.

Samchuk [377] developed an atomic absorption method for the determination of molybdenum in non saline waters, with preconcentration on carbon modified by complex-forming organic reagents and on chelated sorbents. The methods for preparing the modified carbons and chelated sorbents are described. The work was done on a two-beam atomic absorption spectrometer with a graphite atomiser and deuterium background corrector.

2.59.2 Preconcentration

The application of preconcentration techniques is discussed in sections 15.1.7 and 15.1.13.

2.60 Monochloroacetate

2.60.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.4 and 12.2.5.

2.61 Monofluorophosphate

2.61.1 High performance liquid chromatography

Yoza *et al.* [378] applied this technique to the analysis of mixtures of orthophosphate, monofluorophosphate and polyphosphates using a photodiode array detector.

2.62 Nitrate

The quantification of nitrate is important for water quality evaluation in terms of agricultural, industrial and biological pollution. Moreover, the potential health risk from nitrate, especially from its chemically and biologically active toxic metabolite nitrite, leads to increased stringency in nitrate monitoring of waters [379–381]. Owing to the toxicity (risk of anemia, formation of carcinogenic nitrosamines), the nitrate content of drinking waters has been regulated by national authorities and by the European Community Directive 80/778/EEC, which states a maximum admissible concentration (MAC) of 50gm of $\text{NO}_3^- \text{L}^{-1}$ [382]. This directive gives also a guide level of 25mg of $\text{NO}_3^- \text{L}^{-1}$. The US Environmental Protection Agency (USEPA), based in the World Health Organization (WHO) guideline (1984), adopted a MAC value of 45mg of $\text{NO}_3^- \text{L}^{-1}$. The WHO states also a guideline value of 10mg of $\text{NO}_3^- \text{L}^{-1}$ for water intended for bottle fed infants [381].

Achieving good analytical measurements capability for water analysis seems to be a necessity with ‘Europe 93’ and the ratification of the Maastricht Treaty [383]. It is of political importance that quality and comparability of measurement results be improved. Political and legal decisions, such as whether or not water is too polluted for consumption, are based on chemical measurements.

The Institute for Reference Materials and Measurements’ (IRMM) International Measurement Evaluation Programme (IMEP) [383,384] is intended to provide pictures of the ‘state-of-the-practice’ in the assay of toxic or life-essential elements of species (in this case nitrate) in the assay of toxic or life-essential elements or species (in this case nitrate) in different matrices compared to a ‘certified’ reference value obtained by an isotopespecific method, namely isotope dilution mass spectrometry (IDMS).

2.62.1 Spectrophotometric methods

Reduction of nitrate to nitrite by copper activated cadmium followed by estimation of nitrite by one of the methods discussed in this section, usually diazotisation coupling methods, is one of the most widely used methods for the determination of nitrite [385–387].

When it is necessary to analyse a large number of low volume, highly coloured pore waters, the usefulness of the cadmium reduction method is limited because:

- (1) either 100ml of sample is required (Strickland and Parsons [388]), or nitrate levels must be high enough to allow for dilution of 25ml of sample with 75 ml of ammonium chloride solution [385],
- (2) analyst time is excessive for single sample manipulation and maintenance of recommended flow rate ($7\text{--}10 \text{ ml min}^{-1}$) and
- (3) interferences progressively decreased column efficiency [386].

Jones [389] has described a cadmium reduction method which avoids the foregoing problems by shaking the sample with spongy cadmium as an alternative to the use of cadmium columns.

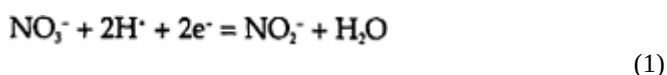
Jones [389] found that when the reduction solution was buffered above pH8 and optimum cadmium contact was used, reduction of 20 μ M nitrate to nitrite was more than 99% complete, even in the presence of sodium chloride concentration corresponding to that of seawater.

Certain metals and phosphate may interfere with nitrate reduction. Precipitation of metal salts onto the cadmium surface may be prevented by addition of EDTA to the buffer solution.

Davison and Woof [390] compared different forms of cadmium as a reducing agent for the batch determination of nitrate. These workers have also carried out interference studies on the batch determination of nitrate in non saline waters by cadmium filings and found that reduction with spongy cadmium is less prone to interference than with cadmium filings. The optimum reduction time or the amount of cadmium filings for mixing reduction efficiency for natural samples or solutions containing interferences was obtained for standard solutions. Possible interfering ions in freshwaters were shown to be phosphate, silicate, hydrogen carbonate, sulphide and some organic compounds.

Earlier work by Davison and Woof [391] had shown that good recoveries on some natural freshwater samples could only be achieved with longer reduction times than had been found to be optimum for standard solutions. Many workers [391–395] have investigated the time dependence of the reduction step and observed that, for the more vigorously reducing forms of cadmium, the efficiency of the reduction attains a maximum and then declines. With less active cadmium preparations, the reduction efficiency slowly approaches a plateau. However, most of these experiments were performed on standard solutions. Conditions have been optimised for studying the time dependence of the reduction efficiency, as reflected by different column lengths at a given flow-rate [396]. As neither standards nor different water samples were studied in the same way, any change in reduction efficiency attributable to the sample water could not be assessed.

The mechanism of reduction must involve the oxidation of cadmium metal as given in the redox reactions (1) and (2):



Anything that can change the ultimate rate of electron transfer of the redox potential of reaction (1) can possibly interfere with the analytical method. Other metal ions and ligands can change the redox potential of reaction (2) and hence possibly decrease or increase the electron availability, which could show up as a positive or negative interference in the method. Alternatively, inorganic or organic complexing agents can interfere by associating with cadmium ions formed at the metal surface so providing a block to the most active reducing sites.

Two types of cadmium were used in this study, filings and a sponge prepared by electrolytic deposition onto zinc rods [390].

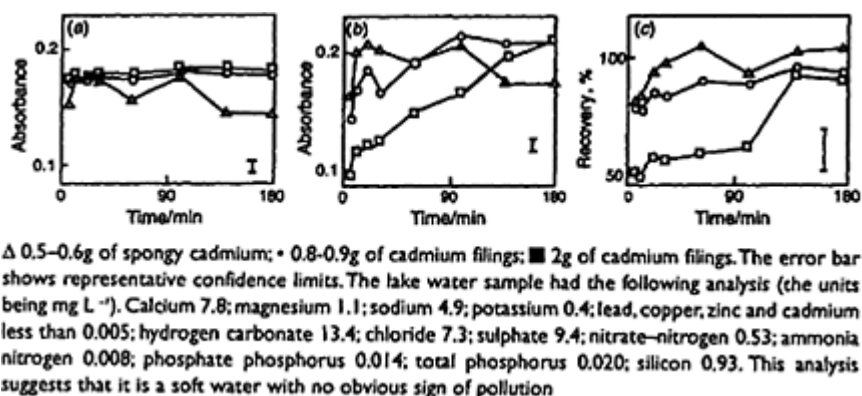


Fig. 2.24 Dependence on reduction time: (a) of absorbance of standards; (b) of absorbance of sample; (c) of recovery of spiked sample

Source: Reproduced with permission from the Royal Society of Chemistry [391]

Fig. 2.24a shows a graph of absorbance vs time for the standards of 0.5mg L^{-1} or nitrate–nitrogen that were measured, at different reduction times, in the same batches as some lake water samples. It was possible to calculate the confidence interval of each point because the measurements were performed in triplicate. However, owing to the confidence interval being fairly constant, and for purposes of clarity, only average values are shown in the figure. The cadmium filings showed a consistent reduction efficiency after 10min for both masses of cadmium used. The spongy cadmium, however, attained a maximum reduction efficiency between 10 and 30min which then declined. The same basic shape for the spongy cadmium results is shown in Fig. 2.24b, the graph of absorbance vs time for a lake water sample, and reference to Fig. 2.24c shows that the recoveries for spongy cadmium are near theoretical for reduction times in excess of 20min. Fig. 2.24b also shows that the reduction efficiency attained by cadmium filings in a lake water sample is greatly reduced for short reduction times, although this effect is much less pronounced when a large amount of cadmium is used for each reduction. Because of the consistent efficiencies that were obtained for the standards (Fig. 2.24a), the recoveries (Fig. 2.24c) have the same shape as the sample absorbances (Fig. 2.24b).

These results suggest the following. First, results obtained when using spongy cadmium are probably less prone to interference although they are less precise. Second, interferences in lake water slow down the reduction by cadmium filings. Third, the interferences can be reduced by either increasing the time of reduction or increasing the amount of cadmium filings used. An increase in the reduction time or in the amount

Table 2.20 Effect of other substances on the determination of nitrate–nitrogen.

Other substances	Concn of other	Added as	Error ^b in determination of nitrate–

	substance ^a mg L ⁻¹	nitrogen (mg L ⁻¹)		
		0.000 mg L ⁻¹ present	0.140mg L ⁻¹ present	2.100mg L ⁻¹ present
Ca ²⁺	100 CaCl ₂			
Mg ²⁺	50 MgCl ₂			
Na ⁺	25 NaCl	0.000	0.000	-0.016
K ⁺	25 KCl			
HCO ₃ ⁻	250 NaHCO ₃	0.000	-0.014	0.016-0.216
SO ₄ ²⁻	50 Na ₂ SO ₄			
HCO ₃ ⁻	125 NaHCO ₃	0.000	-	-0.233
HCO ₃ ⁻	50 NaHCO ₃	0.000	-	-0.077
Zn ²⁺	2 ZnSO ₄	0.000	0.000	-0.011
Cu ²⁺	2 CuSO ₄	0.000	0.000	-0.186
Cu ²⁺	0.1 CuSO ₄	-0.005	-0.003	+0.008
Fe ³⁺	10 NH ₄ Fe (SO ₄) 212H ₂ O	+0.016	+0.025	+0.030
Mn ²⁺	10 MnSO ₄	0.000	+0.003	+0.019
Ni ²⁺	2 NiSO ₄	0.000	+0.003	+0.066
Co ²⁺	2 CoSO ₄			
Al ³⁺	5 AlCl ₃	0.000	0.000	-0.088
Al ³⁺	2.5 AlCl ₃	-	-	-0.033
Pb ²⁺	2 Pbacetate	-0.003	-0.058	-0.786
Pb ²⁺	0.1 Pbacetate	-0.008	-0.005	-0.041
Si	19m Na ₂ SiF ₆	-0.003	-0.055	-0.773
Si	9 Na ₂ SiF ₆	0.000	-0.030	-0.419
Si	23 Na ₄ Si(OH) 4	0.000	-0.090	-1.236
Si	2.3 Na ₄ Si(OH) 4	-0.003	-0.011	-0.132
Orthophosphate (asP)	40 KH ₂ PO ₄	0.000	-0.093	-1.748
Orthophosphate (asP)	2 KH ₂ PO ₄	+0.003	-0.093	-1.354

Pyrophosphate (as P)	2 $\text{Na}_4\text{P}_2\text{O}_7$	-0.000	-0.110	-1.696
Hexametaphosphate (as P)	2 $(\text{NaPO}_3)_6$	-0.003	-0.110	-1.649
EDTA	5 Disodium salt	0.000	-0.005	+0.011
EDTA	5 Disodium salt			
Orthophosphate (as P)	2 KH_2PO_4	0.000	-0.099	-1.422
Cr(VI)	2 CrO_3	+0.003	-0.112	-1.850
S^{2-}	1 Na^+	-0.00/5	-0.088	-0.482
S^{2-}	0.5 Na^+	-0.005	-0.041	-0.167
Alanine	1 Amino acid	+0.003	+0.0008	+0.019
Cysteine	1 Cysteine hydro-chloride	-0.003	-0.055	-0.830
Acetate	2 Na^+	0.000	-	+0.011

^aThe braces denote the simultaneous presence of the indicated substances in the test solutions.

^bIf the other substances had no effect, the results would be expected (95% confidence) to lie within the ranges 0.000 ± 0.0005 , 0.140 ± 0.007 and $2.100 \pm 0.068 \text{ mg L}^{-1}$ respectively.

Source: Reproduced with permission from the Royal Society of Chemistry [391]

of cadmium will produce an increase in the effective reduction capacity to which the solution is exposed. That is to say interferences appear to decrease the surface activity an effect that can be overcome by either prolonging the exposure time or increasing the overall surface area of metal. Davison and Woof [391] studied only the effect of time.

For interference studies it was appropriate to use a reduction time, and an amount of cadmium, that had been shown to be prone to interference from lake water. The results of the interference studies is shown in Table 2.20. The common cations and anions do not interfere, except hydrogen carbonate, and its effect is negligible below 50 mg L^{-1} . Of the metal ions, only lead and copper interfered and then only at such high levels as would not be found in unpolluted waters. When 2 mg L^{-1} of copper were added the results tended to be erratic. This is probably because of an inconsistent induced change in the redox potential of reaction (1) above. Both silicate and phosphate ions, in their various forms, interfered. In order to test whether the interference was due to the complexation of cadmium ions, ethylenediamine-tetraacetic acid (EDTA) was added to complex the cadmium ions preferentially. This addition had no effect and the EDTA itself did not interfere. As expected, the strong oxidising agent chromium (VI) oxide did interfere in the redox process. Sulphite ions have reducing properties, but the interference observed was probably a result of the formation of cadmium sulphide which then blocked the active sites. Of the organic compounds tested, only cysteine interfered.

In order to check whether the interfering compounds were affecting the reduction step

or the colour-development stage, phosphate, silicate, hydrogen carbonate, sulphide and cysteine were added to nitrite determinations with the reduction step omitted; only sulphide interfered. However it is unlikely that it interferes at the same stage in the nitrate determination because all sulphide will have probably have been previously removed as cadmium sulphide.

Fig. 2.25(a) shows how the absorbance, in the presence of known interferences, varies with the time of reduction. The effect of all interfering substances is reduced on increasing the shaking time and near theoretical yields are obtained in the presence of high concentrations of hydrogen carbonate and cysteine after 50 and 140min, respectively. Longer times would be necessary to overcome the problems created by phosphate, silicate and sulphide.

The same time-dependent interference studies were conducted using spongy cadmium and the results are shown in Fig. 2.25(b). The absorbance increased with shaking time up to 20min, and after that it decreased slightly with time. Phosphate, hydrogen carbonate and cysteine did not show any appreciable interferences after this time. Although sulphide and silicate did interfere, their concentrations were much higher than those usually encountered in natural freshwater samples.

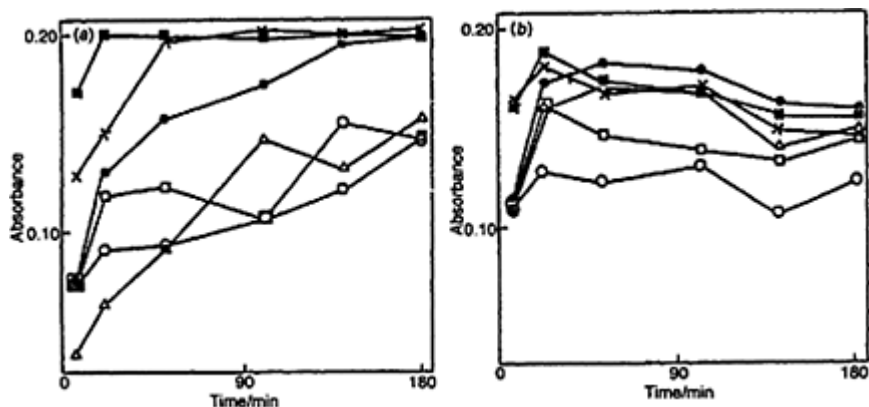


Fig. 2.25 Plot of absorbance vs reduction time: (a) Using 0.5–0.6g of cadmium filings; (b) Using 0.5–0.7g of spongy cadmium for a standard solution of 0.56mg L^{-1} of nitratennitrogen with the following additions: nil; Δ 2mol L^{-1} of phosphate phosphorus; $\square$ 25ml L^{-1} of silicate silicon; $\times$ 250mg L^{-1} of hydrogen carbonate; $\circ$ 1mg L^{-1} of sulphide; $\bullet$ 1mg L^{-1} of cysteine hydrochloride

Source: Reproduced with permission from the Royal Society of Chemistry [391]

Table 2.21 Precision results for nitrate determination using spongy cadmium

Solution	Mean absorbance	Standard deviation ^a mg L ⁻¹		
		S _w ^b	S _b ^c	S _c ^d
0.000mg L ⁻¹	nitrate-nitrogen 0.005	0.0024 (6)	–	–
0.140mg L ⁻¹	nitrate-nitrogen 0.047	0.0042 (6)	0.0072 (5)	0.01 10
2.100mg L ⁻¹	nitrate-nitrogen 0.726	0.0279 (6)	NSe (5)	0.0416

^aThe degrees of freedom for the standard deviations are given in parentheses; ^bWithin-batch;

^cBetween-batch; ^dTotal standard deviation; ^aNot statistically significant

Source: Reproduced with permission from the Royal Society of Chemistry [391]

The analytical implications of this work in the determination of nitrite are as follows. Although cadmium filings are more easily and reproducibly prepared than spongy cadmium, and have been shown to give more precise results [390] for the batch procedure, reduction by spongy cadmium should, perhaps, be preferred because it is much less prone to interferences. Table 2.21 gives basic performance characteristics determined for this method by using 0.5–0.6g of spongy cadmium and a shaking time of 20min. Values for S_p showed that the precision of the method ranged from a relative standard deviation S_r=7.8% at 0.14mg L⁻¹ to S_r=2% at 2.1mg L⁻¹ of nitrate-nitrogen. S_w can be used to calculate the criterion of detection using $ts_w/\sqrt{2}$ where t is Student's t . A value of 0.006g L⁻¹ is obtained for the 95% confidence level.

Reduction conditions must always be optimised for natural samples rather than standards, and, ideally, for each individual water body that is measured. The results suggest a realistic quality control procedure, which can be used to assess the accuracy of measurements on a variety of water samples; two measurements could be made, each at different effective reduction capacities. This measurement technique could be very easily arranged in an automated system by having two channels with two different reduction column lengths. Disparity between the duplicate results would indicate the possible presence of an interfering species.

Olsen [397] demonstrated that 2.5–25μM phosphate may decrease reduction of nitrate by 10–40% in cadmium-copper columns and stated that the effect of phosphate is gradual and varies with the age of the column. These and other interferences are much less likely in the method described by Jones [389] than in a column reduction method because shaking has a continual scouring effect on the cadmium during the reduction process and the cadmium is cleaned before each reduction. According to Nydahl [398], chloride ions can have a strongly retarding effect on the rate of nitrate reduction. However, Jones [389] found that, when the reduction solution was buffered above pH 8 and optimum cadmium contact was used, reduction of 20μmol L⁻¹ nitrate was more than 99% complete, even in the presence of sodium chloride concentration corresponding to that of seawater.

Certain metals and phosphate may interfere with nitrate reduction. Precipitation of metal salts onto the cadmium surface may be prevented by the addition of EDTA to the

buffer solution.

Koupparis *et al.* [399] have described an automated method for the determination of nitrate in river waters with a microcomputer-based stopped-flow mixing system. Nitrate is reduced to nitrite with a copperised cadmium-silver alloy or cadmium tube column fitted to the stopped-flow system, nitrite is determined using fast kinetic, multi-point or single point procedures with N-(1-naphthyl)ethylenediamine dihydrochloride as the colour reagent. Water samples in the range of $0.025\text{--}3\text{mg L}^{-1}\text{ NO}_3^- \text{--N}$ can be processed with a throughput of up to 100 samples per hour and a detection limit of 0.013mg L^{-1} . Interference studies showed that cyanide, dichromate, iodide, sulphide, copper and tin ions cause negative results.

Using this method Koupparis *et al.* [399] carried out a recovery study on river and lake water samples by measuring the nitrite concentration before and after standard addition. Samples were also assayed for nitrite and the equation for the determination of nitrite and nitrate in the mixture was used. The nitrite content was found to be equivalent to less than 0.2mg L^{-1} . Samples higher than 3mg L^{-1} were diluted with distilled water. The results obtained show an average recovery of 100.2% (Table 2.22).

Table 2.22 Recovery data for the determination of nitrate in lake and river water samples with the multipoint kinetic procedure and cadmium alloy column

Sample	Nitrate content ($\text{mg L}^{-1}\text{ NO}_3^- \text{--N}$)			Recovery %
	Before std	After std. addition Expected	Determined	
1	1.90	6.90	7.05	102.2
2	10.50	13.00	13.00	100.0
3	11.95	14.45	14.25	98.6
4	0.10	1.10	1.11	100.9
5	0.40	1.40	1.41	100.7
6	10.70	13.20	13.15	99.6
7	10.90	13.40	13.55	101.1
8	12.90	14.15	14.20	100.4
9	5.20	7.70	7.65	99.4
10	0.39	1.39	1.37	98.6
Average				100.2

Source: Reproduced with permission from Elsevier Science [399]

The effect of various potential interferences was also investigated. Most of the common ions present in water samples do not interfere even in high concentrations. Those ions that showed serious interference rarely are found in water samples at the highest concentrations examined.

The effect of various potential interferences was also investigated. The results of these experiments are shown in Table 2.23. Most of the common ions present in water samples do not interfere, even with high concentrations. Those ions that showed serious interference are rarely found in water samples at the highest concentrations examined.

Lake waters frequently contain a relatively high concentration of organic matter. In determinations of nitrate by the copperised cadmium reduction method this organic matter can interfere by chelating with copper in the reduction system. Hilton and Rigg [400] overcame this difficulty by using an excess of zinc ions to protect the copper catalyst from chelation. They devised a discrete analysis procedure based on these principles for the determination of nitrate.

The Hilton and Rigg [400] method is summarised below:

Reagents

Copper sulphate solution, $2.28\text{g L}^{-1} \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Zinc(II) sulphate solution $51.0\text{g L}^{-1} \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

Sodium hydroxide solution 0.2mol L^{-1} (8g L^{-1}) sodium hydroxide

Table 2.23 Effect of diverse ions on the determination of nitrate by the multipoint reaction-rate procedure with the cadmium alloy wire column.

<i>Interferent</i> ^a	<i>Ion: nitrate</i> ^b	<i>Error (%)</i>	<i>Interferent</i> ^a	<i>Ion: nitrate</i> ^b	<i>Error</i> ^c (%)
Cyanide	100	−99.5	Copper	100	−50.5
	10	−7.0		10	None
	1	None		10	None
Dichromate ^d	10	−21.5	Magnesium	100	+6.5
	1	−10.4		10	none
Iodate	100	−7.5	Mercury	100	−2.5
Iodide	100	−14.1	Tin(II)	10	−88.5
	10	None		1	−15.2
Sulphide ^d	10	−12.0	Nickel ^d	100	−11.0
	1	−2.6		10	None
Cobalt	100	−3.5	Phenol	100	−6.1

^aThe following ions in 100 concentration ratio showed negligible interference: acetate, bromide, carbonate, fluoride, oxalate, perchlorate, sulphate, sulphite, cadmium, calcium, manganese, zinc, silicate, urea, and hypochlorite

^bNitrate concentration 2mg L^{-1}

^cNone means < 2%

^dPermanent decrease in the reduction efficiency of the column; regeneration is needed

Source: Reproduced with permission from Elsevier Science [399]

Reductant solution. Dissolve 0.218g of hydrazine sulphate in 400ml of deionised water. Add 5 ml of copper II sulphate solution and 5 ml of zinc(II) sulphate solution. Make up to 500 ml. Prepare freshly as required.

Diazotisation reagent—dissolve 2.5g of sulphanilamide in 400ml of deionised water. Add 25ml of concentrated phosphoric acid (check concentrated phosphoric acid for low nitrite content prior to use). Dissolve 0.125g of N^{-1} -naphthylethylenediamine dihydrochloride in the resulting solution and dilute to 500ml. Store in a refrigerator.

Apparatus

Pye Unicam URAS system (ACI) automatic chemistry unit with an SP6–550 ultraviolet visible spectrophotometer and a Hewlett Packard 9815A calculator or equivalent. The instrument settings were given as in Table 2.24.

Direct adaptation to the discrete analyser met with little success owing to a non-zero intercept of approximately $50\mu\text{g L}^{-1}$ on the concentration axis, although nitrate and nitrite standards of the same concentration gave the same absorbance. A possible cause of the concentration axis

Table 2.24 Instrument settings for the Pye Unicam AURA discrete analyser cycle time, 15s temperature, 33°C; path length 10mm, and wavelength, 540nm

Reagent	Dispenser colour	Position	Reaction time/min	Syringe size/ μL	Syringe vol/ μL	Stroke/mm
Sample		47	450	400	32.0	
Sodium hydroxide solution	Blue	47	1.5	2000	800	13.8
Reductant solution	Orange	41 ^a	1	1000	250	14.0
Diazorisation reagent	Green	13 ^a	3.25	1000	400	22.5

^aStirrer

Source: Reproduced with permission from the Royal Society of Chemistry [400]

Table 2.25 Precision measurements of nitrate in standard solutions

Solution concn/ $\mu\text{g L}^{-1}$	Mean absorbance	Standard deviation ^a / $\mu\text{g L}^{-1}$		
		S_w	S_b	S_t
0	0.005	3(10)	—	—
200	0.101	5(10)	13(9)	14

400	0.202	6(10)	21(9)	22
600	0.209	11(10)	26(9)	28
800	0.395	18(10)	33(9)	38
1000	0.474	13(9)	27(8)	30

^aThe degree of freedom for within- (S_w) and between batch (S_b) standard deviations are given in parentheses; S_t is the total standard deviation

Source: Reproduced with permission from the Royal Society of Chemistry [400]

intercept was considered to be the presence of an excess hydrazine, reducing nitrate to nitrite prior to diazotisation. The concentration of hydrazine had been set at 190mg L^{-1} in the reduction step. However it was decided to reoptimise this parameter. A hydrazine concentration of 75mg L^{-1} in the reduction stage was then used in the optimisation of the other parameters. The calibration, using the reoptimised concentration for the reduction step, was now found to pass through zero.

The resulting method is linear up to $600\mu\text{g L}^{-1}$ of nitrate as N with a sensitivity of 0.05L absorbance unit per $100\mu\text{g L}^{-1}$. Interpretation of the performance statistics given in Table 2.25 shows a limit of detection of $14\mu\text{g L}^{-1}$ (95% confidence levels). A plot of the concentration of total oxidised nitrogen, determined in a variety of non saline waters, vs the concentration, measured for the same samples using the manual cadmium reduction method [401] gave a good straight line ($r=0.967$, $n=107$) passing through the origin.

Waughman [402] has described a procedure for determining nitrate in agricultural and environmental survey waters. Nitrate in the sample solution is reduced to ammonia by titanous sulphate and the ammonia is then released from the solution and diffused and absorbed onto a nylon square impregnated with dilute sulphuric acid. The nylon is then put into a solution which colours quantitatively when ammonia is present and a spectrophotometer is used to measure the colour.

Reduction of nitrate in nitrite by cadmium or copperised cadmium followed by estimation of the nitrite produced by production of a diazo compound and spectrophotometric estimation is the most commonly used method for determining nitrate. It has the advantage of sensitivity, freedom from interference and automated analysis.

Gauguch and Heath [403] have described a rapid manual cadmium reduction method for nitrate determination in small volumes (5ml) of non saline waters. It involves the preparation of test tubes as reaction tubes which can be used 5–10 times before reactivation of the cadmium filings is necessary. Once the tubes are prepared it is possible to batch-process 30 samples per hour without loss of sensitivity. However, caution is required when applying this method to water with high salinities.

In this method cadmium filings were amalgamated with a 1% (w/v) solution of mercuric chloride for 3min after which the mercuric chloric solution was decanted. The filings were then washed several times with distilled water and stored in the dark under a 0.10mol L^{-1} ammonium chloride solution. Reaction tubes were prepared by adding one small scoop ($0.76\pm 0.07\text{g}$) of the amalgamated cadmium filings into $18\times 150\text{mm}$ borosilicate glass test tubes. Rinse the reaction tubes three times with 0.10mol L^{-1}

hydrochloric acid between successive uses. A sulphanilamide reagent was prepared by dissolving 5g of sulphanilamide in a mixture of 50ml of concentrated hydrochloric and about 300ml of distilled water. This mixture is brought to the final volume of 500ml with distilled water. The *N*-1-naphthyl)-ethylenediamine dihydrochloride reagent was prepared by dissolving 5.05g of dihydrochloride in 500ml of distilled water.

If the sample pH was above 9 its pH was adjusted to between 8 and 9 using dilute hydrochloric acid. 5 ml aliquots of sample were buffered by the addition of 0.1ml 20% /w/v ammonium chloride and then added to the reaction tubes. The reaction tubes were shaken vigorously in an upright position on an oscillatory shaker (about 150 oscillations min^{-1}). After shaking for 25min, a 2.5ml aliquot was removed to another tube into which was mixed 50 μL of sulphanilamide reagent. After at least 2min, but not more than 5min, 50 μL *N*-1-naphthyl)-ethylenediamine dihydrochloride reagent was added and the mixture allowed to react for 10min. The absorbance was determined in 1cm glass cuvettes using a spectrometer.

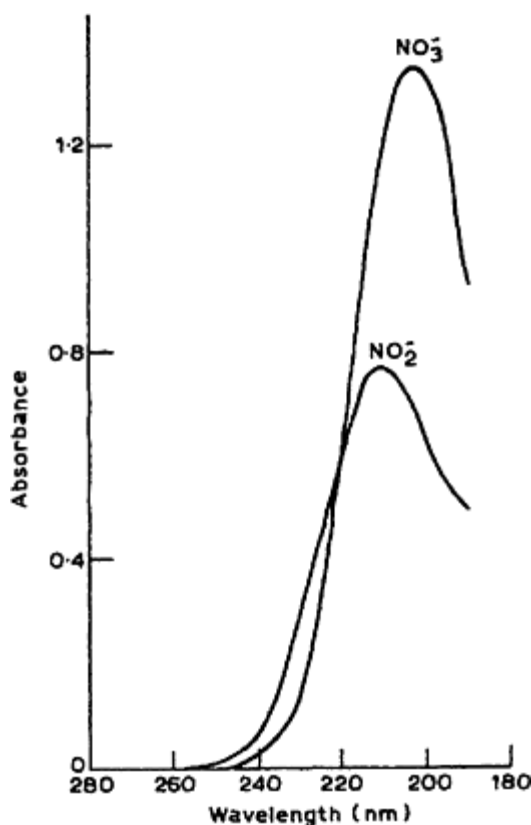


Fig. 2.26 Absorption spectra of nitrate and nitrite standard solutions containing 1mg L^{-1} of nitrogen

Source: Reproduced with permission from the Royal Society of Chemistry [405]

As an alternative to cadmium reduction, Zhang [404] showed that nitrate is reduced with 93% efficiency to nitrite in 8min by ultraviolet light under alkaline conditions. He applied a method based on these principles to the analysis of river water samples. A cadmium reduction column was used to convert the remaining nitrate present in solution to nitrite. Nitrite determinations involved adjustment to pH 7 and sequential addition of sulphanilamide solution (0.6%), alpha- naphthylamine solution (0.6%) and sodium acetate solution (2mol L^{-1}). Adsorbances at 520nm were used to determine nitrite concentrations against a calibration graph. For total nitrogen determinations, river water samples were digested with hydrochloric acid prior to analysis. Addition of potassium persulphate (4.0%) and sodium hydroxide (6mol L^{-1}) solutions and subsequent irradiation for 17min facilitated total nitrogen determination. With this method the coefficient of variation was 1.94% for river waters for a total nitrogen concentration of 1.8mg L^{-1} .

Table 2.26 Nitrate concentrations determined by ultraviolet and 2,4 xlenol methods

Type of water	Absorbances measured in 1cm cells Nitrate-nitrogen (mg L^{-1})	
	Ultraviolet method	2,4-Xylenol method
Butter Sandstone	0.04	0.04 ^a
Butter Sandstone	8.3	8.2
Butter Sandstone	0.005 ^a	0.04 ^a
Butter Sandstone	0.54	0.55
Butter Sandstone	4.5	4.6
Lincolnshire Limestone	7.9	7.9
Lincolnshire Limestone	5.8	5.5
River Thames, Chiswick	11.0	10.9

^a4cm cell

Source: Reproduced with permission from the Royal Society of Chemistry [405]

Miles and Espejoi [405] compared results for nitrate in ground water of low salinity by the 2,4-xylenol spectrophotometric method and by ultraviolet spectroscopy. The ultraviolet procedure is not subject to interference from the major cations present in typical ground waters, and interference by high levels of nitrite can be overcome by addition of sulphamic acid. There was good agreement between nitrate levels determined by both methods on a number of ground water samples.

Nitrite, which absorbs in a similar part of the ultraviolet region is a potential source of interference in this method. A solution containing 1mg L^{-1} of nitrite-nitrogen was scanned between 190 and 260nm and the spectrum is shown in Fig. 2.26 together with that of a 1mg L^{-1} solution of nitrate-nitrogen for comparison. The nitrite absorption

maximum is at about 211nm and it absorbs less strongly than nitrate at a similar concentration. Solutions containing 0–5mg L⁻¹ of nitrate-nitrogen and up to 100µg L⁻¹ of nitrate-nitrogen were prepared and the interference from nitrite is significant only at concentrations about 20µg L⁻¹. Interference by higher concentrations of nitrite can be removed by the addition of 0.1% m/v of sulphamic acid.

Iron does not interfere at concentrations below 100µg L⁻¹ and chloride is without effect at concentrations below 100mg L⁻¹.

In Table 2.26 are compared results obtained for nitrate by ultraviolet spectroscopy and spectrophotometry. Good agreement was obtained for all groundwater samples analysed.

Reduction with hydrazine has also been used to convert nitrate to nitrate as an alternative to cadmium reduction [406,407].

N-phenylthranilic acid forms an intensely coloured oxidation product by reaction with nitrate in a concentrated sulphuric acid medium and this has been used for determining nitrate concentrations in non saline waters[408]. The colour is stabilised by addition of phosphoric acid. Beer's law is obeyed in the concentration range of 0.0–0.35µg of nitrate mL⁻¹ and Sandell's sensitivity is 0.0003µg/cm².

A spectrophotometric determination of nitrate in non saline waters has been reported by Harada [409]. The water sample is first treated with alum and sulphamic acid solution to remove iron and manganese; the supernate is then acidified with hydrochloric acid and treated with sulphamic acid solution to decompose nitrite. The nitrate in the sample is reduced to nitrite with hydrazine sulphate and copper-zinc catalyst; the nitrite is then reacted with sulphamic acid and N-1-naphthylethylenediamine and measured colourmetrically. The relative standard deviation was 6.0–94% for nitrogen concentrations in the range of 0.1–1.0mg L⁻¹.

Garcia Mellian and Cangas Rancaro [410] and Ferrer Saliente [411] described other colourmetric determinations of nitrate in non saline waters. The standard deviation of the latter method is 0.017 and the relative error is 2.16%.

Automated cadmium reduction methods for the determination of nitrate have been reviewed [412],

A study has been carried out of the accuracy of determination of total oxidised nitrogen (nitrate plus nitrate and nitrite in river waters [413].

Airey *et al.* [414] have described a method for the removal of sulphide prior to the determination of nitrate in anoxic estuarine waters. Mercury(II) chloride was used to precipitate sulphide from samples of anoxic water. The sulphide free supernatant liquid was used to estimate sulphide by measuring the concentration of mercury(II). Nitrate was determined by a spectrophotometric method in amounts down to 1µg L⁻¹.

Direct spectrophotometric methods

Apart from cadmium reduction of nitrate to nitrite, other direct spectrophotometric methods for the direct determination of nitrate have been described and are reviewed in Table 2.27. None of these methods, however, has gained the popularity enjoyed by reduction procedures especially those employing cadmium.

The application of this technique is also discussed under multianion analysis in section 14.2.1.1.

2.62.2 Spectrofluorometric methods

All the fluorometric methods for determining nitrate ion are based on redox reactions. These methods are not selective but they can be applied to the determination of parts per billion levels of nitrate.

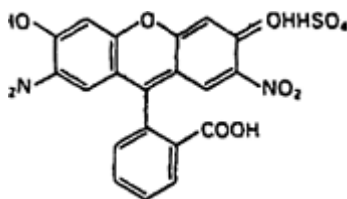
Table 2.27 Non cadmium reduction (ie direct) spectroscopic methods for the determination of nitrate in non saline waters

<i>Chromogenic reagent</i>	<i>D_{max} nm</i>	<i>Solvent extraction pre-concentration</i>	<i>Detection limit</i>	<i>Ref.</i>
Crystal violet	—	Chlorobenzene	<60µg L ⁻¹	[415]
<i>p</i> -Fluorophenol	—	Touene	—	[416]
Tetraphenyl-phosphonium chloride	269	Chloroform	<20mg L ⁻¹	[417]
Salicylic acid	—	None	—	[418]
2,4-Xylenol	—	None	—	[406]
9,9'bianthracene-10, 10'dione	500	None	1µg L ⁻¹	[419]
Phenoldisulphonic acid	—	None	10µg L ⁻¹	[420,421]
<i>o</i> -Toluidine	—	None	10µg L ⁻¹	[422]
Indigo carmine	—	None	6mg L ⁻¹	[423,424]
Brucine	410	—	—	[425]
Chromotropic acid	420	—	—	[426]
3,3'Dimethyl naphthidine	—	—	50µg L ⁻¹	[427]
Dihydroxy coumarin	—	Ethyl aceate	10µg L ⁻¹	[428]

Source: Own files

Fluorescein quenching method

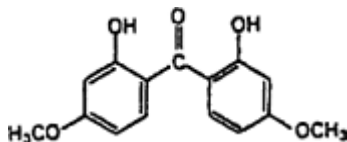
Nitrate oxidises fluorescein in a concentrated sulphuric acid medium to form a non-fluorescent product [429]. As fluorescein fluoresces and the reaction product does not, nitrate can be determined by the measurement of the fluorescent suppression. The authors did not determine the structure of the reaction product, but according to the Colour Index [430] fluorescein reacts with nitrate in concentrated sulphuric acid to form Solvent Orange 16 which has no fluorescence and is possibly the reaction product.



solvent orange

2.2 dihydroxy-4'4-benzophenone method

Afghan and Ryan [431] have described an automated fluorometric method employing 2,2-dihydroxy-4'4-benzophenone which is capable of performing analyses at a rate of 20 samples per hour and has a detection limit of $5\mu\text{g L}^{-1}$ nitrate. The automated procedure incorporates steps to overcome interference by high concentrations of chloride, sulphide and humic acid substances.



Preparation of column to remove organic matter

The XAD-2 column consists of $15\text{cm} \times 0.32\text{cm}$ id glass tubing packed with Amberlite XAD-2 polymeric adsorbent. The glass tubing was plugged at one end with glass wool and an N-6 nipple was butted against the plugged end using a $\frac{1}{2}\text{in}$ length of $\frac{1}{2}\text{in}$ id Tygon tubing for sleeving. A short length of Technicon $\frac{1}{2}\text{in}$ id transmission tubing was attached to the nipple and fitted with a hosecock. The other end of the column was connected to a 65mm filtering funnel using $\frac{1}{2}\text{in}$ id Tygon tubing. The column assembly was secured in a vertical position and filled with distilled deionised water, making sure no air bubbles were trapped below the funnel and hosecock. A washed aqueous slurry of the resin was poured into the funnel and packed into the column by draining water through the bottom of the column. The funnel and Tygon tubing were removed from the top of the column. The N-6 nipple assembly completed with the transmission tubing and hosecock was filled with distilled deionised water and forced over the opening of the column, making sure that no air bubbles were trapped inside. The column was then inserted while running the manifold as shown in Fig. 2.27.

Fig. 2.28 shows uncorrected excitation and emission spectra of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and its reaction product with nitrate under similar experimental conditions as for Fig. 2.27. The sensitivity of the reaction was also compared with similar concentrations of quinine sulphate.

Excitation was carried out at 380nm and emission at 445nm. The fluorescence development did not take place in a medium containing less than 70% sulphuric acid. The sensitivity and the concentration range where the response was linear varied with the concentration of sulphuric acid. A maximum fluorescence was obtained between 83–86% sulphuric acid. Nonlinear calibration curves were obtained when the ratio of sulphuric

acid to water exceeded 92%. Therefore, an 80% sulphuric acid medium was used. In the majority of automated methods, the most convenient way of eliminating interferences is to dilute the sample in the manifold prior to the determination. Because of the high sensitivity of the

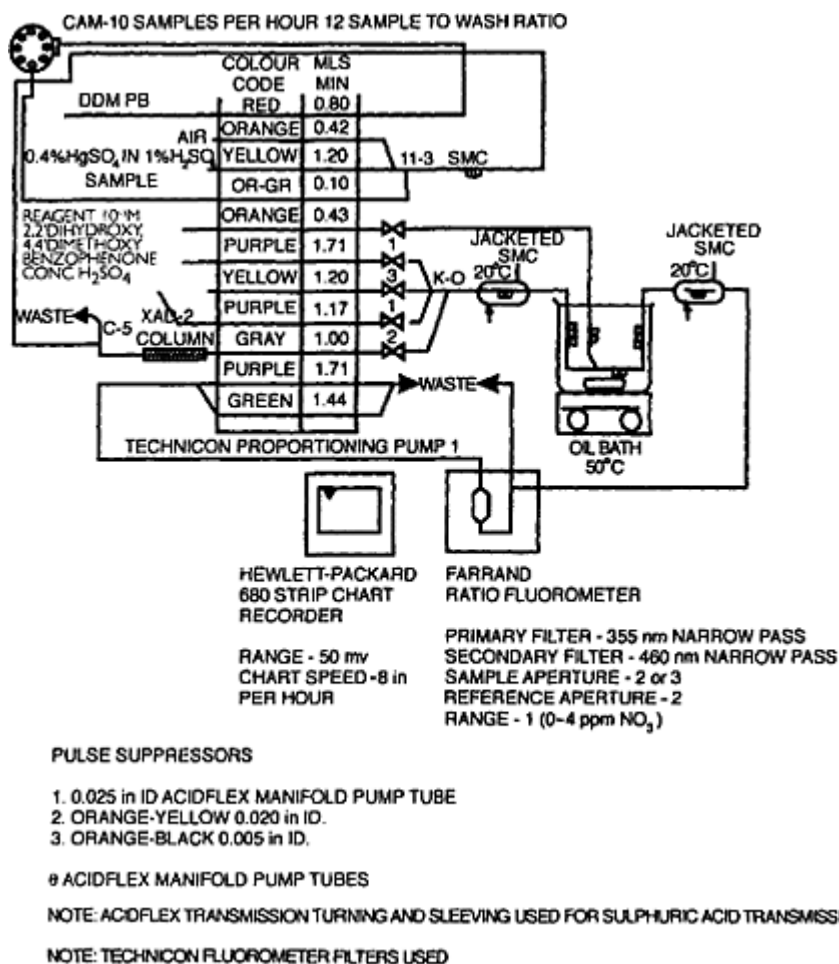


Fig. 2.27 Manifold for fluorometric method (DDM PB=2,2' dihydroxy, 4,4' dimethoxy-benzophenone, 10⁻³M)

Source: Reproduced with permission from the American Chemical Society [431]

method described by Afghan and Ryan [431], it was possible to incorporate a dilution step into the manifold as shown in Fig. 2.27 to tolerate concentration as high as 100, 10 and 1mg L⁻¹ of chloride, fulvic acid and sulphide, respectively. The dilution step was sufficient for the removal of these interferences for the majority of non saline waters.

However in some instances, concentrations of chloride, sulphide and fulvic acid substances may exceed the above levels. Therefore, it was necessary to incorporate an alternate method for the removal of these interferences prior to the determination of nitrate.

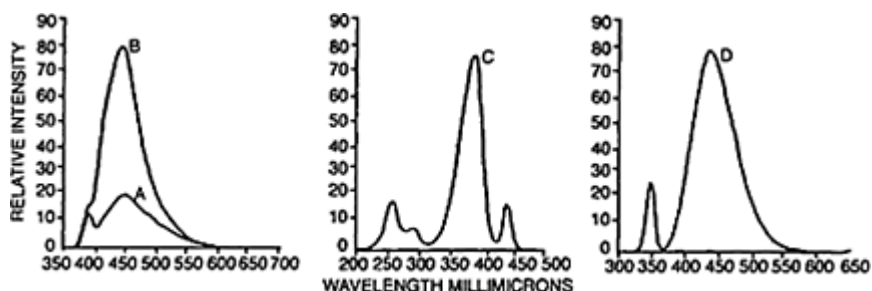


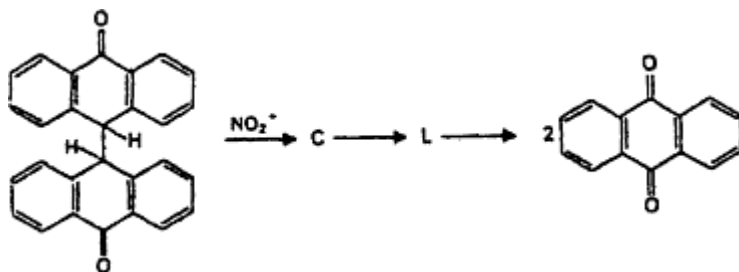
Fig. 2.28 Unconnected fluorescence spectra of solutions run through the manifold In Fig. 2.27. Curve A emission spectrum of DHDMBP; Curve B emission spectrum of $2 \times 10^{-6} \text{ mol L}^{-1}$ nitrate+DMBMBP; Curve C excitation spectrum of $1 \times 10^{-6} \text{ mol L}^{-1}$ nitrate +DHDMBP; Curve D emission spectrum of $1 \times 10^{-6} \text{ mol L}^{-1}$ quinine sulphate in 0.1N sulphuric acid. For all spectra, coarse sensitivity=1, fine sensitivity=80, excitation and emission=2.0. For A and B excitation $\lambda = 385$, for C emission $\lambda = 440$ and D excitation $\lambda = 350$

Source: Reproduced with permission from the American Chemical Society [431]

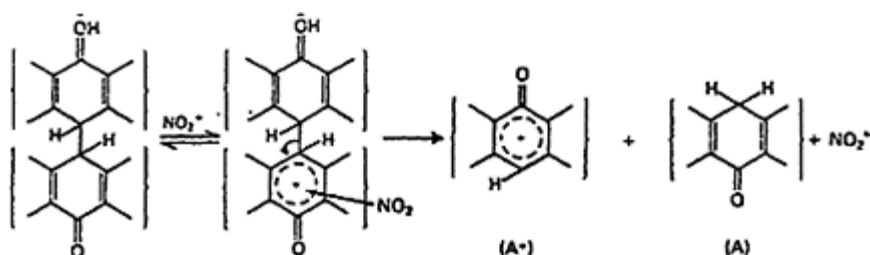
In the procedure the sample is diluted with mercuric sulphate to avoid interference by chloride and sulphide. An XAD-2 resin column was incorporated after the sample dilution step to eliminate interference from fulvic acid substances: ammonia, glycine, urea, amino acids and nitrite were without interference in the procedure.

Bianthranyl method

An extensive study of the kinetics and mechanism of the reaction between nitrate and binthranyl in concentrated sulphuric acid has been carried out [432]. Initially, nitrate reacts with sulphuric acid giving the nitronium cation, which acts on the bianthranyl molecule:



By different oxidative paths, C (coloured species) and L (luminescent compound) are formed. A subsequent step yields anthraquinone. Bianthranyl first degrades via a bianthranyl—nitronium complex, to anthronyl cation (A^+) and anthrone (A) and, later, by different oxidative paths these are transformed into anthraquinone.



The authors differentiated between the final product (λ_{ex} 286, λ_{em} 422nm) and the anthraquinone (λ_{ex} 285 420nm), but as can be observed by their spectral characteristics, these compounds are practically the same.

Resorcinol method

Resorcinol has been proposed as a fluorometric reagent for the determination of nitrate and nitrite [433]. The author suggested the following mechanism for the reaction of nitrate: chloride ion catalyses the conversion of nitrate into nitrite, the resultant nitrite reacts with resorcinol to produce the nitroso compound, which reacts with the excess of resorcinol to form a reddish violet species. This reaction product exhibits intense fluorescence in ammoniacal solution and is probably a phenoxazine derivative.

3-amino-1,5 naphthalenedisulphonic acid method

Motomizu *et al.* [434] describe a flow-injection fluorometric method for determining nitrate in non saline waters. The nitrate is reduced to nitrite in a copperised cadmium column and the nitrite is reacted with 3-amino-1,5 naphthalenedisulphonic acid to form the corresponding azoic acid in a flow-injection system; the salt of this acid is fluorescent in an alkaline medium and the fluorescence is measured. The relative standard deviation was 0.8% for 10 injections of 2×10^{-5} M nitrate, and the detection limit was 1×10^{-5} M nitrate, injection rate was 30 samples/h.

2.62.3 Chemiluminescence methods

Yoshizumi *et al.* [435] described the determination of down to $1 \mu\text{g L}^{-1}$ nitrate by a flow system with a chemiluminescent NOx analyser. Enzymic methods have been used for the determination of nitrate [436]. These methods are based on the enzymic reduction of nitrate to nitrite or ammonia. In one method [437] the nitrite is then estimated by the sulphanilamide-*N*-(1-naphthyl)ethylenediamine dihydrochloride coupling procedure.

Thermal decomposition combined with chemiluminescence analyses has been used to determine nitrate in deposited aerosol particles [438].

2.62.4 Flow injection analysis

Nakashima *et al.* [439] determined nitrate in non saline waters by the flow-injection analysis technique, according to which the sample (650 μL) was injected into the carrier solutions (a mixture of EDTA and ammonium chloride in aqueous solution at pH 8.1) and the nitrate first reduced to nitrite by passage through a column of copperised cadmium. The nitrite was then reacted with a mixture of *p*-aminoacetophenone and *n*-phenylene-diamine and the absorption measured as 456nm. The influence of several variables on the accuracy and sensitivity of the method was investigated. The limit of detection was 1.5 $\mu\text{g L}^{-1}$ and the sample rate about 40 samples per hour. Relative standard deviations for nitrate nitrogen in the range 0.1–0.3 mg L^{-1} were about 1%.

Al-Wehaid and Townshead [440] give details of a procedure for the determination of traces of nitrate (0.02–5 mg L^{-1} nitrogen) in water by flow injection analysis. Trivalent titanium chloride was used to reduce nitrate to nitrite before diazotisation with sulphanilamide and *N*-(1-naphthyl) ethylenediamine, and spectrophotometric determination at 530nm. Divalent copper was the only common ion that caused interference and this could be removed by an on-line cation exchange mini column.

Discrete injection segmented flow analysis has been used [441] to determine nitrate and phosphate in small volume samples.

An automatic flow-injection analyser for spectrophotometric monitoring of nitrite in the field by reduction with copperised cadmium and derivatisation by *N*-1-naphthylethylenediamine dihydrochloride and sulphanilamide has been described [442]. The linear calibration range on the method was 0–12 $\text{mg nitrate nitrogen per litre}$.

Various other workers [443–445] have studied the application of this technique in the determination of nitrates.

2.62.5 Electrochemical methods

Electrochemical methods that have been used to determine nitrate include polarography [446,447] and voltammetric analysis [448]. Bodini and Sawyer [449] described a voltammetric determination of nitrate at the $\mu\text{g L}^{-1}$ level. This electrocatalytic method utilises the concomitant reduction of cupric chloride and cadmic chloride on pyrolytic graphite to catalyse the reduction of nitrate ion.

Table 2.8 Instrumental components

Components	Model or size	Manufacturer
Microwave generator	MR-3S	Ito Chotanpa Co Ltd
Microwave cavity	TM ₀₁₀ type	laboratory constructed
discharge tube	6mm od 3mm id	laboratory constructed
Monochromator	JE-50E	Nippon Jarrell-Ash Co Ltd

Lens	f:60mm, 25mmØ	
Photomultiplier	R 787	Hamamatsu TV Co Ltd
Power supply picoammeter	part of ICAP-500	Nippon Jarrell-Ash Co Ltd
Chart recorder	B-181H	Rigakudenki Co Ltd

Source: Reproduced with permission from the American Chemical Society [451]

2.62.6 Atomic absorption spectrometry

Cresser [450] showed that nitrate can be rapidly reduced to ammonia by the action of titanium(III) sulphate at room temperature. Subsequent displacement of the ammonia by a current of air enables the gas-phase molecular absorbance the ammonia to be measured using an atomic absorption spectrophotometer and thus provides a sensitive and selective method for the determination of nitrate. Ions which affect the reduction of nitrate by titanium salts, such as cobalt, copper, iron and zinc, interfere with this method and must be removed if present in large amounts.

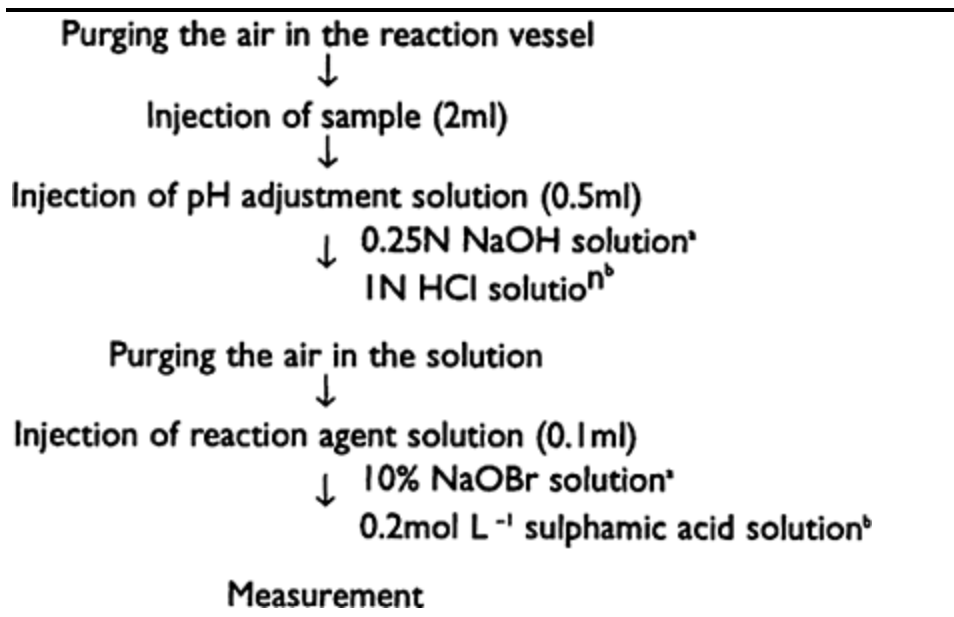
2.62.7 Helium microwave induced emission spectrometry

Ultratrace amounts ($\mu\text{g L}^{-1}$) of nitrate, nitrite (and ammonium) have been determined in pond waters by atmospheric pressure helium microwave induced emission spectrometry utilising a gas generation technique [451]. The instrument components are summarised in Table 2.28. The instrumental set-up consists primarily of the plasma system, the optical measurement system and the gas generation system.

Ammonium ion is oxidised to nitrogen gas by sodium hypochlorite in an alkaline medium and nitrite ion by sulphamic acid in an acidic medium. Nitrate ion is reduced to nitrite in a cadmium/copper column and then determined as above. The nitrogen produced by the chemical reduction is introduced into the helium flow via a three-way valve system connecting the reaction vessel. Plasma is generated by a microwave generator and the emission signals are measured at 391.4nm. Experimental procedures are summarised in Table 2.9.

Four wave-lengths listed in Table 2.30 were used for the determination of nitrogen. These peaks of nitrogen-containing species provided different

Table 2.29 Experimental procedures for nitrogen gas generation

^aIn the case of ammonium nitrogen^bIn the case of nitrite-nitrogen

Source: Reproduced with permission from the American Chemical Society [451]

Table 2.30 Detection limits and dynamic ranges for ammonium and nitrite-nitrogens at different emission lines and bands

Wavelength, nm	Ammonium N		Nitrite N	
	Detection limit, mg L ⁻¹ N	Detection range	Dynamic limit mg L ⁻¹ N	Dynamic range
337.1 (N ₂)	0.004	~3000	0.008	~100
391.4(N ₂ ⁺)	0.004	~200	0.004	~200
336.0 (NH)	0.02	~50	0.006	~100
746.8 (N)	0.009	~5000	0.01	~3000

Source: Reproduced with permission from the American Chemical Society [451]

detection limits and dynamic ranges. The detection limits and dynamic ranges obtained for ammonium and nitrite nitrogens are also summarised in Table 2.30. the detection

limit and dynamic range for nitrate were very similar to those for nitrite. The detection limit was defined as the signal level corresponding to twice the standard deviation of the blank signals.

As can be seen in Table 2.30, the N_2^+ main system bandhead at 391.4nm provided the lowest detection limit, while the N_2 'second positive' system bandhead at 337.1nm and the nitrogen atomic line at 746.8nm were observed to have wide dynamic ranges (more than three orders of magnitude). The emission signal of the NH band maximum ('A' system) at 336.0nm was the largest of four analytical wave lengths but the detection limits of this band, especially for ammonium nitrogen were not so good because of the significantly large blank signals at 336.0nm. The relative standard deviation of eight replicate measurements was about 7% at the 10-fold concentration of the detection limit and was about 4% at the 100-fold concentration for all the analytical wavelengths.

The effect of various concomitants possibly coexisting in water samples was investigated. The samples containing 0.4mg L^{-1} ammonium nitrogen or 0.3mg L^{-1} nitrate nitrogen were analysed in the presence of $100\text{--}20000\text{mg L}^{-1}$ of the inorganic ions. Of the organic compounds, amino acids and urea were examined where the analysis was done in the presence of 0.5–100-times concentration (in molar concentration) of the concomitants. The results, summarised in Table 2.31, show that only a few inorganic ions and organic compounds interfere with nitrogen analysis by helium microwave induced plasma emission spectrometry.

The results of nitrate determinations in pond water quoted in Table 2.32 show that results obtained by this procedure are consistent with those obtained by spectrophotometry. No nitrite was found in the sample by either method.

2.62.8 Isotachoelectrophoresis

The application of this technique is discussed under multi anion analysis in section 14.6.1.1.

2.62.9 Ion selective electrodes

Schechter and Gruener [452] developed a nitrate-selective electrode and applied it to highly mineralised borehole waters. Results obtained by this procedure were compared with those obtained by the standard phenoldisulphonic acid spectrophotometric method. These workers concluded that the electrode method is satisfactory under laboratory conditions but not as a field method because of the detailed calibration and complex controls required.

To evaluate the net influence of most common anions occurring in water, Schechter and Gruener [452] made measurements in a variety of synthetic solutions containing 1.50mg L^{-1} nitrate-nitrogen and varying amounts of nitrite, hydrogen carbonate, carbonate, chloride and sulphate. The results are presented in Table 2.33.

It is observed that the level of interfering ion, the total ionic strength and the level of nitrate do influence the measured potential. For most anions occurring in water, there are major additive influences from nitrite and chloride.

Table 2.31 Interferences of inorganic ions and organic compounds with determination of ammonium and nitrite-nitrogens (observed at 391.4nm)

<i>Concomitant</i>	<i>Concn mg L⁻¹</i>	<i>Relative sensitivity Ammonium N^a</i>	<i>Nitrite N^b</i>
none		100 ^c	100 ^c
Na ⁺	13000	100	115
K ⁺	20000	98	195
Mg ²⁺	500	98	104
Ca ²⁺	1000	97	102
Al ³⁺	100	103	102
Fe ³⁺	1000	96	101
Fe ²⁺	100	114	71
Mn ²⁺	100	84	99
Co ²⁺	100		106
Cu ²⁺	100	103	107
Zn ²⁺	100	99	102
Cl ⁻	20000	100	100
NO ₃ ⁻	1500	105	107
SO ₄ ²⁻	4000	107	99
PO ₄ ³⁻	500	102	70
Alanine	7m mol L ⁻¹		100
	1m mol L ⁻¹	97	
	7m mol L ⁻¹		95
Serine	1m mol L ⁻¹	90	
Glutamic acid	7m mol L ⁻¹		99
	1m mol L ⁻¹	94	
	7m mol L ⁻¹		99
Urea	0.015m mol L ⁻¹	114	

^aThe concentration of the test solution was 0.4mg L⁻¹ as N; ^bthe concentration of the test solution was 0.3mg L⁻¹ as N; ^cdefined as 100

Source: Reproduced with permission from the American Chemical Society [451]

Table 2.32 Analytical results in the determination of nitrate-nitrogen in pond water

Sample no ^a	Nitrate-nitrogen content, mg L ⁻¹ as N	
	Plasma emission ^b	Colorimetry
1	0.010±0.002	0.013±0.001
2	0.019±0.002	0.021±0.001

^aSamples 1 and 2 refer to the surface water samples taken from the Sanshiroike pond at the University of Tokyo

^bMeasured at 391.4nm

Source: Reproduced with permission from the American Chemical Society [451]

Table 2.33 Anions interference in nitrate-nitrogen determination by specific ion electrode

Anion	Added mg L ⁻¹		Nitrate as nitrogen added mg L ⁻¹				
			0	1	5	10	25
Nitrate as nitrogen detected mg L ⁻¹							
Nitrite	5	1.20	1.30	5.00	10.50	26.10	53.20
	10	1.50	1.70	5.60	10.50	28.20	58.10
	50	4.40	4.50	8.40	13.50	28.70	60.40
Bicarbonate	50	0.25	1.10	5.80	11.50	25.00	50.00
	250	0.40	1.50	7.30	12.00	26.10	51.50
	500	0.50	1.60	7.50	13.80	27.00	52.50
Carbonate	50	1.00	1.50	6.00	11.40	27.00	54.00
	250	1.15	1.70	6.40	12.00	29.00	58.00
	500	1.20	1.70	6.70	12.50	29.00	59.50
Chloride	50	1.30	1.30	5.80	11.50	27.00	52.00
	250	2.50	2.10	7.00	13.20	28.00	56.00
	500	3.60	3.00	8.00	15.20	30.00	59.10
Sulphate	1000	5.20	4.80	9.80	17.00	34.00	64.20
	50	0.20	1.00	4.90	10.40	25.00	50.00
	200	0.30	1.10	5.00	10.10	25.10	50.00
	500	0.60	1.00	5.00	10.00	25.20	49.70
	1000	0.70	0.90	4.80	9.80	24.90	49.30

Source: Reproduced with permission from the American Waterworks Association [452]

Nitrite is seldom present in high concentrations in borehole water. As to the strongly

interfering chloride, it must be initially removed by precipitation with silver sulphate if more accurate determinations are to be made. The elimination of chlorides was also performed by treatment with cationic ion exchange resin, prepared in the silver form. In this study better results were obtained by silver sulphate precipitation.

In Table 2.34 nitrate determinations on well water and spring water samples by ion selective electrodes and phenoldisulphonic acid spectrophotometry are compared. Good agreement was generally obtained between results obtained by the two methods.

Potentiometric titration using an Orion 93–07 nitrate-selective electrode and an Orion 90–02 reference electrode has been used [453] to determine nitrate in lake waters. Of the variants of this procedure, the Gran method [454] was found to be most suitable. Six known additions (0.0, 0.10, 0.15, 0.20, 0.25 and 0.30ml of 10–2mol L⁻¹ sodium nitrate) were added to 10 ml of the sample and after each addition the electrode potential was checked and recorded. Analysis was performed with constant stirring and in the presence of 0.1ml of silver fluoride to each 10ml of sample in order to maintain a constant ionic strength and to eliminate interferences from such as chlorides or sulphates.

Table 2.34 Comparison of specific ion electrode and PDSa method for nitrate-nitrogen determination in well water

Nitratenitrogen level range mg L ⁻¹	No of samples	Nitrate-nitrogen mg L ⁻¹		Conductivity mmho		Chlorides mg L ⁻¹	
		Electrode ^b	PDS ^b	Min	Max	Min	Max
<5.0	4	2.92	2.60	0.45	1.10	76	140
5.0–10.0	45	8.78	8.02	0.50	3.15	40	750
10.1–20.0	71	15.24	14.45	0.70	3.15	111	740
20.1–30.0	12	26.15	25.00	0.80	2.70	95	600
>30.0	16	35.94	34.86	1.80	2.90	500	580
Total	148						

^aphenoldisulphonic acid

^bmean value

Source: Reproduced with permission from the American Waterworks Association [452]

For calculating the nitrate concentration by Gran's method, the known transformation of the Nernst equation was employed:

$$\text{antilog } E/S = \text{const} + a_{\text{NO}_3^-}$$

where E is the emf of the electrochemical cell, S the electrode function of the nitrate electrode (found to be 55mV per decade). The graph obtained represents the dependence between $\text{antilog } E \cdot S$ and the added quantity of standard solution. The intersection of the

graph with the horizontal axis represents the volume of standard solution containing a quantity of nitrate equal to that in analysed solution. Table 2.35 shows the experimental results for eight different samples.

Cox and Litwinski [448] described a voltammetric ion selective electrode for the determination of nitrate down to $6.7 \times 10^{-6} \text{M}$. The electrolysis cell used was equipped with anion-exchange membrane sheath. An instrument has been described [455] which is based on ion selective electrode measurements, with an acidic buffer solution which ensures that alkaline earth carbonates do not deposit, and variations in sample ionic strength are decreased. A feature is the automatic checking and autocorrection for sensor drift, carried out at two concentrations at preset time intervals. Monitoring trials have shown that the instrument can produce accurate and consistent records without manual intervention almost indefinitely.

Nitrate has been determined by a nitrate-selective electrode [441] consisting of a porous polymer wick sealed with liquid ion-exchanger (tris (4,7-diphenyl-1, 10-phenanthroline) nickel(II) in 2-nitro-*p*-cymene).

Table 2.35 Nitrate-nitrogen content (mg L^{-1}) in lake water samples analysed by Gran method

S. No.	Gran
1 (standard)	
1.06	1.06
2	1.87
3	1.93
4	2.80
5	2.94
6	2.89
7	2.05
8	1.82
9	2.35

Source: Reproduced with permission from American Water Works Association [452]

Chloride and bicarbonate interferences are overcome by the addition of silver sulphate and 0.5mol L^{-1} phosphate pH buffer respectively.

Synott *et al.* [456] compared ion selective electrodes and gas-sensing electrode techniques for the measurement of nitrate in non saline waters. The gas electrode method is based on the reduction of nitrate to ammonia by titanium trichloride and detection of the ammonia by an ammonia electrode. The results indicated satisfactory reproducibility and correlation between the two methods, except for sea water where the high concentration of dissolved salts made the membrane electrode method unreliable. The

gas-sensing method, however, was unaffected by the presence of chloride in high concentrations and also enabled the operator to compensate for the presence of trace quantities of free ammonia in the sample.

Csiky *et al.* [457] used disposable clean-up columns of chemically bonded alkylaminosilica for the selective removal of humic substances prior to measurements with a nitrate ion selective electrode. Using the clean-up procedure, recoveries averaged 95% and reproducibility was independent of humic acid concentration. Without clean-up, recovery was always greater than 100%, increased with humic acid concentration and changed with time. The nitrate concentrations found in non saline waters after clean-up were in good agreement with determinations by ion chromatography.

O'Hara and Okazaki [458] studied the effect of surfactants on the determination of nitrate in river and stream waters using a nitrate ion selective electrode. The interferences due to anionic surfactants and their elimination by the addition of cationic surfactants was examined. The interference of dodecylbenzenesulphonate below 1 mg L^{-1} was unimportant.

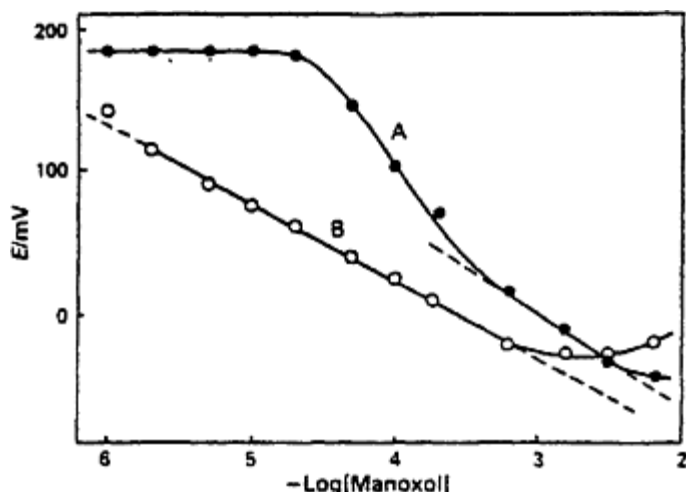


Fig. 2.29 Effect of Manoxol OT on the response of nitrate-selective electrodes with solidsilver contact (a) and internal reference solution (B) in the presence of 10^{-1}M potassium nitrate

Source: Reproduced with permission from the Royal Society of Chemistry [459]

The interference of $1\text{--}10\text{ mg L}^{-1}$ dodecylbenzenesulphonate could be mostly eliminated by the addition of a cationic surfactant such as cetyltrimethylammonium bromide. An anomalous response behaviour occurs in the presence of some cationic surfactants.

Hulanicki *et al.* [459] also studied the effect of surfactants on the response of nitrate selective electrodes with polyvinyl chloride membranes. The electrodes investigated had either an internal reference solution or a solid-silver contact. The latter type was found to be less sensitive to surfactant interferences as shown in Fig. 2.29.

Crumpton *et al.* [460] give details of equipment and procedure for determination of nitrate, based on alkaline reduction with titanous chloride in gas-tight reaction vials and determination of the ammonia produced by means of gas-sensing ammonia probes. The method was simple and reliable and could be applied to very small sample volumes. Results obtained by this method and by the cadmium reduction method are compared.

Various other workers have studied the application of ion selective electrodes to the determination of nitrate in non saline waters [451,461–466].

2.62.10 Ultraviolet spectroscopy

Munoz [467] adapted the ultraviolet procedure for the determination of nitrate to an automatic discrete-sample system, the AMA-40 system for the determination of nitrate in waters at low mg L^{-1} levels. Results indicate that the automated system is simple to set up and is easily applicable to routine determinations of nitrate in water samples, giving excellent repeatability of results.

Brown and Bellinger [468] have proposed an ultraviolet technique which is applicable to both polluted and unpolluted fresh waters and some estuarine waters. Humic acid and other organics are removed on an ion exchange resin. Bromide interference in sea water samples can be minimised by suitable dilution of the sample but this raises the lower limit of detection such that only on relatively rich (0.5mg L^{-1} nitrate) estuarine and inshore waters could the method be used. Chloride at concentrations in excess of $10,000\text{mg L}^{-1}$ does not interfere.

The method is either not affected by, or can allow for, interference from phosphate, sulphate, carbonate, bicarbonate, nitrite, coloured metal complexes, ammonia, dyes, detergents, phenols and other ultraviolet absorbing substances.

The method incorporates three features designed to reduce interferences.

- (a) Humic acid interference is reduced by carrying out measurements at 225nm, a higher wavelength than that used by previous workers (210–229nm).
- (b) Removal of inorganic interferences, particularly the removal of bromide interference in sea water, by diluting the sample fivefold, the removal of nitrite by the addition of sulphamic acid and the removal of metals by passage through Amberlite IR120 cation exchange resin.
- (c) Removal of ultraviolet absorbing organics by passage through a specific ion exchange resin such as Amberlite XAD-2.

In Table 2.36 nitrate determination by this method in the presence of various interfering substances is compared with two alternate methods, namely phenoldisulphonic acid and ion selective electrode methods. It is seen that, in general, the method proposed by Brown and Bellinger [468] is less subject to interference.

Saito *et al.* [469] used ultraviolet spectrophotometry to determine nitrate in non saline waters, interference by nitrite was eliminated by ion chromatography.

2.62.11 Mass spectrometry

Heumann and Unger [470] have described a mass spectrometric determination of nitrate

in mineral waters. The method is based on the technique of isotopic dilution analysis. The formation of negatively charged nitrite thermal ions from the nitrate in the water permits the nitrate to be detected in the mass spectrometer. Using nitrogen-15 labelled nitrate as a radioactive tracer for the isotopic dilution method,

Table 2.36 The effects of various interferences on the determination of nitrates by three methods. For all determinations (with the exception of non saline river waters) the concentration of $\text{NO}_3^- \text{N}$ was 1.125 mg L^{-1} . All concentrations are given in mg L^{-1}

<i>Interference</i>	<i>Phenoldisulphonic acid</i>		<i>Method UV method</i>		<i>Selective ion electrode</i>	
	<i>Uncorrected</i>	<i>Corrected</i>	<i>Uncorrected</i>	<i>Corrected</i>	<i>Uncorrected</i>	<i>Corrected</i>
Chloride						
100	0.62	1.07 ^a	1.08	1.08		1.55 ^d
1000			1.05			
Bicarbonate-carbonate						
100	1.13		1.06		7.87	1.24 ^e
260	1.23					
1000			1.13			
Bicarbonate-chloride						
100Cl:200HCO ₃						1.58 ^e
100Cl:100HCO ₃						1.46 ^e
50Cl:100HCO ₃						1.46 ^e
Nitrate						
0.304	1.11		1.48	1.10 ^b		
1.500						1.31 ^e
3.0–4	1.13			1.06 ^b		
Ammonium						
1.4	0.98					
14.0	0.66		1.08			1.13 ^e
1400.0			1.08			
<i>Interferences</i>	<i>Phenoldisulphonic add</i>		<i>Method UV method</i>		<i>Selective ion electrode</i>	
	<i>Uncorrected</i>	<i>Corrected</i>	<i>Uncorrected</i>	<i>Corrected</i>	<i>Uncorrected</i>	<i>Corrected</i>
Phenol						
1.0	1.10		1.29	1.10 ^c		1.13 ^c

10.0		1.86	1.08 ^c	
Daz'				
1.0		1.12		2.48 ^e
10.0		1.56	1.05 ^c	202.5 ^e
Unpolluted river water				
humic acid-inorganic				
salts NO ₃ -N by				
polarography	1.69	1.77	1.77 ^c	3.15 ^a
1.170				

^aAddition of exact amount of silver sulphate to precipitate chloride with no excess silver

^bAddition of sulphamic acid (final conc, in sample approximately 20mg L⁻¹)

^cTreatment with Amberlite XAD-2 resin

^dAddition of saturated silver sulphate (1ml to 10ml sample). Not recalibrated. Addition of 2mol L⁻¹ acetic acid to sample (0.09ml per 30ml sample). Not recalibrated

^eCalibrate for presence of 3ml saturated silver sulphate and 0.09mol L⁻¹ acetic acid in 30ml sample

^fDaz—a commercially available household detergent

Source: Reproduced with permission from Elsevier Science [468]

nitrate could be quantitatively determined down to the $\mu\text{g L}^{-1}$ level. The method is also applicable to nitrite, after separation of nitrate ions, which can be performed by ion exchange in the alkaline pH range.

Wolff *et al.* [471] have determined nitrate in water samples by isotope dilution analysis using a small thermionic quadrupole mass spectrometry. The isotope dilution experiments were carried out using the Institute for Reference Materials and Measurements' 15N-enriched nitrate spike reference material IRMM-627. Nitrate was isolated from the matrix by precipitating it as nitron nitrate, from which emission of negative thermal nitrite ions was found to be best. The ions were produced in the ion source of a small, low-cost, easy-to-handle thermionic quadrupole mass spectrometer equipped with a secondary electron multiplier coupled to an ion counter. The procedure developed was applied to the measurement of nitrate in a certified reference material (simulated rainwater, CRM 409 from Community Bureau of Reference), in sparkling mineral water and in tap water. Results were compared with those obtained using ion chromatography. Good agreement (within 1%) was found between the concentration determined by isotope dilution mass spectrometry, the values from ion chromatography, and the certified value. The procedure developed allowed accurate and traceable determinations of nitrate in water samples, with an expanded uncertainty (coverage factor $k=2$) of 2–5% and the detection limit was found to be $2\mu\text{mol kg}^{-1}$.

The application of thermionic quadrupole mass spectrometers has also been discussed in Heumann *et al.* [472] and Rever *et al.* [473].

2.62.12 Enzymic assay

Enzymic methods have been used for the determination of nitrate [436,474]. These methods are based on the enzymic reduction of nitrate to nitrite or ammonia. In one method [436] the nitrite is then estimated by the sulphanilamide-*N*-(1-naphthyl) ethylenediamine dihydrochloride coupling procedure.

Kiang *et al.* [474] reduce nitrate with nitrate reductase and nitrite with nitrite reductase using an air gap electrode to monitor the ammonia produced by the reduction of nitrate. Between 5×10^{-5} and 1×10^{-2} mol L⁻¹ nitrate can be determined by this procedure.

2.62.13 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.1, 12.2.4, 12.2.5 and 12.2.6.

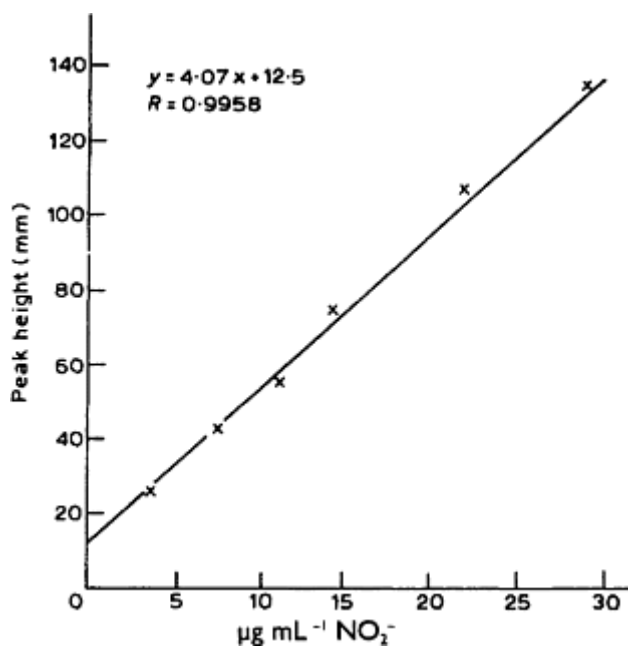


Fig. 2.30 Calibration curve for nitrate ion for the range 5–40 $\mu\text{g mL}^{-1}$ as sodium nitrate

Source: Reproduced with permission from Alfred Huethin Verlag GmbH [475]

2.62.14 High performance liquid chromatography

High performance liquid chromatography on a small bore column packed with microparticulate silica based ion exchange material has been used [475] to determine

down to 0.1mg L^{-1} nitrate in water, without interference from other ions associated with potable, pond, river and stream water.

Detection of the separated peaks was achieved using a Pye LC-UV variable wavelength ultraviolet detector fitted with a $8\mu\text{L}$ flow cell and set at 265nm . The chromatographic system consisted of Partisil $10\mu\text{m}$ SAX column, and a mobile phase consisting of 10^{-3}M potassium hydrogen phthalate ($\text{pH } 3.95$) in deionised water.

In Fig. 2.30 is shown a calibration curve obtained for a set of nitrate standard solutions. This was linear (correlation coefficient= 0.9958) and was defined by the equation **$y = 4.07x + 12.5$** . Using this calibration line a series of water samples was studied and the nitrate levels measured.

Schroeder [476] has determined nitrate in non saline waters and wastewaters by high performance liquid chromatography using aqueous phosphoric acid/sodium dihydrogen phosphate as the mobile phase and UV detection. The optimum nitrate concentration was $0.3\text{--}3\text{mg L}^{-1}$ as nitrate with a linear response for $<3\text{mg L}^{-1}$ as nitrogen. Relative standard deviations in the optimum range were $<1\%$, and the detection limit was 0.0007mg L^{-1} as nitrogen. Various potential interferences, including nitrite, are separated from the nitrate on the high performance liquid chromatography column.

The application of this technique is also discussed under multianion analysis in sections 13.1.1.3, 13.1.1.4 and 13.1.1.5.

2.62.15 Ion exchange chromatography

Sherwood and Johnson [477] have described an ion exchange chromatographic determination of nitrate and amperometric detection at a copperised cadmium electrode. The chromatograms obtained in this procedure resolve nitrate from dissolved oxygen.

2.62.16 Micelle chromatography

The application of this technique is discussed under multianion analysis in section 13.5.1.2.

2.62.17 Gas chromatography

Christensen and Tiedje [478] used a denitrifier (*Pseudomonas chlororaphis*) in determining nitrate to nitrite at sub-ppb levels in non saline waters. The denitrifier reduces the nitrous oxide to nitrogen and does not reduce the nitrous oxide any further; the released nitrous oxide is measured with a ^{63}Ni electron capture gas chromatograph detector, with very little background interferences. The optimum measurement range was from 0.5 to $50\mu\text{g L}^{-1}$ of nitrate nitrogen and the detection limit was $0.2\mu\text{g L}^{-1}$ of nitrogen.

2.62.18 Miscellaneous

Kiang *et al.* [474] reduce nitrate with nitrate reductase and nitrite with nitrite reductase using an air gap electrode to monitor the ammonia produced by the reduction of nitrate.

Between 5×10^{-5} and 1×10^{-2} M nitrate can be determined by this procedure.

Kretzschmar and Kretzschmar [479] have reported an enzymic-photometric method for the determination of nitrate in non saline waters.

Other techniques for determining nitrate include paper chromatography of diazo dyes to reduce interference by metals [480], stopped flow analysis [481], direct injection enthalpimetry [482] and a nitrogen-15 isotopic tracking method [483].

2.63 Nitrite

Analysis of nitrite ion is important due to its role in environmental processes and its toxicity and suspected carcinogenicity in humans, as

Table 2.37 Effect of diverse species on determination of 0.1 mg L^{-1} of nitrite (100 ml of solution extraction method)

Tolerance limit (ppm)	Species
800	SO_4^{2-} , NO_3^- , PO_4^{3-} , HCO_4^- , SiO_3^{2-}
150	Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Zr^{4+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+}
100	Li^+ , Be^{2+} , Cr^{3+} , Mo(VI) , W(VI) , Ni^{2+} , Sb_3^- , Bi^{3-} , Se(IV) , Te(IV) , F, Br
50	Fe^{3+}
40	I^- , aniline, HCHO, phenol
10	SO_3^{2-} , SO^{2-}
2	Cu^{2+}

Source: Reproduced with permission from Elsevier Science [488]

well as its normal function in humans. Measurement of nitrite ion has recently been examined as a surrogate for in vivo nitric oxide production [484–486]. Sensitive and selective methods are needed to measure nitrite ion at low levels in the complex matrices found in water, foods and biological fluids. The wide variety of analytical techniques has been reviewed recently [487].

2.63.1 Spectrophotometric methods

2.63.1.1 Diazotisation spectrophotometric methods

Spectrophotometric methods for determining nitrite are generally based on conversion of nitrite to nitrous acid then diazotisation of an aromatic amine by the nitrous acid, followed by coupling of the diazotised product with an amine or phenol to produce a dye which is evaluated spectrophotometrically. Numerous diazotisation-coupling reagent

systems have been studied, as discussed below.

(a) *Diazotisation reagent: o-Nitroaniline*

Coupling reagent: *N*(1-Naphthyl)ethylene diamine dihydrochloride

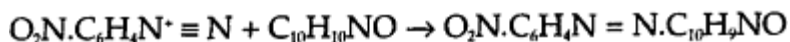
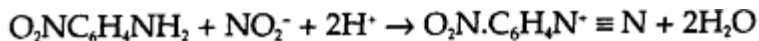
Chaube *et al.* [488] developed a method based on these reagents in which the coupled red-violet dye is extracted into isoamyl alcohol prior to spectroscopic evaluation at 545nm.

The effects of foreign species are shown in Table 2.37 which gives concentrations of foreign species that cause 2% error in the determination of 0.1mg L⁻¹ of nitrite by the extraction method (100ml samples). Copper(II), iron(II) and sulphur dioxide interfere but the interference of up to 100ppm of sulphur dioxide can be eliminated by oxidising it to sulphate with hydrogen peroxide. Bismuth and iron(III) require masking with tartrate.

(b) *Diazotisation reagent: p-nitroaniline*

Coupling reagent: 2-methyl-8-quinolinol

Tsao and Underwood [489] give a procedure for the determination of low concentrations of nitrite in non saline water which involves diazotisation with *p*-nitroaniline and coupling of the diazonium salt with 2-methyl-8-quinolinol, followed by solubilisation of the azo dye in aqueous hexadecyltrimethylammonium bromide.



(c) *Diazotisation reagent: p-nitroaniline*

Coupling reagent, 8-quinolinol

This method [490] very similar to that of Tsao and Underwood [489] except that it does not include the use of hexadecyltrimethylammonium bromide as a solubilisation agent for the dye.

Norwitz and Keliher [491,492] determined nitrite in non saline water using composite reagents containing sulphanilamide, sulphanilic acid, or 4-nitroaniline as the diazotisation reagents and aromatic amino and *N*-(1-naphthyl) ethylenediamine as the coupling agent. As a result of this work they recommended the following composition for the composite coupling reagents: 0.25% sulphanilamide, 0.0060% *N*-(1-naphthyl)ethylenediamine and 5.42% hydrochloric acid; 0.50% sulphanilic acid, 0.0050% *N*-(1-naphthyl)ethylenediamine, and 0.29% hydrochloric acid; and 0.25% 4-nitroaniline, 0.010% *N*-(1-naphthyl)ethylenediamine and 15.0% sulphuric acid. The wavelengths of maximal absorption were 542, 541 and 542nm respectively. The effects of varying the ratios of the reagents, the overall amount of the reagents, the amount of acid, and the reaction temperature were studied, as was the effect of methanol on the colours. The importance of the ratios of reagents as well as the overall quantities was demonstrated.

(d) Diazotisation reagent: 4-aminosalicylic acid

Coupling reagent: naphth-1-ol

Flamerz and Bashir [493] studied the effects of this method on foreign ions that often accompany nitrite in water samples (Table 2.38).

The method is more selective towards anions than cations; this is not unexpected because these azo dyes are commonly used chromogens for metal ions. However, an ion exchange procedure can be used to remove the seriously interfering ions.

Table 2.38 Effect of diverse ions on the determination of nitrite

<i>Interferent</i>	<i>Permissible amount in the presence of 10µg of nitrite (µg)^a</i>
Ammonia	150
Carbonate	50
Chloride	180
Cyanide	75
Fluoride	120
Iodide	140
Hydrogen carbonate	110
Nitrate	80
Phosphate	110
Sulphide	4
Sulphite	25
Calcium	60
Cadmium	9
Cobalt (II)	8
Copper(II)	10
Iron(III)	7
Magnesium	15
Mercury(II)	30
Lead(II)	30
Tin(II)	20
Phenol	170

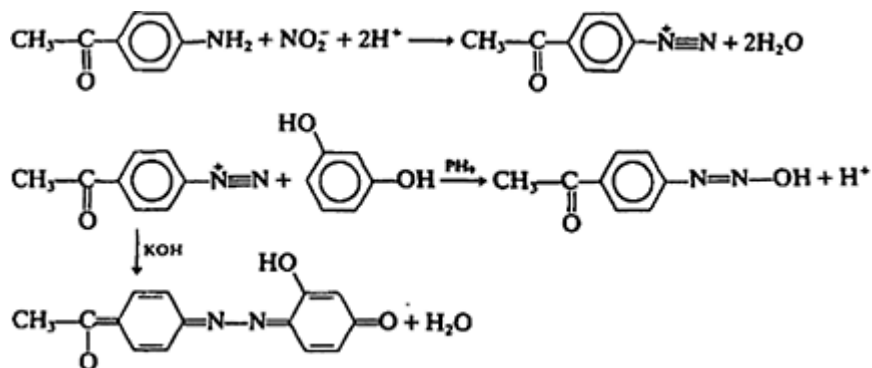
^aAmount of diverse ion causing an error of less than 2% in the determination

Source: Reproduced with permission from the Royal Society of Chemistry [493]

(e) Diazotisation reagent: *p*-aminoacetobenzophenone

Coupling reagent: resorcinol

Suggested reaction sequence:



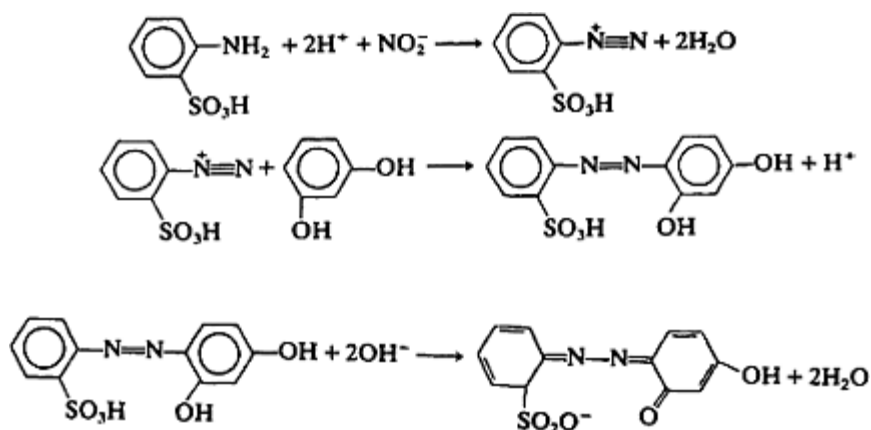
Wu and Liu [494] have described a spectrophotometric technique based on these reactions. The method is based on the diazotisation of *p*-aminoacetophenone followed by coupling with resorcinol in a sodium carbonate/sodium acetate medium to form a bright gold water-soluble azo dye. Mercuric chloride is added to eliminate the interference of sulphide and a composite EDTA/sodium hexametaphosphate reagent is used to mask foreign ions.

Wu and Liu [494] examined the effect of various amounts of foreign ions on the determination of nitrite. Most of the cations and common anions do not interfere; sulphide, thiosulphate, tetrionate and iodide interfere but their effect can be mitigated by adding mercuric chloride solution as indicated in the method above.

(f) Diazotisation reagent: *orthanilic acid*

Coupling reagent: resorcinol

Bashir *et al.* [495] have described a sensitive method based on these reagents which operates over the range 1–12 µg nitrite with a relative standard deviation, depending on concentration, in the range 0.4–3.5%. Cobalt interferes seriously in this method at the 4mg L⁻¹ level while sulphate is without interference even when present in the sample at concentrations between 1 and 1.5g L⁻¹.



Numerous other publications have appeared on the application of diazotisation-coupling to the spectrophotometric determination of nitrite in non saline water. These are reviewed in Table 2.39.

2.63.1.2 Non-diazotisation spectrophotometric methods

Spectrophotometric methods for the determination of nitrite which are dependent on colour forming reactions other than diazotisation and

Table 2.39 Diazotisation-coupling systems for the spectrophotometric determination of nitrite in non saline water

<i>Diazotisation agent</i>	<i>Coupling agent</i>	<i>Mox nm</i>	<i>Concn range</i>	<i>Limit of detection</i>	<i>Ref.</i>
4-amino-I-naphthalene sulphonic acid	1-naphthol	530	3–10µgN	–	[496]
naphthalene-2,3-diamine		355			[497]
Sulphanilamide	<i>n</i> -(1-naphthyl) ethylene diamine flow injection analysis	–	–	0.05µM	[443]
4'-amino-acetophenone	<i>N</i> -phenyl-I-naphthy lamine	618	0.1–4µg L ⁻¹	–	[498]
4-nitroaniline	1-naphthol	–	–	–	[499]
Sulphanilic acid	8-amino-naphthalene-2-	525	–	–	[496]

	sulphonic acid			
Miscellaneous	Miscellaneous	–	–	– [500]
8-amino phenyl	N-(1-naphthyl)	–	–	– [496]
Mercaptoacetic acid	ethylene diamine	–	–	– [501]

Source: Own files

coupling include reaction with 2,3-dimethyl-1-phenyl-pyrazolin-5-one [502], 2-mercaptoethanol [503], mercaptoacetic acid [504], dihydroxy-4-imino-2-oxochroman [505] and zirconyl ion [500,506,507].

Gabbay *et al.* [500] described a rapid spectrophotometric method in which nitrites react with resorcinol in an acidic medium and the nitroso product forms a pale yellow chelate with the zirconyl ion. The absorbance of the chelate is measured at 347nm. The method is suitable for the determination of nitrite ion in a 1cm cell in the range from a few parts per 100 million to about 1mg L⁻¹.

Beer's law holds up to a concentration of 7mg L⁻¹ of nitrite, as was demonstrated by the calibration graph, which was a straight-line graph passing through the origin over this range.

The effects of various potential interferences were investigated. Some of the problematic interferents expected in the diazotisation methods such as sulphite, copper (II), iron(II) or iodide, are tolerated in this procedure.

5,7-dihydroxy 4-imino-2-oxochroman has been used as a chromogenic reagent for the spectrophotometric determination of nitrite in river waters [505].

The reagent was reacted with nitrate nitrogen in acidic medium, the product added to a mixed solvent *n*-butyl alcohol and ethyl acetate, and absorbance measured at 361nm. The amount of nitrite nitrogen was determined from the calibration curve. The relative standard deviation was 0.3% for the determination of 0.1mg L⁻¹ of nitrite. Beer's law was obeyed over the range 0.005–0.280mg L⁻¹ nitrite nitrogen.

Montes and Laserna [508] have described a spectrophotometric reaction rate method for the determination of nitrite in water with pyridine-2 aldehyde-2-pyridylhydrazone. In acidic medium the rate of the bromate oxidation of pyridine-2-aldehyde 2-pyridylhydrazone is accelerated by nitrate. This kinetic principle was exploited for the determination of sub-microgram quantities of nitrite in river samples. The reaction was monitored spectrophotometrically at 372nm. The mean relative standard deviation for nitrite determinations in polluted river water was 3.2%. Ammonium and nitrate ions did not interfere but interferences from copper(II) and palladium(II) ions and electroactive substances, were marked. The sensitivity of the kinetic method was less than for established polarographic and chemiluminescence methods. However, this method was more rapid than other spectrophotometric or polarographic procedures.

Ibraheem and Bashir [509] used para-aminoacetophenone as the diazotising reagent and *N*-(1-naphthyl)ethylenediamine as the coupling reagent for a sensitive and simple method for nitrite determination. The reddish-purple coloured azodye complex was monitored by its absorption maximum at 550nm. Optimal conditions affecting the colour

reaction and interferences due to foreign ions were examined. Concentration curves were linear over the range 1–20 µg nitrite per 25 ml final volume.

There are numerous other reports dealing with the spectrophotometric determination of nitrite in non saline waters. The reagent *N,N*-bis(2-hydroxypropyl)aniline reacts with nitrite in an acidic medium to form a reddish product ($\lambda_{\text{max}} = 500\text{nm}$), which gradually changes to a yellowish product ($\lambda_{\text{max}} = 370\text{nm}$). The reddish product was used for determining nitrite in river water using a flow-injection method [510]. The calibration graph was linear from 3 to 64 µg L⁻¹ of nitrite nitrogen and the relative standard deviation for nine determinations was 0.7% for a solution containing 16 µg L⁻¹ of nitrite nitrogen; sampling rate was 50 samples/h. The solid reagents *p*-amino-benzenesulphonic acid and *N*-1-naphthylethylenedimine react with nitrite to generate a product which is measured photometrically [511]. The method has recoveries of 95–105%, and relative standard deviations of 0.5–7.9% for eight measurements of nitrite concentration at <1 ppm; the detection limits at 544 nm were 0.002 and 0.0005 mg L⁻¹ nitrite nitrogen for cuvette pathlengths of 1 and 10 cm respectively. Reaction of nitrite with 5,7-dihydroxy-4-amino-2-oxochroman in acid medium produces a complex which is extracted into a solvent mixture of butanol and ethyl acetate for spectrometric determination at 361 nm [512]. This method gives a relative standard deviation of 0.4% for seven measurements of nitrite nitrogen at the 0.140 ppm level. Other spectrophotometric determinations of nitrite in waters can be found in the following references [501, 508, 513–518]. Nitrite in 10 to 50 mL volumes of water was injected into an anion exchange resin column and then eluted with 4M sodium chloride. Nitrite in the eluate was measured spectrophotometrically at 210 nm. The detection limit was 0.1 µg L⁻¹ nitrite and the anions nitrate, chloride and sulphate did not interfere over a considerable range of concentrations.

2.63.2 Spectrofluorometric methods

The method using *p*-chloroaniline and 2,6-diaminopyridine [519] is highly sensitive (limit of detection 2 µg L⁻¹) and apparently selective, as the authors did not investigate the effect of diverse ions on the method. They consider that interferences can be expected from those ions which either are not compatible with the nitrite ion or can effect the diazotisation and coupling reactions. 2,3-diaminonaphthalene [497] is also a sensitive fluorometric reagent for nitrite (0–850 µg L⁻¹), but all these methods have the disadvantage of being complicated as they rely on solvent extraction. The method developed with 5-aminofluorescein is simple and is sensitive to 0.05 µg L⁻¹.

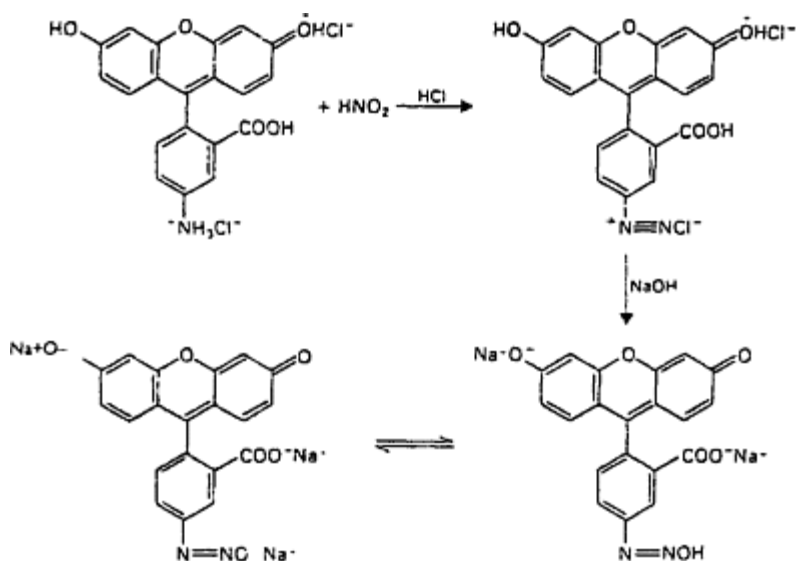
Benzidine has been used for the determination of microgram amounts of nitrite [520]. This anion oxidises the benzidine and produces a shift in its emission maximum from 387 to 348 nm and in its excitation maximum from 295 to 275 nm. Also, the intensity decreases by about two-thirds.

Rubio *et al.* [521] have described a spectrofluorometric method for determining nitrite whereby the nitrite ion oxidises pyridoxal-5-phosphate-2-pyridylhydrazone in acidic media to give a fluorescent product. Although less sensitive than other methods, it was selective, simple and rapid and could be applied in the 0.1–1.0 mg L⁻¹ nitrite range.

2.63.2.1 Methods based on redox reactions

A method based on the increase in the fluorescence intensity of 5-aminofluorescein when it reacts with nitrite has been proposed for the determination of this anion [522]. The reaction has not been studied, but the authors propose the following mechanism (see over).

The shape of the calibration graph depends on the dye concentration and the nitrite working range. In general, as the 5-aminofluorescein concentration decreases, the calibration graph curves. It is conceivable that there is another reaction or other reactions present that affect the fluorescence intensity.



Other methods for the determination of nitrites are based on the formation of triazoles. Thus, nitrite has been determined with 2,3-diaminonaphthalene, which is transformed into 2,3-naphthotriazole [497].



Nitrate does not interfere in this method but it can be determined by reduction to nitrite with hydrazine sulphate [523].

A sensitive fluorometric method has been proposed for measuring nitrite ions based on the diazotisation of *p*-chloroaniline and coupling with 2,6-diaminopyridine [519]. The resulting azo product then is further derivatised with ammoniacal copper(II) sulphate to produce a highly fluorescent triazole compound in acidic media that is extracted into benzene.

Hydroxide ion considerably quenches the fluorescence. This is probably due to a proton transfer between the excited hydrogen-bonded aminopyridine and hydroxide ion, followed by radiationless decay of the imine anion. Although this procedure is lengthier than the Griess method, it provides a five-fold increase in sensitivity of nitrite detection.

2.63.3 Chemiluminescence methods

Dunham *et al.* [487] have described an improved method of flow injection analysis for aqueous nitrite ion which exploits the sensitivity and selectivity of the nitric oxide chemiluminescence detector. Trace analysis of nitrite ion in a small sample (5–160 μL) is accomplished by conversion of nitrite ion to nitric oxide by aqueous iodide in acid. The resulting nitric oxide is transported to the gas phase through a semi-permeable membrane and subsequently detected by monitoring the photoemission of the reaction between nitric oxide and ozone. Chemiluminescence detection is selective for measurement of nitric oxide, and, since the detection occurs in the gas-phase, neither sample coloration nor turbidity interfere. The detection limit for a 100 μL sample is 0.04 $\mu\text{g L}^{-1}$ of nitrite ion. The precision at the 10 $\mu\text{g L}^{-1}$ level is 2% relative standard deviation, and 60–180 samples can be analysed per hour. The results from a standard colorimetric measurement are compared with those from the new chemiluminescence method in order to further validate the latter method. A high degree of selectivity is obtained due to the three discriminating steps in the process:

- (1) the nitrite ion to nitric oxide conversion conditions are virtually specific for nitrite ion,
- (2) only volatile products of the conversion will be swept to the gas phase (avoiding turbidity or colour in spectrophotometric methods), and
- (3) the nitric oxide chemiluminescence detector selectively detects the emission from the nitric oxide plus ozone reaction. The method is free of interferences, offers detection limits of low parts per billion of nitrite ion, and allows the analysis of up to 10 μL -ized samples per hour, with little sample preparation and no chromatographic separation. Much smaller samples can be analysed by this method than in previously reported batch analysis methods, which typically require 5 mL or more of sample and often need chromatographic separations as well.

2.63.4 Flow injection analysis

This technique has been applied [524] to the fluorometric determination of nitrite in river water using 3-aminonaphthalene-1,5-disulphonic acid as fluorescing agent. The reagent solution was prepared by dissolving sodium 3-aminonaphthalene-1,5-disulphonate (0.035g) in 0.01M hydrochloric acid (100ml) and mixing 3ml of this solution with 0.1M EDTA, concentrated hydrochloric acid (50ml) and distilled water (244ml). The reagent stream was then mixed with a carrier stream of distilled water, passed through a mixing coil and mixed with an alkaline solution stream of sodium hydroxide (20%). The aromatic amine was derivatised, in acidic medium, with nitrite to form a diazonium salt which was converted, in alkaline medium, to a fluorescent azoic acid salt. Fluorescence intensity was recorded (470nm) with a spectrofluorometer. Nitrite levels as low as

$0.01\mu\text{g L}^{-1}$ were detected by this method.



Fig. 2.31 Schematic flow diagram for the determination of nitrite R_1 , *p*-aminoacetophenone solution (5g plus 10ml conc. hydrochloric acid diluted to 500ml diluted to 40ml to 1L); R_2 , *m*-phenylenediamine solution (13.8g *m*-phenylene dihydrochloride, diluted in 500ml water, diluted 40ml to 1L); P, double plunger micro pump (1.7ml min^{-1}); DT, damping coil ($0.5\text{mm id}\times 20\text{m}$); S, loop valve sample injector (sample volume $650\mu\text{L}$); WB, water bath 30°C ; MC 1, mixing coil ($1\text{mm id}\times 150\text{cm}$); MC 2, mixing coil ($1\text{mm id}\times 100\text{cm}$); F, line filter; SP, spectrophotometer with flow cell (light path 10mm, $8\mu\text{L}$); RE, recorder, BPT, back pressure coil ($0.5\text{mm id}\times 5\text{m}$); W, water

Source: Reproduced with permission from Elsevier Science [525]

Motomizu *et al.* [510] have also performed a flow injection analysis-spectrophotometric determination of traces of nitrite in water based on the nitrosation reaction with *N,N'*-bis (2-hydroxypropyl) aniline.

Nakashima *et al.* [525] have described a spectrophotometric determination of nitrite at the $\mu\text{g L}^{-1}$ level in non saline waters by flow injection analysis. The limit of detection is $0.2\mu\text{g L}^{-1}$ for sample injections of $650\mu\text{L}$. The sampling rate is about 30 per h and the relative standard deviation is less than 1.3%.

A diagram of the flow system is shown in Fig. 2.31. The absorbance was measured with a Shimadzu double-beam spectrophotometer UV-140-02 with a 1-cm flow cell ($8\mu\text{L}$) and recorded by a Rikadenki R022 recorder. A double-plunger micro pump (Kyowa Seimitsu KHU-W-52) is used. The sample solution ($650\mu\text{L}$) is injected by a 6-way injection valve into the reagent R_1 stream. The water bath, in which the mixing coils were heated to accelerate the reactions. Temperature is controlled by a Taiyo Thermo Minder Jr-10. The flow lines are made from polytetrafluoro-ethylene (PTFE) tubing 1mm and 0.5mm id). The mixing coils (1mm id) MC1 and MC2 are optimally 1.5 and 1.0m long, respectively, and are wound around plastic rods (6mm od). The damping coils (0.5mm id) are 20m long, to cancel the pulse from the reciprocal pump. The back-pressure tubing (0.5mm id) are 5m long, to prevent formation of bubbles.

The reagent solutions R_1 and R_2 are prepared by diluting 40ml of the appropriate stock solutions to 1L; the pH of R_1 is adjusted to 1.3 and the pH of R_2 to 2.4. Both reagent solutions give the same response for three months (maximum period tested) if kept in a refrigerator when not in use.

The flow rates of R_1 and R_2 are 1.7ml min^{-1} each. Sample solutions are filtered through a $0.45\mu\text{m}$ Millipore filter. From the sample loop, $650\mu\text{L}$ of sample solution is injected into the reagent R_1 stream. Peak heights are measured at 456nm against water as reference. The concentration of nitrite is evaluated from the peak heights by using a

calibration graph prepared from freshly prepared nitrite standards.

A calibration run was obtained using $0\text{--}30\mu\text{g L}^{-1}$ nitrite-nitrogen standards. The method is claimed to be one of the most sensitive flow injection procedures available for nitrite. The relative standard deviations of 10 injections each of solutions containing 10, 20 and $30\mu\text{g L}^{-1}$ nitrite-nitrogen were 1.3, 1.1 and 0.39% respectively. Samples with higher concentrations of nitrite can be directly determined by decreasing the sample volume injected and the recorder sensitivity. Linear calibration graphs were then obtained up to 3mg L^{-1} nitrite-nitrogen (the maximum concentration tested). The sampling rate was about 30 samples per h.

The effect of various ions on the determination of nitrite was also investigated. No interference was caused by less than 50mg L^{-1} Ca^{2+} , Mg^{2+} , K^{+} , NH_4^{+} , HCO_3^{-} , SO_4^{2-} , Cl^{-} , SiO_3^{2-} , NO_3^{-} or $\text{H}_2\text{PO}_4^{-}$ in the determination of $30\mu\text{g L}^{-1}$ nitrite-nitrogen.

In Table 2.40 some results obtained upon applying this method to various non saline water samples are shown.

Trojanek and Bruckenstein [526] have described a novel flow through penumato amperometric detector the determination of nanogram and sub-nanogram amounts of nitrite by flow injection analysis.

This gas porous electrode structure that detects volatile electroactive species in a flowing liquid stream is described and evaluated for its utility in flow injection analysis. The electrode is fabricated by depositing a porous gold layer on one side of a porous Teflon membrane. The gold serves as the amperometric electrode which consumes dissolved, volatile species that is transported from the flowing solution through the membrane to the metallised face where it is electrolysed. Nitrite ion is determined by reaction in the carrier stream to produce nitric oxide and iodine, and both are electroxidised at the gold electrode. The detection limit is 30pg of nitrite ion. Dissolved, non-volatile electroactive species do not interfere.

Zagatto *et al.* [527] have also discussed the application of flow injection analysis to the determination of nitrite in non saline waters.

Vinas *et al.* [528] determined nitrite in non saline waters and waste-waters by a method based on reverse flow injection analysis.

Workers at Tecator Ltd have devised flow injection analysis methods, based on the sulphanilamide-N-(1-naphthyl) ethylenediamine reaction for the routine determination of nitrite in various concentration ranges between 0.05–1, 10–100 and 30–100mg L^{-1} [529–532].

2.63.5 Cathodic stripping voltammetry

Adsorptive cathodic stripping voltammetry was used by Van den Berg *et al.* [533] for determining nanomolar levels of nitrite in freshwater and

Table 2.40 Recovery of nitrite added to non saline water samples

Sample	Amount of nitrite-N ($\mu\text{g L}^{-1}$)	Recovery %

	<i>Added</i>	<i>Found</i>	<i>Recovered</i>	
River water	none	5.0		
	5.0	10.3	5.3	106
	10.0	15.2	10.2	102
River water	none	1.4		
	5.0	6.4	5.0	100
	10.0	10.8	9.4	94
Lake water	none	2.2		
	5.0	7.2	5.0	100
	10.0	12.5	10.3	103
Pond water	none	3.0		
	5.0	8.1	5.1	102
	10.0	12.8	9.8	98
Well water	none	2.4		
	5.0	7.6	5.2	104
	10.0	12.7	10.3	103
Rain water	none	2.6		
	5.0	7.8	5.2	104
	10.0	13.2	10.6	106
Irrigation water	none	4.9		
	5.0	10.0	5.1	102
	10.0	14.3	9.4	94
Irrigation water	none	5.3		
	5.0	10.3	5.0	100
	10.0	14.9	9.6	96

^aEvaluation of recoveries of nitrite was based on the addition of nitrite to 16ml of sample solution in a 20ml calibrated flask

Source: Reproduced with permission from Elsevier Science [525]

seawater. The nitrite is first derivatised by diazotisation with sulphanilamide and then coupled with 1-naphthylamine to form an azo dye. This azo dye adsorbs on the mercury drop electrode and its reduction is fully reversible. The concentration of the dye is linearly related to the height of the reduction peak for concentrations of nitrite in the range 0.3–200nM. The relative standard deviation was 2% for a concentration of 4nM nitrite, and the detection limit as 0.3nM for an adsorption time of 60s.

2.63.6 Polarography

Nitrites have been determined by oxidation at a glassy carbon electrode [526,534] electrocatalytically using a molybdenum catalyst [535] and polarographically using differential pulse polarography using the reaction between nitrite ion and diphenylamine to produce diphenyl-nitrosamine [536].

Differential pulse absorptive volumetric analysis has been used to determine $\mu\text{g L}^{-1}$ levels of nitrate in water [537].

Barsotti *et al.* [538] determined nitrite in amounts down to $0.4\mu\text{g L}^{-1}\text{N}$ and nitrite by differential pulse polarography. Nitrate is reduced on a cadmium column to diphenylnitrosamine and then determined polarographically. Cadmium interference is removed by adjustment of pH and complexing with EDTA. Nitrite is determined directly as the diphenylnitrosamine.

In order to separate the cadmium(II) peak from that of diphenyl nitrosamine, advantage was taken of the fact that organic polarograms are usually pH dependent, while those of reversible inorganic ions are not. Changing the pH from 1.0 to 4.0 shifts the diphenyl nitrosamine peak, without loss of peak height, hence sensitivity, but causes no change in the cadmium(II) peak. A pH of 1.0 is used for the formation of diphenyl nitrosamine since the rate is fast at that pH with no decomposition. At a pH of 4.0 a peak separation of 140mV occurs which is sufficient to determine nitrite ion in the presence of cadmium (II) to a level of approximately $200\mu\text{g L}^{-1}$. At this pH the EDTA complex of cadmium(II) has a stability constant of approximately 10^{16} . Thus, the addition of EDTA at a pH of 4.0 results in the complete disappearance of the cadmium(II) peak and total removal of any interference. Therefore, by an adjustment of pH and the addition of EDTA to the nitrite ion procedure, nitrate could be determined.

Liu *et al.* [539] have described a polarographic method for the determination of nitrite in non saline waters.

2.63.7 Isotachoelectrophoresis

The application of this technique is discussed under multianion analysis in section 14.6,.1.1.

2.63.8 Ultraviolet spectroscopy

Espinola [540] has described a direct ultraviolet spectroscopic method for the determination of nitrite in non saline waters. By using an addition technique and a reference nitrate/nitrite solution, he compensated for the interference caused by the overlapping of the nitrate and nitrite bands, which is normally a limiting factor in the analysis of mixtures of nitrite with large excesses of nitrate. The detection limit was $5 \times 10^{-5}\text{mol L}^{-1}$ nitrite, which corresponded to a minimal detectable amount of 2.3mg L^{-1} nitrite in the presence of up to a 20,000 times greater amount of nitrate.

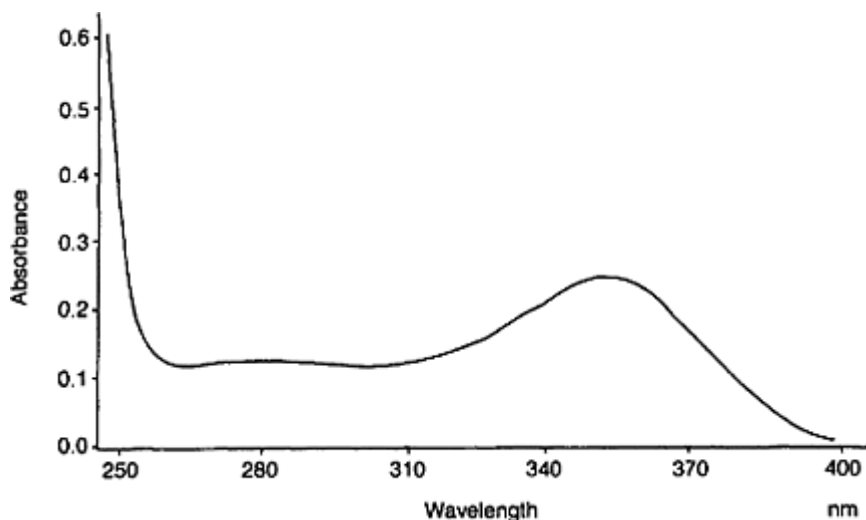


Fig. 2.32 Near ultraviolet spectrum of nitrite in aqueous solution. $10^{-3} \text{ mol L}^{-1}$ NaNO_2 ; H_2O as reference. Mod. 15 Cary spectrophotometer; optical path 10cm

Source: Reproduced with permission from Marcel Dekker Inc. [540]

The near-ultraviolet spectrum of sodium nitrite in aqueous solution is shown in Fig. 2.32. In aqueous solution the same general characteristic spectrum as in the nitrate medium is maintained, but a small blue shift is observed. At low concentrations, the very intense higher energy bands do not interfere with the lower energy bands of either nitrate or nitrite.

From spectra obtained independently it might be inferred that the broadening of the nitrate band would not strongly interfere with that of the nitrite at λ_{max} if the mutual concentrations did not exceed $10^{-1} \text{ mol L}^{-1}$ nitrate and $10^{-2} \text{ mol L}^{-1}$ nitrite. However, in reality the analysis of a mixture containing these proportions is unfeasible because the broadened nitrate band deforms the nitrite band causing a large error.

In the spectrophotometric analysis of nitrite in the presence of nitrate, it is fortunate that the nitrite ion in molten nitrate, as well as in aqueous solutions, has an absorption minimum in the region of the nitrate band, and an absorption maximum at 355nm.

When the concentration of nitrite is greater than $10^{-2} \text{ mol L}^{-1}$ if the concentration of nitrate does not exceed $10^{-1} \text{ mol L}^{-1}$ the absorbances of nitrite in the presence of nitrate can be measured at the maximum wavelength vs a suitable reference solution. The reference solution must contain approximately the same concentration of nitrate as in the unknown sample. For concentrations of nitrite $10^{-2} \text{ mol L}^{-1}$ or less, and 1 mol L^{-1} nitrate, the resulting error caused in the molar absorptivity of nitrite is no longer negligible. This error can be avoided by using the

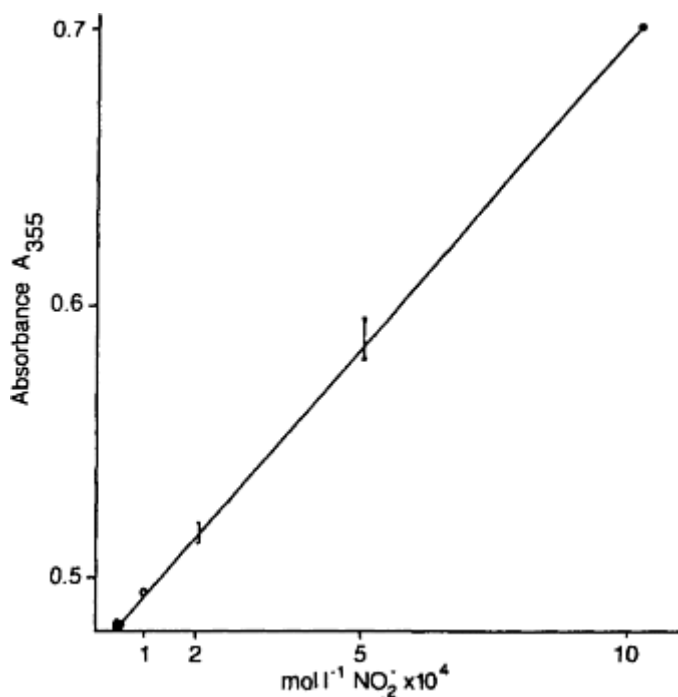


Fig. 2.33 Working curve for the nitrite analysis in the presence of large nitrate excess. Cary spectrophotometer mod. 15, with 50Å/div., optical path 10cm

Source: Reproduced with permission from Marcel Dekker Inc. [540]

addition technique outlined below. In this technique, all solutions are made with the same concentration of nitrate; then, a known and accurately measured amount of nitrite is added to all solutions except to the reference blank.

All solutions, including the blank, are prepared to contain the same concentration of nitrate. To all solutions, except the blank, a known and exactly measured amount of nitrite is introduced to bring its concentration to the $2 \times 10^{-3} \text{ mol L}^{-1}$ range; this concentration was calculated from the known molar absorptivity of nitrite ($E_{355}=24.0$) in order to raise the absorbance of the sample into the region of minimum photometric error. Therefore, the solutions to be analysed for nitrite contain the same added background concentration of nitrate and nitrite.

The excellent results obtained under these conditions for a range of nitrite standards are shown in Fig. 2.33.

2.63.9 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.1, 12.2.4 and 12.2.5.

2.63.10 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.1.3, 13.1.1.4 and 13.1.1.5.

2.63.11 Ion exclusion chromatography

Kim and Kim [541] have described an extremely sensitive determination of nitrite in drinking water (tap water and underground water) and environmental samples (rain, lake water, and soil) by ion exclusion chromatography with electrochemical detection. Potential interferences in the determination of nitrite by the standard spectrophotometric method or by the ion exchange chromatographic method with either conductivity or ultraviolet detection were eliminated. The detection limit was $0.1 \mu\text{g L}^{-1}$ without preconcentration. No nitrite was observed from tap water or underground drinking water. The recoveries of nitrite added to tap water at 0.02, 0.1 and 1mg L^{-1} levels were between 96 and 104.5%. The average coefficient of variation was 4.7%. The recovery results were in good agreement with those obtained by the standard spectrophotometric method. Nitrite concentrations between 0.068 and 0.19mg L^{-1} were observed in rain within a week period. A greater variation, between 0.015 and 0.26mg L^{-1} was observed in lake water.

2.63.12 Micelle chromatography

The application of this technique is discussed under multianion analysis in section 13.5.1.2.

2.63.13 Gas chromatography

Funazo *et al.* [542] have given details of a procedure for the determination of nitrite in river water by gas chromatography after reaction with *m*-nitroaniline and hypophosphorous acid to convert nitrite to nitrobenzene.

It is well known that nitrite diazotises aromatic amines in acidic media and that the resulting diazonium ions are reduced by hypophosphorous acid to form benzene derivatives. The reactions are formulated as follows.

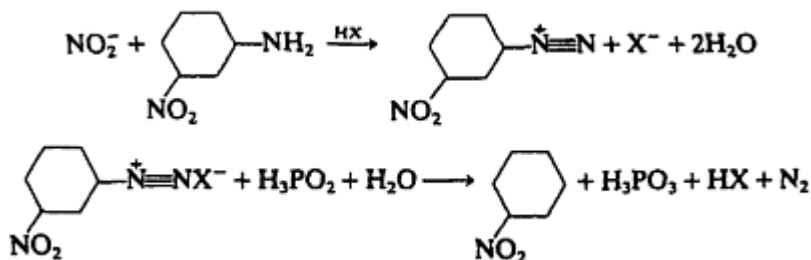


Table 2.41 Results of interference study the concentration of nitrite was $0.10\mu\text{g mL}^{-1}$

Ion	Concentration/ mg L^{-1}	Relative peak area ^a	95% Confidence interval
Standard	–	100.0 $\pm$ 2.0	97.5–102.5
Cl^-	20000	101.2 $\pm$ 2.3	98.3–104.1
Cl^-	100	99.4 $\pm$ 2.1	96.8–102.2
Br^-	100	100.4 $\pm$ 2.2	97.7–103.1
F^-	100	98.8 $\pm$ 1.9	96.4–101.2
SO_4^{2-}	100	97.8 $\pm$ 1.3	96.2–99.4
HCO_3^-	100	99.1 $\pm$ 1.5	97.2–101.0
H_2PO_4^-	100	98.6 $\pm$ 2.5	95.5–101.7
NO_3^-	100	111.9 $\pm$ 1.3	110.3–113.5
NO_3^-	10	99.6 $\pm$ 1.8	97.4–101.8
NH_4^+	100	100.4 $\pm$ 1.1	99.0–101.8

^aMean $\pm$ standard deviation for five replicate analyses (between batch). The peak area of nitrobenzene converted from the standard solution was arbitrarily assigned a value of 100

Source: Reproduced with permission from the Royal Society of Chemistry [542]

An electron capture detector was used to monitor the gas chromatographic effluent. The detection limit and determination range of nitrite are $0.5\mu\text{g L}^{-1}$ and $1.00\text{--}1000\mu\text{g L}^{-1}$ respectively, which are much lower than those of the widely used colorimetric method for the determination of nitrite (detection limit $16\mu\text{g L}^{-1}$).

The gas chromatographic method was tested in the presence of several ions normally found in environmental samples. In Table 2.41 the peak area of nitrobenzene produced from the standard solution containing $100\mu\text{g L}^{-1}$ of nitrite was arbitrarily assigned a value of 100. The concentrations of the ions (100mg L^{-1}) added to the standard nitrite solution were much higher than those in environmental samples. The results indicated that these anions, except for nitrate, do not interfere in this method. Moreover, chloride added as sodium chloride at a concentration of 2.0% to the standard solution has no effect, which suggests the possibility of applying this method to the analysis of seawater. However, nitrate interferes positively at a concentration of 100mg L^{-1} although this interference is not found at 10mg L^{-1} .

Derivatisation-electron capture gas chromatography has been used to determine $\mu\text{g L}^{-1}$ quantities of nitrite in water without interference from halides, nitrate, phosphate, sulphate, bicarbonate, ammonium and alkali metals and alkaline earth metals [543].

2.63.14 Miscellaneous

Nitrites have been determined by oxidation at a glassy carbon electrode [526,534],

electrocatalytically using a molybdenum catalyst [535] and polarographically using differential pulse polarography using the reaction between nitrite ion and diphenylamine to produce diphenyl-nitrosamine [536]. Other techniques for determining nitrite include paper chromatography of diazo dyes to reduce interference by metals [480], stopped flow analysis [544] and direct injection enthalpimetry [482]. Derivatisation-electron capture gas chromatography has been used to determine $\mu\text{g L}^{-1}$ quantities of nitrite in water without interference from halides, nitrate, phosphate, sulphate, bicarbonate, ammonium and alkali metals and alkaline earth metals [543].

Mureta *et al.* [545] have studied the effect of freezing on the stability of nitrite in aqueous solutions. Losses of nitrite of 38–57% occurred during 15 days of frozen storage.

A Weisz ring-oven method for determining nitrite in non saline waters in the 0.1–2mg L^{-1} range gave a maximum relative error of $\pm 4\%$ [546]. This method was based on the reaction of nitrite with *p*-aminobenzoic acid to form a diazonium ion, which was then coupled with 8-hydroxyquinoline in an alkaline medium to give a reddish orange azo dye. The method is claimed to be simple, economical and reasonably accurate.

Sanchez-Pedrinio *et al.* [547] utilised the inhibitory effect of nitrite ions on the photochemical reaction between iodine and EDTA in a method for the determination of nitrite in non saline waters.

Strehlitz *et al.* [548] have described a nitrite sensor based on highly sensitive nitrite reductase mediation-coupled amperometric detection. Down to 0.1 μM nitrite can be detected.

2.64 Nitrate and nitrite

2.64.1 Titration methods

A standard method published by the Department of the Environment, UK [549] describes a technique for the determination of total oxidised nitrogen in non saline waters. In this method nitrite and nitrate are reduced to ammonia under alkaline conditions using Devadas alloy. Ammonia is then distilled out and determined by titration with 0.01N hydrochloric acid in amounts down to 3mg L^{-1}N .

2.64.2 Spectrophotometric methods

Two groups of workers [550,551] have discussed methods for the determination of nitrite and nitrate in river waters.

Okada *et al.* [550] describe a technique for determining nitrite in river waters where the nitrite in the water diazotises *p*-aminoacetophenone, which is then coupled with *m*-phenylenediamine at pH 1.5–3. The 2,4-diamino-4'-acetylazobenzene formed is then measured using a spectro-photometer at 460nm. Determination of nitrate is carried out using the same method, after the nitrate has been reduced to nitrite in a cadmium-copper column. By this method nitrite has been determined at levels of 1 $\mu\text{g L}^{-1}$. The ions normally present in river waters do not interfere in this procedure. No interference is caused by less than 10^{-2}M calcium, magnesium, sodium, potassium, bicarbonate,

sulphate, chloride or ammonium.

Workers at the Water Research Centre UK [551,552] have carried out detailed investigations of the accuracy of determination of total oxidised nitrogen and nitrite in river waters by the Griess-Ilosvay automated spectrophotometric procedure. Broadly, each of the 11 participating laboratories achieved total errors of not greater than $\pm 20\%$ of the determined concentration or 0.1 mg L^{-1} of nitrogen (whichever was the larger for different sample concentrations).

The values of S_t for the two standard solutions, the river water and the spiked river water were compared with the appropriate target value using the F-test, and were accepted as satisfactory provided S_t was not significantly greater ($p=0.05$) than the appropriate target. For both total oxidised nitrogen and nitrite all laboratories achieved a precision that was not significantly (0.05 probability level) greater than the target value.

Nagashima *et al.* [553] determined nitrate and nitrite by using second derivative spectrophotometry after conversion to nitrogen monoxide. Detection limits are $5 \times 10^{-6} \text{ mol L}^{-1}$ for nitrate and $1 \times 10^{-6} \text{ mol L}^{-1}$ for nitrite.

A dual wavelength spectrophotometric determination of nitrate and nitrite in non saline water has a relative standard deviation of $<2\%$ and recoveries of $>95\%$ [554]. The method is based on the reaction of nitrate and nitrite with 2,6-xynolol in a sulphuric acid solution.

An automated procedure utilising a Technican Autoanalyser has been described for the determination of nitrate and nitrite in non saline waters [555].

In another study, total nitrogen (organic and inorganic) in non saline water was oxidised by potassium persulphate at $120\text{--}124^\circ\text{C}$ and the resulting nitrate was measured spectrophotometrically at 220 and 275nm [556]. The detection limit was 0.05 mg of nitrogen L^{-1} , relative standard deviations were $<7\%$, and recoveries were in the range of 94–105%.

2.64.3 Chemiluminescence method

Cerny *et al.* [557] and Braman and Hendrix [558] have described chemi-luminescence methods for the determination of nitrite plus nitrate in non saline waters.

Braman and Hendrix [558] used vanadium(III) reduction with chemi-luminescence detection to determine nanogram amounts of nitrite plus nitrate. In this method nitrite in water samples is reduced at room temperature to nitric oxide in acidic medium containing vanadium(III). Nitrate is also rapidly reduced after heating to $80\text{--}90^\circ\text{C}$. Nitric oxide is removed from the reaction solution by scrubbing with helium carrier gas and is detected by means of a chemiluminescence NO_x analyser. The method has the advantage of not requiring highly acidic solutions for nitrate reduction and has been applied to the analysis of a variety of environmental waters.

2.64.4 Continuous flow analysis

A standard Department of the Environment UK method [559] for the determination of total oxidised nitrogen employs continuous flow colorimetry employing sulphanilamide chromogenic reagent with the addition of a copper/hydrazine reducing reagent for the

reduction of nitrate to nitrite. Detection limits are $0.05\text{--}0.26\text{mg L}^{-1}$ (nitrate plus nitrite) and $0.01\text{--}0.05\text{mg L}^{-1}$ (nitrite).

2.64.5 Segmented flow analysis

Marti and Hale [560] compared automated segmented flow and discrete analysers for the determination of nitrite, nitrate, ammonia and phosphate. The discrete analyser provided a 50% increase in the rate of analysis compared with segmented flow analysis. The accuracy and precision were comparable. While both methods are in agreement, the rate of analysis (60 samples per h) was faster by discrete analysis than segmented flow analysis (40 samples per h).

This technique has been applied to the determination of nitrite and nitrate in concentration ranges $0\text{--}0.5$, $0\text{--}5$, $0\text{--}20$, $0\text{--}40$ and $0\text{--}100\text{mg L}^{-1}$ (as N).

2.64.6 Flow injection analysis

This technique has been used to determine nitrite and nitrate in non saline waters [561]. Van Staden [561] converts nitrate to nitrite using a pre-valve in-valve reduction technique before the sampling valve. Lerique and Lighetto [562] describe an analyser which depends on three principles: injection of sample into a continuous, non-segmented flux of reagent, a reproducible residence time for the samples, and controlled dispersion of the sample. These objectives are achieved by independent peristaltic pumps for each of the four analysis channels, a very precise injection system and a specially designed replaceable manifold. Nitrite determination is based on the sulphanilamide/naphthyl ethylenediamine reaction with a colorimetric measurement at 540nm . Nitrates are reduced to nitrites using a cadmium catalyst and the nitrites determined as above. The apparatus is connected to a microprocessor, can analyse 300 samples per h, and results for each sample are printed out within about 20s.

Workers at Tecator Ltd, UK in a series of application notes discuss the determination of total nitrite plus nitrate by flow injection analysis at concentrations between 0.05 and 500mg L^{-1} [563–568].

2.64.7 Polarography

Polarography has been applied to the determination of nitrites and nitrates [569,570]. In the polarographic technique, total nitrate and nitrite are determined. The nitrite is decomposed by the addition of methyl alcohol, and nitrate only is determined on a second polarogram. Boese *et al.* [570] described a method based on the enhancement of the differential pulse polarographic peak current of ytterbium by nitrate and nitrite.

Holak and Specchio [571] determined nitrite and nitrate in non saline waters by differential pulse polarography with simultaneous nitrogen purging.

2.64.8 Amperometry

Nygaard [572] has described a pneumatoamperometric technique for the determination of

nitrite and nitrate. These ions are reduced to nitric oxide with hydroquinoline and then nitric oxide purged from the sample and oxidised at a membrane covered anodically polarised platinum electrode.

2.64.9 Column coupling capillary isotachophoresis

This technique offers many similar advantages to ion chromatography in the determination of anions, namely multiple ion analysis, little or no sample preparation, speed, sensitivity and automation. Very similar advantages are offered by capillary isotachophoresis. Zelinski *et al.* [190] applied the technique to the determination of nitrite, nitrate, fluoride, chloride, sulphate and phosphate in river water.

The application of this technique is also discussed under multianion analysis in section 14.6.1.1.

2.64.10 Ion selective electrodes

Zhou [573] has described the use of an ammonia sensor probe followed by reduction for the determination of nitrate plus nitrite in non saline waters.

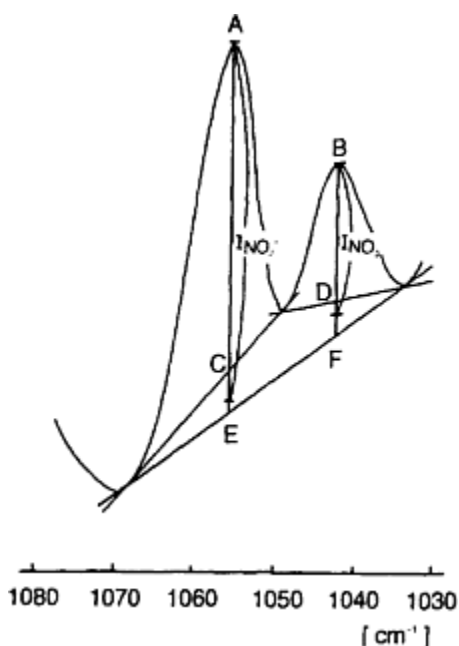


Fig. 2.34 The spectrum of the mixed solution of the coloured product and nitrate. The base lines for the analysis are determined as follows:

$$I_{\text{NO}_3^-} = \frac{BD + BF \times DF}{AE + BF}, I_{\text{NO}_2^-} = \frac{AC + AE \times CE}{AE + BF}$$

The concentrations of the $\text{NO}_2^- = 0.2 \text{ mg L}^{-1}$ and $\text{NO}_3^- = 100 \text{ mg L}^{-1}$

Source: Reproduced with permission from Elsevier Science [577]

2.64.11 Ultraviolet spectroscopy

Suzuki and Kuroda [574] and Koida *et al.* [575] used ultraviolet spectroscopy for the direct simultaneous determination of nitrite and nitrate in non saline waters.

The sum of nitrite and nitrate concentrations in non saline waters have been determined by measuring the absorbance of a solution at 219nm, the isosbestic point for these two species [576]. Beer's law is obeyed over the concentration range of 0–2.0mg L⁻¹ (nitrate plus nitrite) and the coefficient of variation of the method is 4.2–7.5%.

2.64.12 Resonance Raman spectroscopy

Furaya *et al.* [577] investigated the simultaneous determination of nitrite and nitrate using resonance Raman spectroscopy. Fig. 2.34 shows an example of the spectra of the sample solutions which contain much larger quantities of nitrate relative to those of nitrite. This spectrum demonstrates that the key band of nitrate can be measured almost independently of the adjacent band of the coloured product corresponding to nitrite. This result shows clearly the possibility of the simultaneous determination of nitrite and nitrate and also proves the excellent selectivity of Raman spectrometry.

Plots of $I_{\text{NO}_3^-}/I_{\text{NO}_2^-}$ against $C_{\text{NO}_3^-}/C_{\text{NO}_2^-}$ give the most satisfactory result ($I_{\text{NO}_3^-}$, $I_{\text{NO}_2^-}$ are peak heights of the nitrate band at 1045cm⁻¹ and that of the band at 1056cm⁻¹ corresponding to nitrite, respectively; $C_{\text{NO}_3^-}$, $C_{\text{NO}_2^-}$ are concentrations of nitrate and nitrite) $I_{\text{NO}_3^-}$ and $I_{\text{NO}_2^-}$ are estimated as shown in Fig. 2.34. The plots of peak heights or areas of the 1045cm⁻¹ band against $C_{\text{NO}_3^-}$ does not give such satisfactory results regardless of the selections of base lines. Thus the process of the simultaneous determination of nitrite and nitrate is as follows.

- (1) Sample waters are treated to form the coloured product from nitrite by the colour reaction
- (2) From the resonance Raman band of the coloured product at 1250cm⁻¹, the concentrations of nitrate are determined.
- (3) From the spectra in the 1030–1080cm⁻¹ region $I_{\text{NO}_3^-}/I_{\text{NO}_2^-}$ is measured, and, using the analytical curve shown in Fig. 2.34 $C_{\text{NO}_2^-}$ is estimated by operation (2), and the concentrations of nitrate ($C_{\text{NO}_3^-}$) are determined.

2.64.13 Helium microwave induced emission spectrometry

Ultratrace amounts (µg L⁻¹) of nitrite, nitrate and ammonium have been determined [451] in pond waters by atmospheric pressure helium microwave induced emission spectrometry utilising a gas generation technique. The instrumental set up consists primarily of the plasma system, the optical measurement system and the gas generation system. Ammonium ion is oxidised to nitrogen gas by sodium hypochlorite in an alkaline medium and nitrite ion by sulphonic acid in an acidic medium. Nitrate ion is reduced to nitrite in a cadmium/copper column and then determined as above. The nitrogen produced by the chemical reduction is introduced into the helium flow via a three-way valve system connecting the reaction vessel. Plasma is generated by a microwave

generator and the emission signals are measured at 391.4nm.

The N_2^+ 'main' system bandhead at 391.4nm provided the lowest detection limit, while the N_2 'second positive' system bandhead at 337.1nm and the nitrogen atomic line at 746.8nm were observed to have wide dynamic ranges (more than three orders of magnitude). The emission signal of the NH band maximum ('A' system) at 336.0nm was the largest of the four analytical wavelengths investigated but the detection limits of this band, especially for ammonium nitrogen, were not so good because of the significantly large blank signals at 336.0nm. The relative standard deviation of eight replicate measurements was about 7% at the 10-fold concentration of the detection limit and was about 4% at the 100-fold concentration for all the analytical wavelengths.

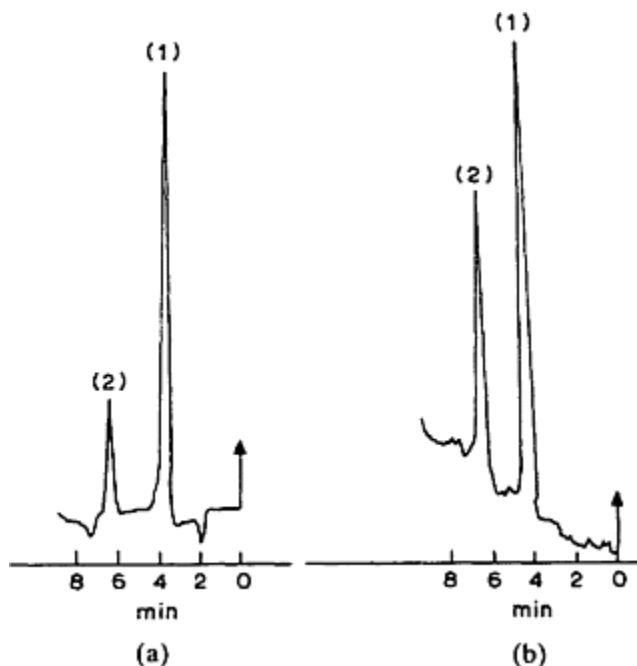


Fig. 2.35 (a) Extract from 100ml of water spiked with 1 μ g of nitrate in 0.5ml of eluent, aliquot volume 20 μ L (b) standard, 200ng of ol-nitrophenol (2). (1) is an oxygen peak

Source: Reproduced with permission from Springer Verlag [578]

2.64.14 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.1, 12.2.4 and 12.2.5.

2.64.15 High performance liquid chromatography

Alawi [578] has described a simple and specific high performance liquid

chromatographic method for the determination of nitrite and nitrate in non saline water based on the nitration of an excess of phenol by nitrate or oxidised nitrite ions; the ortho-nitrophenol produced is extracted, separated on a reversed phase column and quantified using an amperometric detector in the reduction mode. Nitrite, if present, is first oxidised to nitrate by addition of 1% hydrogen peroxide. The method has been successfully applied to waters containing nitrate plus nitrite at the $5\mu\text{g L}^{-1}$ level. By using a larger sample volume (500ml) and injecting a larger aliquot (100 μL) onto the column the sensitivity could be improved, giving a lower limit of about $1\mu\text{g L}^{-1}$.

Fig. 2.35 shows representative chromatograms and illustrates the analysis of nitrate in water. Recoveries were $82.6\pm 2.37\%$ for nitrate and $76.9\pm 1.94\%$ for nitrite in the $0.01\text{--}1\mu\text{g mL}^{-1}$ concentration range.

This method is free from interferences, which when coupled with the specificity and the high sensitivity of the electrochemical detection mode, renders it suitable for the determination of trace levels of nitrate and nitrite in surface, ground and main water.

This technique has been applied to the determination of nitrate and nitrite in water [579]. Chemically bonded amine materials have been used to remove interference by humic substances prior to the ion chromatographic determination of nitrate and sulphate in non saline waters.

High performance liquid chromatography on a small bore column packed with microparticulate silica based ion exchange material has been used [580] to determine down to 0.01mg L^{-1} nitrate in water without interference from other ions associated with potable, pond, river and stream water.

Detection of the separated peaks was achieved using a Pye LC-UV variable wavelength ultraviolet detector fitted with a $8\mu\text{L}$ flow cell and set at 265nm. The chromatographic system consisted of a Partisil $10\mu\text{m}$ SAX column, and a mobile phase consisting of 10^{-3}mol L^{-1} potassium hydrogen phthalate (pH 3.95) in deionised water.

The method for the detection of non-ultraviolet absorbing ionic species relies on the technique of indirect photometric detection. In conventional high performance liquid chromatography where an ultraviolet detector is employed, the mobile phase is selected for many reasons and among them is the property of low absorbance at the monitoring wavelength. Compounds which elute and which have a significant absorbance at the set detector wavelength are thus observed as peaks of high absorbance against the low background absorbance of the solvent. This situation may be reversed however. Thus the mobile phase may contain an ultraviolet absorbing substance which will (after equilibration of the column) give a high, but constant, background absorbance. The presence of a non-absorbing species (such as an inorganic anion) in the mobile phase would thus be expected to cause a drop in absorbance. The elution of a non-absorbing species under these chromatographic conditions is therefore recognised as a peak corresponding to increased transmission, ie decreased absorption. Indirect detection of non-absorbing species may thus be achieved using a conventional variable wavelength ultraviolet high performance liquid chromatographic detector.

Lee and Field [581] have discussed a technique of post column fluorescence detection of nitrite, nitrate, thiosulphate and iodide anions in high performance liquid chromatography. These anions react with cerium(IV) to produce fluorescent species in a post-column packed bed reactor.

Alawi [582] has discussed an indirect method for the determination of nitrite and nitrate in surface, ground and rain water by reaction with excess phenol (nitrite ions first being oxidised to nitrate) and extraction of the o-nitrophenol produced, followed by separation on a reversed phase high performance liquid chromatography column with amperometric detection in the reduction mode. Recoveries were 82% for nitrate and 77% for nitrite in the concentration range 10–1000 $\mu\text{g L}^{-1}$. The method is claimed to be free of interferences from other ions.

Using a radial compression C_{18} column and a mobile phase of aqueous tetramethylammonium phosphate Kok *et al.* [583] analysed mixtures of nitrate and nitrite at the 0.1mg L^{-1} level (3 σ) and compared the results obtained with those found by ultraviolet spectroscopic screening methods.

Marengo *et al.* [584] have discussed experimental design and partial least squares for the optimisation of reversed phase ion interaction liquid chromatographic separation of nitrite, nitrate and phenylenediamine isomers. Levels down to 0.5mg L^{-1} of these substances were determined.

The application of this technique is also discussed under multianion analysis in sections 13.1.1.3, 13.1.1.4 and 13.1.1.5.

2.64.16 Ion exchange chromatography

Davenport and Johnson [585] used ion exchange chromatography on Amberlite IRA-900 strongly basic resin to determine nitrate and nitrite in water. 0.01M perchloric acid was used as eluent and an electrochemical cadmium electrode detector was used.

Sherwood and Johnson [477] have described an ion exchange chromatographic determination of nitrate and amperometric detection at a copperised cadmium electrode. The chromatograms obtained in this procedure resolve nitrate from dissolved oxygen.

2.64.17 Micelle exclusion chromatography

Okada [375] has used micelle exclusion chromatography to determine nitrite and nitrate in the presence of other anions (bromide, iodide and iodate) in water. The method is based on partition of ions to a cationic micelle phase and shows different selectivity from ion exchange chromatography.

The application of this technique is also discussed under multianion analysis in section 13.5.1.2.

2.64.18 Miscellaneous

Marti and Hale [560] compared automated segmented flow and discrete analysers for the determination of nitrite, nitrate, ammonia and phosphate. The discrete analyser provided a 50% increase in the rate of analysis compared with segmented-flow analysis. The accuracy and precision were comparable. While both methods are in agreement, the rate of analysis (60 samples per h) was faster by discrete analysis than segmented-flow analysis (40 samples per h).

Nagashima *et al.* [586] determined nitrate and nitrite by using second derivative

spectrophotometry after conversion to nitrogen monoxide. Detection limits are $5 \times 10^{-6} \text{M}$ for nitrate and $1 \times 10^{-6} \text{M}$ for nitrite.

Nygaard [572] has described a pneumatoamperometric technique for the determination of nitrite and nitrate. These ions are reduced to nitric oxide with hydroquinone then nitric oxide purged from the sample and oxidised at a membrane covered anodically polarised platinum electrode.

Martiadou-Nikolopoulou and Kouimtzis [587] studied the effects of *N*-cetylpyridinium chloride, dodecylhydrogen sulphate sodium salt, dodecylbenzene sulphonate and Triton-X-100 on the spectrophotometric determination of nitrite and nitrate in aqueous samples. Two methods were used for nitrate determination, one based on the nitration of salicylic acid (higher nitrate levels) and one based on nitrate reduction to nitrite (low nitrate levels) followed by nitrite determination. Cationic and non-ionic surfactants did not interfere with nitrite determination whereas anionic surfactants caused significant interferences which could be eliminated by treating the water with *n*-cetylpyridiniumbromide.

A study has been carried out of the accuracy of determination of total oxidised nitrogen (nitrite plus nitrate and nitrite in river waters [413].

Various workers have reviewed methods for the determination of total nitrogen in non saline waters [588–590].

2.65 Nitriloacetate

2.65.1 Polarography

Nitrolacetic acid has been preconcentrated from water at pH 3 by passage through an anion exchange column and subsequent elution with sodium chloride [591] prior to estimation by polarography.

2.65.2 Ultraviolet spectroscopy

Longbottom [592] preconcentrated nitrolacetic acid on a strong anion exchange resin, then desorbed it with sodium tetraborate at pH 9 prior to estimation by ultraviolet spectroscopy.

2.66 Octanedioate

2.66.1 Gas chromatography

The application of this technique is discussed under multianion analysis in section 14.1.1.1.

2.67 Octane sulphate

2.67.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.68 Octane sulphonate

2.68.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.69 Octanoate

2.69.1 Gas chromatography

The application of this technique is discussed under multianion analysis in section 14.1.1.1.

2.70 Oxalacetate

2.70.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.71 Oxalate

2.71.1 Spectrofluorometric methods

There are few fluorometric methods for the determination of oxalate. These methods have similar sensitivities but the most selective is that using resorcinol [361].

Oxalate has been determined by reduction of non-fluorescent Ce(IV) to fluorescent Ce (III) [361]. Other reductor ions give the same reaction.

Bishop [236] proposed spectrofluorometric tests for the detection of oxalate.

2.71.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.72 Palmitate

2.72.1 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.6.

2.73 Perchlorate

2.73.1 Ion selective electrode

Jain *et al.* [593] have described a liquid membrane perchlorate selective electrode.

2.73.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5.

2.74 Phthalate

2.74.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.75 Phosphate

Phosphorus in non saline waters can exist in a multiplicity of forms, including ortho-, pyro-, poly-, meta-, organic, colloidal, and suspended phosphorus. Each of these forms is capable of being measured either partly or wholly (depending upon the reaction conditions) as orthophosphosphate through hydrolysis and reaction with molybdate. Strickland and Parsons [594] therefore attempted to define a labile fraction of phosphorus (soluble reactive phosphorus) as the amount of phosphorus able to pass a 0.45µm Millipore filter and reacting within 3min with acid molybdate. This fraction is not equivalent to orthophosphate, nor dissolved inorganic phosphorus, but rather some ill-defined intermediate.

It becomes evident, therefore, that methods will measure differing proportions of the total phosphorus depending upon the reaction conditions employed and whether all or some of the above-mentioned phosphorus-containing fractions are present in any one sample.

The ability of the phosphate manifold to recover added phosphorus was tested to a maximum level of 400µg L⁻¹. The resultant linear response indicates that the method is

able to recover orthophosphate in the presence of other elements normally present which may cause

Table 2.42 A precision of $\text{PO}_4\text{-P}$ determinations

Sample	Day			Sample mean
	1 $\mu\text{g L}^{-1}$	2 (mean of 10)	3	
1	14.2	14.6	14.3	14.4
2	263.5	263.5	264.3	263.7
3	9.4	9.6	9.4	9.5
4	21.5	21.5	21.1	21.4
5	100.4	100.8	100.7	100.6
Day mean	81.8	82.0	82.0	81.9
LSD between			P=0.05	P=0.01
sample means			0.4	0.6
day means			0.3	0.5
Any pair of sample $\times$ day means			0.8	1.0
Relative SD				1.0%

Source: Reproduced with permission from Fisheries Research Board, Canada [594]

interference. Adding Hg(II) showed no effect to a level of 50mg L^{-1} . Similarly no interference was recorded from silica added as sodium silicate up to a level of 100mg L^{-1} silicate.

The excellent precision of this manifold at low levels of phosphate phosphorus is illustrated in the statistical analysis given in Table 2.42. The overall relative standard deviation was 1% and there were no significant differences ($P=0.01$) between days or in the sample $\times$ day interactions. There is no doubt that this method is very precise even at low levels of phosphate phosphorus.

Bickford and Willett [595] showed the filtration of water samples through Gelman membranes which contained wetting agents prior to analysis for phosphate caused interferences (low phosphate results) in molybdenum blue spectrophotometric methods for phosphate. This effect was due to the release of some substance from the membrane. It is recommended that low extractable membranes are used when the filtrate is required for the determination of phosphate or inorganic phosphorus.

Boyd and Tucker [596] found that Millipore membrane filters ($0.45\mu\text{m}$), Gelman glass-fibre filters and Whatman No. 42 and No. 1 filter papers were suitable for preparing pond water samples for orthophosphate determinations. The stannous chloride reduction method was considered as accurate and precise as the ascorbic acid reduction method for

orthophosphate, but more sensitive; nevertheless, the longer stability of the coloured sol by the latter method made it more suitable for analysing pond waters for filtrate orthophosphates. Concentration of filtrable orthophosphate changed with time of storage at 25°C in polyethylene bottles for up to 48h; samples should ideally be analysed within 1h of collection, although storage for 2–8h does not greatly affect the concentration.

Recently, eutrophication in lakes and reservoirs has become an important problem. Phosphorus is a critical nutrient aiding the eutrophication process. The principal sources of phosphorus in environmental waters are agricultural effluents, municipal waste waters, industrial waste waters, etc.

As the eutrophication of lakes, streams and reservoirs has increased in recent years, sanitary engineers have become increasingly aware of the widespread use of phosphorus in the environment and the important role it has in the eutrophication process. Phosphates have been applied as plant fertilisers for many centuries in one form or another but the development of synthetic fertilisers has greatly increased the amount applied. Metaphosphates are often used to treat water used in cooling systems and boilers to control corrosion. With the banning of alkyl benzene sulphonate for household detergents in the mid 1960s, phosphate builders were used for synthetic detergents and this greatly increased the phosphorus content of domestic wastewater. Phosphates occur naturally in bodies of water and littoral sediments but their increased use and subsequent discharge into the environment has greatly increased the concentrations in the environment in recent years. Since phosphorus is an essential nutrient for the growth of aquatic plants and organisms, the result in many instances had been the overgrowth of algae and aquatic plants to the point that the usefulness of the body of water for other purposes has been greatly impaired.

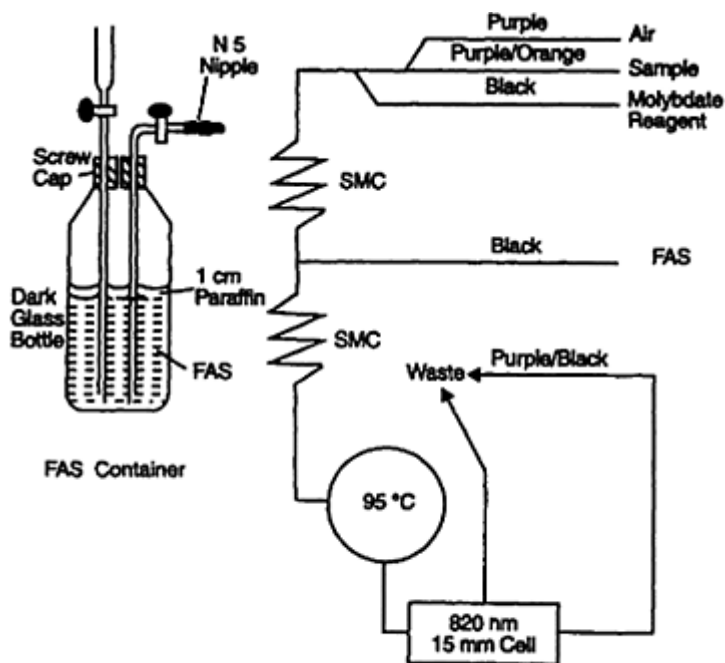
The importance of phosphorus in the eutrophication of surface waters is well known. Extensive monitoring is needed to provide data on this nutrient for effective water quality management. An indispensable key to the accomplishment of this objective are methods for analysing phosphates that are accurate, specific, and reliable.

Most colorimetric determination procedures in common use are based on the formation of 12-molybdophosphoric acid and its reduction to a blue heteropoly compound. There are quite a few reductants that can be used for the formation of phosphomolybdenum blue. A few are used for the high range determinations, such as vanadomolybdophosphoric acid and amino acid. Stannous chloride has been most widely used for low range determinations.

2.75.1 Spectrophotometric procedures

2.75.1.1 Methods based on formation of molybdenum blue

Pakalns and Stedman [597] have discussed the effect of surfactants on the Spectrophotometric determination of phosphate by direct and by solvent



33.7g ammonium molybdate plus 800ml water. Add 493ml conc. sulphuric acid to 1L water and when cool add to the molybdate and make up to 2L.

Fig. 2.36 Flow sequence for automated determination of phosphate

Source: Reproduced with permission from Elsevier Science [600]

extraction procedures. For direct methods cationic detergent caused considerable interference, but there was little interference by biodegradable anionic detergents. The ascorbic acid method is recommended for routine determination of phosphate in most waters. For the extraction procedure the levels of cationic and non-ionic detergents must not exceed 2 and 10mg L⁻¹ respectively. The maximal level of anionic detergents should be 8mg L⁻¹.

Problems with standard methods for the determination of phosphate by standard molybdenum blue methods has prompted development of a method based on the use of hydrazine-molybdic acid reagent [598].

Goulden and Brooksbank [599] have described an automated method for eliminating arsenate interference in the determination of phosphate in non saline waters by the molybdenum blue method. The arsenate is reduced to arsenite by thiosulphate in an acidic medium before the colour-producing reagents are added.

Skjemstad and Rieve [600] have reported three automated procedures for the simultaneous determination of phosphate, ammonia and nitrate plus nitrite at µg L⁻¹ levels in non saline waters. Phosphate is estimated by reaction with molybdate and reduction to molybdenum blue with ferrous ammonium sulphate.

Throughout the methods, deionised water with a conductivity of less than 1µs (micro

siemen) was used for standards, reagents and rinsing of glassware. All sample tubes and glassware were washed with 'BRIJ-35' detergent each time before use and soaked in 5N hydrochloric acid at frequent intervals. All samples were filtered through a Millipore 0.45µm filter before analysis.

Their determination of phosphate utilised the manifold and flow sequence are illustrated in Fig. 2.36.

Harmsen [601] used derivative spectrophotometry to determine phosphate in turbid water samples using the conventional molybdenum blue spectrophotometric procedure. Turbidities less than 0.8 did not interfere with adsorbance. Precautions were needed for phosphorus concentrations higher than 3mg L⁻¹. Nevertheless recovery tests were accurate to within 4%.

Stainton [602] has discussed errors in molybdenum blue methods for determining orthophosphate in non saline waters. He suspected that the release of orthophosphate from colloidal phosphorus was the source of such errors as had been shown by previous workers, and he therefore studied the effect of a variety of the more popular molybdenum blue methods on the colloidal phosphorus fraction. All variations on the method caused a significant loss of phosphorus from the fraction. Phosphorus originating from the colloidal fraction tested as orthophosphate, gave an overestimate of the true orthophosphate present.

Sulphide interference in the determination of phosphate by molybdenum blue methods has been discussed by De Jonge *et al.* [603].

Tarapchak *et al.* [604] have shown that when the molybdenum blue method was applied to samples of Lake Michigan water, differences in the period of exposure of samples to acid molybdate and differences in molybdate concentration, can affect the accuracy of the results.

Studies by Tarapchak [605] have indicated that methods using molybdenum blue to determine orthophosphate in surface waters may result in an over-estimation of the amount of available phosphorus. Evidence was obtained that molybdenum accelerates hydrolysis of organic phosphorus in the presence of acid and also either causes hydrolysis or forms complexes with organic phosphorus before acidification. Possible ways for limiting these effects are discussed.

Yoshimura *et al.* [606] have carried out microdeterminations of phosphate by gel-phase colorimetry with molybdenum blue. In this method the blue species of molybdophosphate are strongly adsorbed on Sephadex gels. Almost all the blue species in a 50cm³ sample solution are concentrated in 0.20g of Sephadex G-25 (fine) within 10min. Direct absorptiometry of the heteropoly acid concentrated in the gel phase was developed for the determination of the phosphate at parts per billion levels in non saline waters. The coloured gel beads, on which the blue species reduced by ascorbic acid in the presence of antimonyl ions were adsorbed, are packed into a 10mm cell; the attenuances at 836 and 416nm are measured; and the attenuation difference is used for the determination of traces of phosphate. The use of cells of other length (5, 2 and 1mm) give a wide concentration range for calibration from parts per billion to parts per million levels. This method is simple in operation and has a high reproducibility of measurements.

Towns [607] determined phosphate in non saline waters by ascorbic acid reduction of

phosphomolybdic acid. These workers examined the standard molybdenum blue method using 1cm cuvettes. The 'standard methods' version has been examined with polystyrene cuvettes over the concentration range 0.01–0.5mg L⁻¹. Erratic performance encountered at concentrations greater than about 1mg L⁻¹ is shown to be due to incomplete colour development during the prescribed measurement interval. Deviation from Beer's law behaviour occurring near 1mg L⁻¹ P is shown to be due to a transition from 'molybdenum blue' formation to 'heteropoly blue' formation. Incorporation into the standard method of a mild (75°C) short-term (20min) heating of the developing samples provides effective quantitation of the higher concentration range by a linear calibrations function and makes measurement time less critical. Example calibrations and colour development plots are presented and discussed in terms of the molybdenum blue and heteropoly blue formations. Support is given to the involvement of molybdate dimers in the 'blue' formation under the conditions of the 'standard method'.

Traces of orthophosphate in non saline waters have been determined by the stopped-flow time difference analysis technique in combination with the molybdenum blue method and preconcentration solvent extraction (with isobutyl alcohol) of 12-molybdophosphate [608]. The reductant was stannous chloride. The apparent molar (PO₄³⁻) absorptivity of the coloured product was $\sim 2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 730nm, and the detection limit was 0.3µg of phosphate L⁻¹. The calibration curve was linear from 0 to 5µg of phosphate L⁻¹, with a relative standard deviation <3% and a recovery of 100 ± 6% at a concentration of 20µg of phosphate L⁻¹.

Hassan and Salem [609] have described a sensitive spectrophotometric method for the rapid determination of phosphate in non saline water based on the reaction between phosphomolybdate and resazurine (at 495nm) or *p*-resolic acid (at 470nm). Phosphate can be determined in concentrations of 0.02–0.08mg L⁻¹ and 0.02–0.16mg L⁻¹ with resazurine and *p*-resolic acid reagents, respectively.

Quin and Fu [610] have described a spectrophotometric method using potassium persulphate as the oxidising agent for determining total nitrogen (at 200–210nm) and total phosphorus at 700nm) in river water. The method is reported to have recoveries of 98.0–108.0% for total nitrogen and of 92.3–107.0% for phosphorus; the corresponding detection limits were 0.010 and 0.019mg of nitrogen and phosphorus.

Taga and Kan [611] describe a flotation-spectrophotometric determination of phosphate in river water. The method has a relative standard deviation of 1.45% (n=6) for 0.4µg of phosphorus.

To and Randall [612] have reported on the use of ascorbic acid as a reductant and compared its reliability to that of a method using stannous chloride for reducing phosphate to the phosphomolybdenum blue complex. They report that, using ascorbic acid, the colours are more stable than occurs when stannous chloride is used. Consequently, the ascorbic acid method is more amenable to automation, although there are some limitations to the method. In the preparation of the combined reagent, care should be taken that all reagents reach room temperature and that they are mixed in order as prescribed. Otherwise turbidity and sometimes even a precipitate may form.

The ascorbic acid solution and the combined reagent are very unstable. They have to be prepared weekly and stored in the refrigerator when not in use. Otherwise the reagents will turn yellow and become useless.

There are interferences from some ions such as arsenates, nitrites and hexavalent chromium. Downes [613] gives details of an automated method for determination of reactive phosphorus in concentrations lower than 0.5mg L^{-1} in non saline waters which also contained arsenic, silicon and mercuric chloride preserving agent. The addition of thiosulphate in acid solution removes various interferences. Potman and Lijkema [614] have discussed the determination of phosphate in small samples of water.

Lei *et al.* [615] give details of a procedure for the determination of traces of phosphorus in non saline waters by absorption spectrometry, using a long capillary cell to lower the limit of detection.

Nurnberg [616] found that iron and hydrogen sulphide, often present in anoxic lake waters, interfere with the determination of soluble reactive phosphorus. Methods for reducing the interference are indicated. They propose an alternative to more complicated procedures for soluble reactive phosphorus in anoxic waters for determination of total (unfiltered reactive phosphorus). Results are on average only 2% lower, and the method can be automated if required.

Hydrogen sulphide concentrations higher than 1mg L^{-1} and ferrous iron concentration above 0.20mg L^{-1} produce interferences in the soluble reactive phosphate analysis (eg 80% underestimation of soluble reactive phosphorus (Fig. 2.37).

Ferrous iron is not problematic if the sample is kept anoxic before and during filtration. On the other hand vigorous aeration is obligatory if hydrogen sulphide is present.

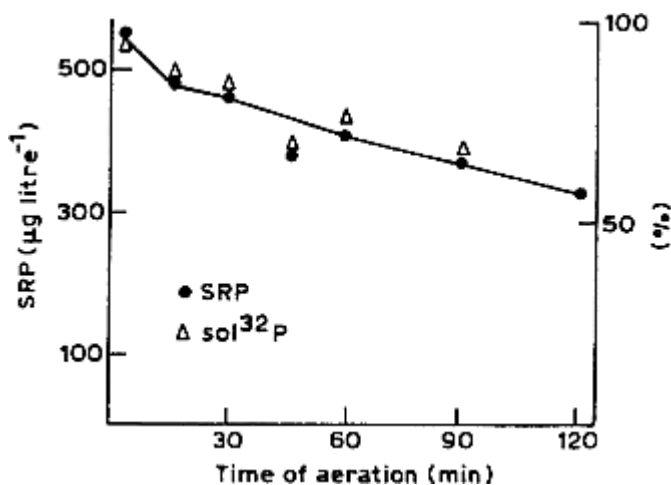


Fig. 2.37 Removal of soluble phosphorus during aeration in water from the anoxic hypolimnion of Lake Maga, 16m 11 August 1981. The iron concentration is 3.15mg L^{-1} . Circles represent soluble reactive phosphorus (SRP), triangles soluble radioactive phosphorus

Source: Reproduced with permission from Elsevier Science [616]

Worsfold *et al.* [617] give a detailed illustrated description of equipment for automatically monitoring phosphate in the field by the molybdenum blue method. It incorporated a flow-injection manifold for injecting the reagent into the sample stream

and a double-beam photometric detector incorporating light-emitting diodes and photodiodes. The response was linear over the range 0–2000 µg phosphorus and the limit of detection was 12 µg L⁻¹. There was no interference by silicate at a concentration of 10 mg L⁻¹.

The Water Research Association UK [618] have issued a standard method for the determination of phosphorus in waters, effluents and sewages. In this method, which is capable of determining 3–6 µg L⁻¹ phosphate a 200 ml sample is reacted with acidic molybdate reagent and ascorbic acid to form a reduced molybdenum blue complex.

The complex is extracted into 10 ml *n*-hexanol (ie preconcentration factor of 20) and the colour of the reduced molybdenum blue complex measured spectrophotometrically at 680 nm.

The Water Research Association UK [619] has issued a method, based on similar principles, which is capable of determining down to 0.5–0.7 µg L⁻¹.

Interferences of silicate, germanate, chromate and nitrate are negligible. Arsenate at the 0.05–0.1 mg L⁻¹ level and nitrite at 0.2–0.5 mg L⁻¹ level do interfere.

In both these methods precautions are used when preparing sampling bottles involving the use of iodised low density polyethylene or nylon sampling bottles.

2.75.1.2 Methods based on malachite green

The only alternative spectrophotometric methods for the determination of phosphate to those based on molybdenum blue appear to be those which utilise malachite green as the chromogenic reagent [620,621]. Fernandez *et al.* [620] have discussed an automated version of the malachite green micromethod for determining inorganic phosphate in non saline waters. The molar absorptivity of the technique was six times more sensitive than that of molybdenum blue methods. Reproducibility was very good and interferences from silicate and arsenate were easily removed.

Motomizu *et al.* [622] have described a spectrophotometric method for the determination of phosphate in river waters based on the measurement at 650 nm of the colour produced with molybdate and malachite green. The limit of detection is in the µg L⁻¹ range. In this method the sample solution was acidified with sulphuric acid and heated in a water bath above 90°C for 40 min and subsequently it was coloured with molybdate and malachite green. The colour was stabilised by adding poly (vinyl alcohol).

The interference of diverse ions was examined and the results obtained are shown in Table 2.43. The amounts of ions, except silicate, generally present in river water are much smaller than those listed in Table 2.43. Silicate ion at concentrations above 5 × 10⁻⁵ M reacts gradually with molybdate to form heteropolyacid and this results in positive errors, but large amounts of silicate ion were eliminated by acidifying the sample solution and filtering it through a membrane filter (pore size 0.45 µm).

Table 2.43 Effect of diverse ions

Phosphorus taken: 3.72 µg

Tolerance limit^a

Ion

HCO ₃ ⁻	6mg
Al ³⁺	3mg
Fe ³⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Ca ²⁺ , K ⁺ , NO ₃ ⁻	1mg
Mg ²⁺ , Na ⁺ , NH ₄ ⁺	0.5mg
Si(IV)	15µg
ClO ₄ ⁻	5µg
W(VI)	4µg
As(V)	2µg
V(V)	1µg

^aThe tolerance limit is defined as the concentration level at which the interference causes an error of not more than ±2%

Source: Reproduced with permission from the Royal Society of Chemistry [622]

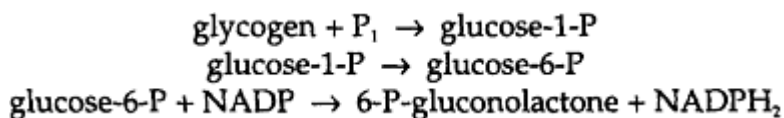
Matsubara *et al.* [623] have described a rapid method for the determination of trace amounts of phosphate (and arsenate) in water by spectrophotometric detection of their heteropoly acid-malachite green aggregates following preconcentration by membrane filtration.

The application of this technique is also discussed under multianion analysis in sections 14.2.1.1 and 14.2.2.1.

2.75.2 Spectrofluorometric methods

Several types of method for the determination of orthophosphate exploit the high sensitivity of fluorometric techniques. The ability of phosphate to inhibit the fluorescence of chelates led to the investigation of various metal-chelate systems for maximum sensitivity in the detection of trace amounts of phosphate. Several metal chelates of aluminium, gallium and zirconium with morin, 3-hydroxyflavone and quercetin have been examined but none proved as satisfactory as aluminium-morin for the determination of phosphate. Strongly complexing, coloured and metallic ions have a detrimental effect on this method. For the technique to be specific, phosphate must be separated from a number of cations and anions that interfere in the fluorometric analysis.

The enzymatic method proposed by Shulz *et al.* [624] with glycogen is specific but the treatment is too slow. This selective method for determining inorganic phosphate is based on a series of three enzymic reactions at neutral pH. Glycogen phosphorylase is used to catalyse the reaction between inorganic phosphorus (P_i) and glycogen, forming glucose-1-phosphate, which with phosphoglucomutase is converted into glucose-6-phosphate. Finally, with glucose-6-phosphate dehydrogenase and the addition of NADP, 6-P-gluconolactone and NADPH₂ are formed in proportion to the inorganic phosphate present:



The NADPH_2 formed is determined by measuring its fluorescence. This method is very sensitive because in terms of amount there is no real sensitivity limit as the NADPH_2 formed can be measured by enzymic cycling. In terms of concentration, the sensitivity is limited mainly by the degree to which phosphate can be removed from the reagents. As the analytical reaction takes place under neutral conditions, inorganic phosphate can be measured in the presence of very unstable organic phosphate.

Land and Edmonds [625] have studied fluorescence quenching by phosphate on aluminium morin, aluminium-3-hydroxyflavone, gallium-morin, gallium-3-hydroxyflavone, gallium-quercetin, zirconium-morin and zirconium-3-hydroxyflavone systems. They have found that only the first of these is suitable for determining the phosphate ion. The percentage of alcohol affects the aluminium-morin system considerably, as a large percentage causes non-linearity in fluorescence quenching. This method suffers from many interferences by cations and anions, which led to the suggestion of a method for isolating the phosphate ion. Guyon and Shults [626] also studied this system and applied it to the determination of phosphate in well and pore waters. The interfering fluoride ions are removed by boiling the slightly acidic sample and the cationic interferences by precipitation with hydroxide ions.

Phosphorus can be determined as orthophosphate by the formation of the ion-association complex of molybdophosphate with the basic dyestuff Rhodamine B [627]. After the extraction of excess of dye reagent into chloroform, the Rhodamine B-molybdophosphate is extracted into chloroform-butanol (4+1). A study of the stoichiometry in the ion-association complex revealed a combining ratio of 3mol of Rhodamine B to 1mol of molybdophosphate. This is in accordance with the formation of an unchanged complex of the type $[\text{RhB}^+]_a[\text{PMo}^{3-}]$.

The orthophosphate ion is also determined by precipitation of quinine molybdophosphate in 0.5M sulphuric acid. The excess of the quinine reagent is removed by washing the precipitate with 0.5M sulphuric acid and the complex is dissolved in the solvent mixture acetone-0.5M sulphuric acid (9+1) [628]. The authors suggested that the precipitate corresponds to the composition $(\text{C}_2\text{O}_4\text{H}_2\text{N}_2)_3(\text{PMo}_12\text{O}_{40})_2$; similar to that of quinine-molybdovanadophosphate as proposed by Ripau and Siteu [629].

Wang *et al.* [630] have also described a method based on quenching of Rhodamine 6G fluorescence for the determination of phosphate in non saline waters.

2.75.3 Flow injection analysis

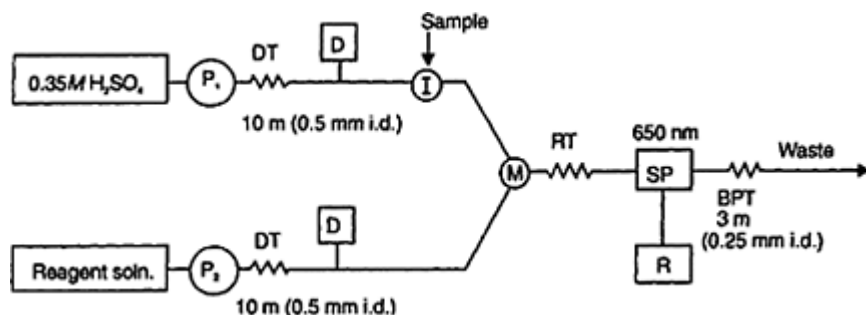
Janse *et al.* [631] have optimised conditions for the determination of phosphate by flow injection analysis. The flow rates of the water carrier stream and the reagent streams, the injection volume and the lengths of coils are the parameters on which the procedure was optimised.

Motomizu *et al.* [632] determined phosphate in river water by flow injection analysis.

The technique used malachite green in acidic medium as chromogenic reagent and spectrophotometric measurements are made at 650nm (Fig. 2.38). The procedure is very sensitive and can be used at a high sampling rate.

In Table 2.44 tolerable levels of coexisting ions likely to occur in river water samples are shown.

Only orthophosphate can be determined by this method. However, the condensed phosphates can easily be hydrolysed to orthophosphate by



Reagent solution. Dissolve 19.4g of ammonium heptamolybdate tetrahydrate, 0.092g of malachite green (oxalate) in about 500ml of distilled water, add 250ml of ethanol and 70ml of concentrated sulphuric acid and dilute to 1000ml with distilled water. This solution is 0.1 mol L^{-1} in molybdenum and $2.2 \times 10^{-4} \text{mol L}^{-1}$ in malachite green. Filter through a $0.45 \mu\text{m}$ membrane filter before use. This solution is stable for at least one month if stored in the dark.

Fig. 2.38 Schematic flow diagram. P1 and P2, pumps; DT, damping coil (0.5mm $\times$ 10m); D, air damper; I, sample injector; M, mixing joint; RT, reaction coil (1mm $\times$ 7.5m or 0.5mm $\times$ 5m); SP, spectrophotometer with flow cell; R, recorder; BPT, back pressure coil (0.25cm $\times$ 3m)

Source: Reproduced with permission from Elsevier Science [632]

Table 2.44 Tolerable concentrations of coexisting ions. Phosphorus taken: $120 \mu\text{g L}^{-1}$

Ion	Maximum tolerable concentration, mol L^{-1}
Na^+, Cl^-	0.1
$\text{Mg}^{2+}, \text{Ca}^{2+}$	0.01
$\text{Al}^{3+}, \text{K}^+, \text{Fe}^{3+}, \text{NO}_3^-, \text{HCO}_3^-$	10^{-3a}
SiO_3^{2-}	10^{-4}
$\text{WO}_4^{2-}, \text{VO}_3^-$	10^{-5}
AsO_4^{3-}	2×10^{-6}

^aMaximum tested

Source: Reproduced with permission from Elsevier Science [632]

heating the acidified solution for 30min in a water bath at about 90°C. In this work the water samples were made 0.35mol L⁻¹ in sulphuric acid in stoppered test-tubes, heated for about 45min in a water bath at about 95°C cooled to room temperature and injected into the carrier system.

Workers at Tecator Ltd [633–635] have described flow injection methods for the determination of between 0.025 and 5mg L⁻¹ of phosphate. These methods are fairly conventional employing to stannous chloride reducing system.

Fogg and Bselbu [636] developed a sequential flow injection voltammetric determination at a glassy electrode of phosphate (and nitrite) by injection of reagents into a sample stream. Good precision was obtained in the range 5–500μM phosphate.

A flow-injection method for determining phosphate concentrations in the field is described by Worsfold *et al.* [617]. The colour-forming reagents are injected into the sample stream and the absorbance is measured with a compact double-beam photometric detector having light-emitting diodes and photodiodes. The response is linear over the range 0–2000μg of phosphate L⁻¹ and the detection limit is 2μg of phosphate L⁻¹; there is no interference from 10mg of silicate L⁻¹.

Motomizu and Oshima [637] determined orthophosphate in non saline waters by a spectrophotometric method involving flow injection coupled with solvent extraction. The ion pair formed between molybdophosphate and malachite green was extracted into benzene-4-methyl-2-pentanone and the absorbance was measured at 630nm. The carrier stream was 0.005M in sulphuric acid and the reagent stream contained ammonium molybdate, malachite green and sulphuric acid. The calibration graph was linear for concentrations <30ng of phosphate mL⁻¹ on injecting 10μL samples. The detection limit was 0.1ng of phosphate mL⁻¹, and the sampling rate was 40 samples/h.

Schulz and Thiele [638] described a modified flow injection analysis procedure based on the formation of molybdenum blue using stannous chloride as reducing agent for the determination of orthophosphate in water, waste water and sludge samples. The results were compared statistically to those obtained by the standard method DJN 38402 part 71.

Pauer *et al.* [639] described a flow injection analysis method for the determination of phosphate using the molybdenum blue colorimetric method with tin(II) chloride stabilised with hydrazinium sulphate as reducing agent. The method was suitable for 10–500μg L⁻¹ phosphate. Precision of 0.50% at 500μg L⁻¹ phosphate was obtained. Silicon concentrations of less than 30mg L⁻¹ did not interfere with the technique. Interference by the preservative mercury(II) was negated by adding the same amount to both samples and standard solutions. A carry over of less than 1% was achieved at 90 samples per hour.

Yuan and Qu [640] and Freeman *et al.* [132] have studied the application of flow injection analysis to the determination of phosphates in non saline waters. The application of this technique is also discussed under multianion analysis in sections 14.4.1.3 to 14.14.1.6.

2.75.4 Atomic absorption spectrometry

Phosphate (and arsenate and arsenite) have been determined in non saline waters by a technique based on flotation spectrometry and extraction-indirect atomic absorption spectrometry using malachite green as an ion-pairing reagent [641].

2.75.5 Polarography

Hight *et al.* [642] give details of a procedure for the determination of phosphate in aqueous samples by differential pulse polarography, based on determination of molybdenum in 2-phosphomolybdic acid. Phosphate is first converted to the phosphomolybdate complex which is then extracted into iso-butyl acetate. High sensitivity is achieved by measuring the polarographic wave due to the catalytic reduction of perchlorate or nitrate in the presence of molybdenum(VI). The method is suitable for samples as small as 3.5ml which contain as little as $9\mu\text{g L}^{-1}$ of phosphorus. The average relative deviation is 3.0% at the 0.045mg L^{-1} phosphorus level and 1.6% at the 1–2mg L^{-1} level.

Iso-butyl acetate is then removed by evaporation and the residue dissolved in dilute sodium hydroxide, followed by acidification with perchloric acid. Phosphate is then determined indirectly by measurement of the catalytic current of perchlorate or nitrate in association with molybdenum(VI).

2.75.6 Anodic scanning voltammetry

Matsunaga *et al.* [643] have discussed the differential pulse anodic voltammetry of phosphates.

2.75.7 Column coupling isotachopheresis

This technique offers very similar advantages to ion chromatography in the determination of anions in water, namely multiple ion analysis, little or no sample pretreatment, speed, sensitivity and automation. Very similar advantages are offered by capillary isotachopheresis. Zelinski *et al.* [325] applied the technique to the determination of 0.02–0.1mg L^{-1} quantities of phosphate, chloride, fluoride, nitrate, nitrite and sulphate in river waters.

The application of this technique is also discussed under multianion analysis in section 14.6.1.1.

2.75.8 X-ray fluorescence spectroscopy

Yamamoto [644] precipitated trace amounts of phosphate in river water by adding ammonium molybdate and 8-quinolinol to form $(\text{C}_9\text{H}_7\text{ON})_3\cdot\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot 2\text{H}_2\text{O}$. The precipitate was collected on a membrane filter and the phosphorus was determined by X-ray fluorescence spectrometry. The calibration curve was linear over the range of 0.3–10 μg of phosphate. Iron(III) (<0.15mg) and lead (<0.3mg) did not interfere.

2.75.9 Enzymic methods

Enzymic methods have been developed for the determination of phosphates in non saline waters. Stevens [645] gives details of an automated enzymatic method for determination of orthophosphate. Results of analysis of water samples by this method and by the soluble reactive phosphorus method indicated that a form of phosphorus was present which was determined as soluble reactive phosphorus but not as enzymatic orthophosphate; the presence of an hydrous ferric oxide-orthophosphate complex is postulated.

Steinberg *et al.* [646] described an automated enzymic method for phosphate based on the property of orthophosphate of inhibiting the hydrolysis of certain fluorogenic substrates by means of the alkaline phosphatase of *Esch. coli*. A particular substrate is 4-methylumbelliferyl phosphate which has a maximal excitation frequency of 360nm. Results obtained are compared with values given by the molybdenum blue method, which point to discrepancies in the latter. A detection limit of $0.1\mu\text{g L}^{-1}$ phosphate phosphorus is reported.

Chrost *et al.* [647] described a method for determining enzymically hydrolysable phosphate based on determination of inorganic phosphate released after the hydrolysis of organophosphoric esters by free, dissolved phosphohydrolases (mainly phosphatase) produced by biota. The method gave higher values in hypereutrophic waters than the molybdenum blue procedures and similar values for less eutrophic waters. The method was recommended for eutrophic waters where the orthophosphate concentration exceeded $25\mu\text{g L}^{-1}$ phosphorus.

2.75.10 Ion chromatography

Various workers have applied this technique to the determination of phosphate in non saline waters [648–650].

The application of this technique is discussed under multianion analysis in sections 12.2.1, 12.2.4, 12.2.5 and 12.2.6.

2.75.11 High performance liquid chromatography

Sakurai *et al.* [651] have described a high performance liquid chromatographic procedure for the determination of down to 0.5mg L^{-1} phosphate in waste water and river waters. The method is based on the solvent extraction of molybdoheteropoly yellow with methyl propionate. 0000

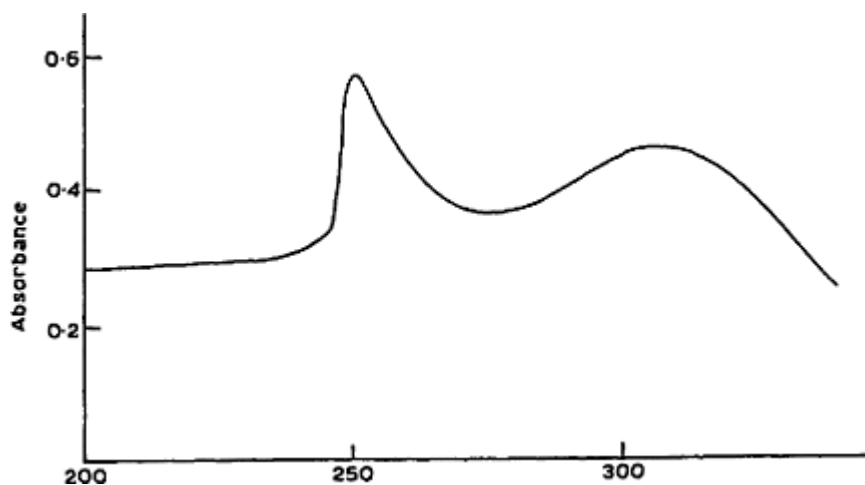


Fig. 2.39 Absorption spectrum of molybdophosphoric acid

Source: Reproduced with permission from Springer Verlag [651]

The corresponding silicon compound is not extracted into this solvent. Thus, the interference by silicon is excluded even at concentrations as high as 10mg L^{-1} . A wavelength of 251nm at the ultraviolet detector gave an absorption maximum of phosphorus molybdoheteropoly yellow in methyl propionate as shown in Fig. 2.39.

Fig. 2.40 shows good agreement in calibration curves obtained for orthophosphate in distilled water and in wastewater. Fig. 2.41 shows a typical chromatogram obtained by this technique.

High performance liquid chromatography has also been used to [237] to determine orthophosphate, diphosphate and triphosphate.

Speciation and quantitative analysis of orthophosphate, diphosphate and triphosphate are performed by using high performance liquid chromatography with inductively coupled argon plasma emission spectrometric detection. High performance liquid chromatography is used to separate mixtures of phosphates on an anion exchange column using tartrate magnesium buffer. The inductively coupled plasma is used as a selective detector by observing P(II) emissions at 214.9nm. The detection limit is 0.5, 1 and $3\mu\text{g}$ respectively for ortho-, di- and triphosphate respectively.

Phosphorus was monitored at 214.9nm (second order). The analog signal was taken out through the profile mode of a computer program. In order to filter noise, a $50\text{K}\Omega$ resistor and $20\mu\text{F}$ condenser were installed before the recording giving an approximate time constant of 1s.

Among the eluants examined, oxalate plus magnesium gave the best resolution, tartrate plus magnesium gave the second best but formate

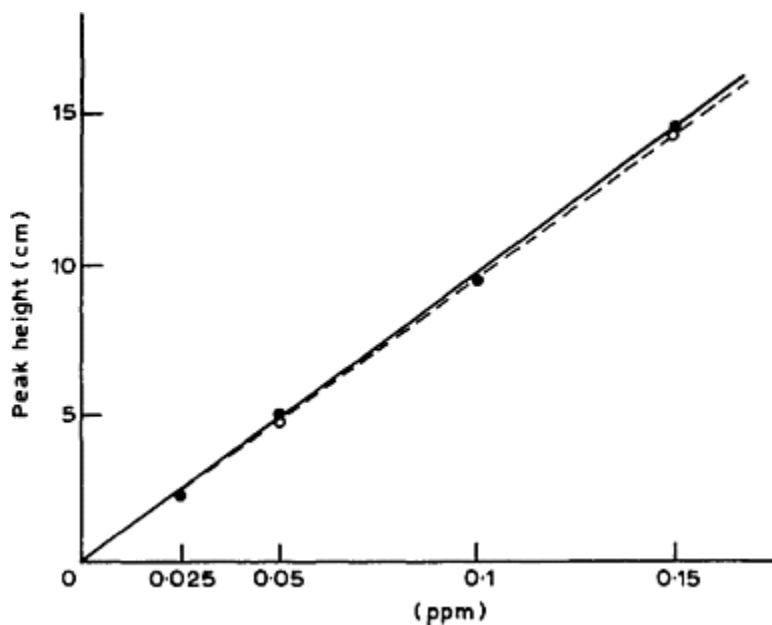


Fig. 2.40 Calibration curves (°—°) P in aqueous solution (°- - °) P in waste water

Source: Reproduced with permission from Springer Verlag [651]

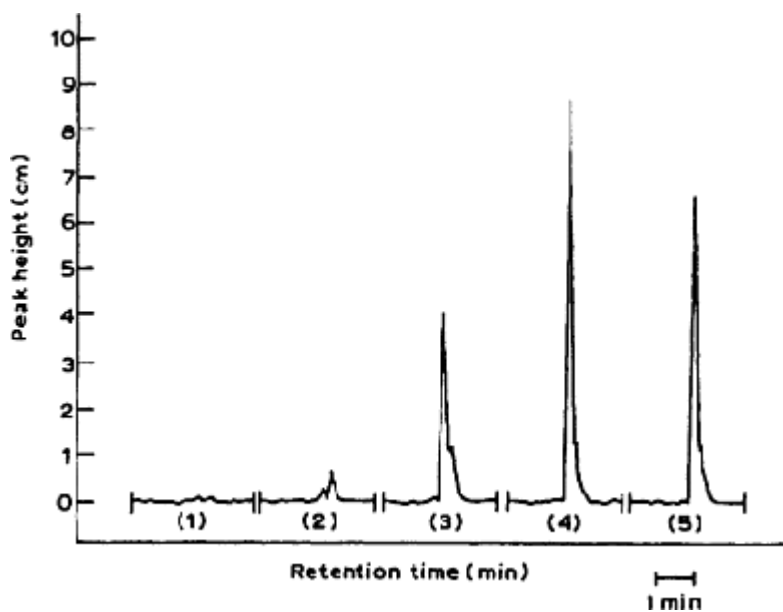


Fig. 2.41 Some chromatograms as example: (1) methyl propionate; (2) reagent

blank; (3) orthophosphate (P: 5ng); (4) orthophosphate (P: 10ng); (5) sample solution (P: 8.5ng)

Source: Reproduced with permission from Springer Verlag [651]

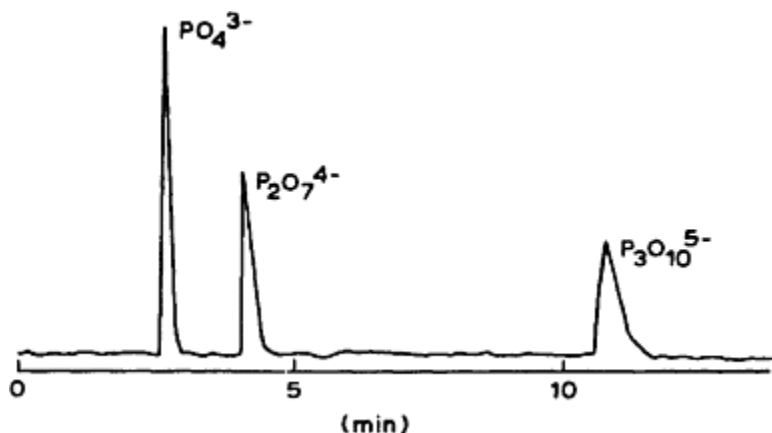


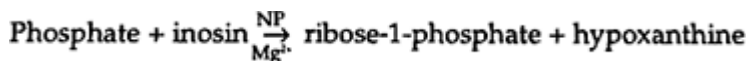
Fig. 2.42 Chromatogram of orthophosphate, diphosphate and triphosphate.

Column is μ -Gondapak- NH_2 and the eluant was oxalate-Mg buffer at the flow rate of 1.0 ml min^{-1} , $50\mu\text{L}$ of mixed solution which contains 10^{-3}M each phosphate

Source: Reproduced with permission from Springer Verlag [651]

plus magnesium and acetate plus magnesium gave poor resolutions. Oxalate plus magnesium buffer should be freshly prepared as it is subject to decomposition. The column should be rinsed after use.

In Fig. 2.42 is shown a typical chromatogram, obtained by this technique for a mixture of orthophosphate, pyrophosphate and $\text{P}_3\text{O}_{10}^{5-}$. Morgan and Danielson [652] have described the development of an enzymatic method of determining phosphate eluted from a reverse phase high performance liquid chromatographic column. The method is applicable to sewage effluents and non saline water samples. It is based on the nucleoside phosphorylase catalysed conversion of inosine and orthophosphate to hypoxanthine. This method is claimed to give better results than standard molybdenum blue spectrophotometric methods.



The inosine and hypoxanthine were separated by reversed phase high performance liquid chromatography and the amount of hypoxanthine produced was related to the phosphate concentration. Quantitation of the hypoxanthine peak was found to be linear with orthophosphate up to about 30 mg L^{-1} . A detection limit of 0.75 mg L^{-1} could be obtained after dialysis of the commercial enzyme. Interference studies showed that the enzymatic assay unlike the colorimetric molybdate blue technique was essentially unaffected by

complex matrices such as polyphosphates and phosphoesters.

Fig. 2.43 shows a typical chromatogram for a standard $42\mu\text{g L}^{-1}$ phosphate solution and hypoxanthine peaks resulting from various

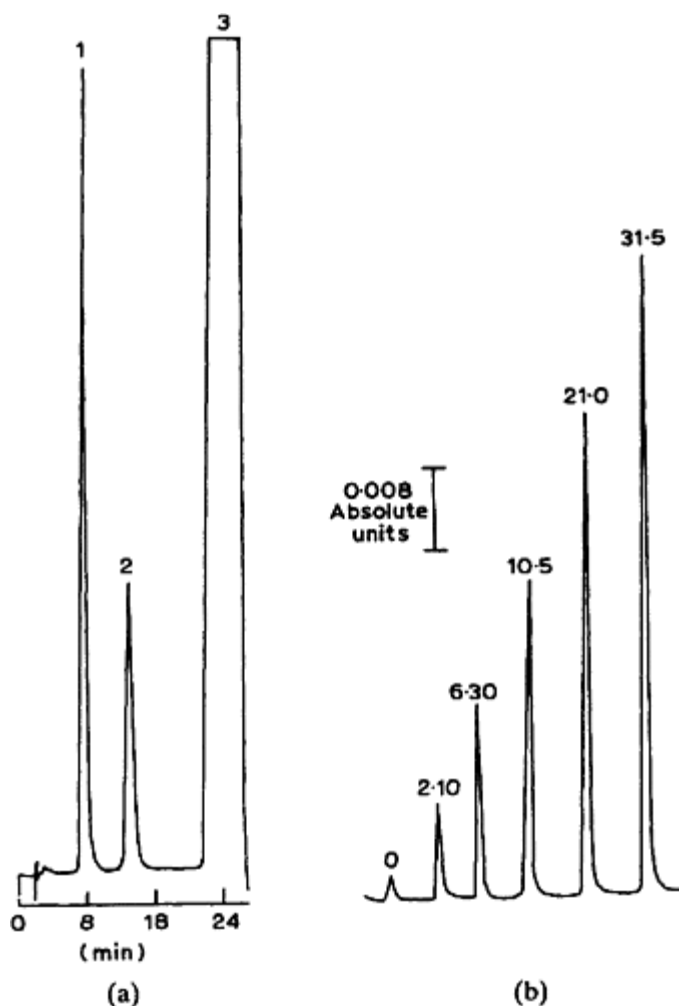


Fig. 2.43 (a) Sample chromatogram of a 42mg L^{-1} phosphate sample. Absorbance units full scale, $\text{su.f.s.}=0.08$. Peaks: 1=hypoxanthine; 2=m-aminophenol; 3=inosine. (b) Hypoxanthine peak for various phosphate concentrations in mg L^{-1} (indicated above each peak)

Source: Reproduced with permission from Springer Verlag [651]

phosphate samples after reaction with the enzyme. The calibration curve had a slope of 0.043 ± 0.002 and an intercept of 0.124 ± 0.033 with a correlation coefficient of 0.998.

Linearity up to 30 mg L^{-1} was observed. Relative standard deviation of triplicate runs was 10% or less. The detection limit, twice the signal of the blank, was determined to be 1.5 mg L^{-1} .

Fig. 2.44 is a plot of phosphate concentration given by the enzymatic method vs that found by the molybdate blue method. The line fit to these points had a slope of 0.999 ± 0.046 and an intercept of 0.421 ± 1.222 with a correlation coefficient of 0.996.

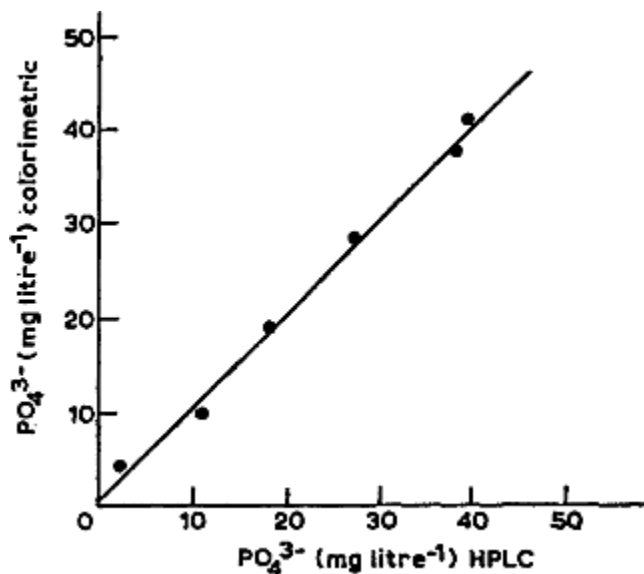


Fig. 2.44 Concentration of phosphate obtained by the colorimetric method versus the concentration obtained by the enzymatic high performance liquid chromatographic method

Source: Reproduced with permission from Springer Verlag [651]

To compare the selectivity of the enzymatic method with that of the molybdate blue method, interference studies were conducted for both methods. The first study was the effect of tripolyphosphate in the sample. The molybdate blue method showed a positive deviation with increasing amounts of tripolyphosphate. The reason for this positive deviation can be attributed to the acid hydrolysis of tripolyphosphate to orthophosphate. The enzymatic method also showed a slight positive deviation probably due to orthophosphate impurity in the triphosphate used.

2.75.12 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.3.

2.75.13 Gas chromatography

Hashimoto *et al.* [653] converted phosphates to phosphine prior to gas chromatographic analysis in their method for the determination of phosphates in non saline waters.

2.75.14 Preconcentration

The application of this technique is discussed under multianion analysis in section 15.1.8.

2.75.15 Miscellaneous

Various other methods for the determination of phosphate in water include atomic absorption inhibition titration of magnesium absorption [437,654], neutron activation analysis of the tungstophosphate [437,654, 655], X-ray fluorescence spectrometry following adsorption of phosphate onto silica gel modified with N-substituted diamine functional groups [656], radio-activation analysis as the ^{185}W tungstomolybdophosphoric acid complex [657] and differential pulse anodic voltammetry [643].

Herve and Kauppi [658] studied the effects of filtration on the determination of phosphate phosphorus in run off waters. The effect of filtration was to reduce the amount of phosphorus reacting with molybdenum in turbid water samples. The GF/C and 0.45 μm membrane filters gave similar results but a much smaller reduction occurred with the black ribbon filter (pore size 7.4 μm). The total reactive phosphorus concentration method was thought to over-estimate the level of available phosphorus in turbid waters because of the severity of the acid treatment embodied in the method.

Ryden *et al.* [659] have studied the adsorption of inorganic phosphates by laboratory ware, including glass, polypropylene and polycarbonate. They conclude that the use of acid washed glassware should be discouraged and a polycarbonate which has been previously 'phosphated' by treatment with hot hydrochloric acid followed by potassium dihydrogen phosphate is the most suitable sample container material.

Nelson and Romkous [660] have shown that, after freezing of water samples followed by storage at -20°C for 3d, the soluble phosphate concentration decreased by 2–27%. Rapid freezing with liquid nitrogen produced about half the effect of slow freezing. No decrease in the phosphate concentration was found when samples were stored at 2°C (for 3d) or when they were frozen slowly after removal of sediments by centrifuging.

Lindquist and Cox [661] determined phosphate in lakewater by cathodic stripping chronopotentiometry at a copper electrode. Good agreement was obtained with results obtained by spectrophotometric procedures.

Shapiro [662] fixed lakewater samples for phosphate determination by adding aqueous ammonium molybdate to the sample immediately after collection. As soon as convenient the samples were extracted with isobutyl alcohol and the organic layers stored for up to two weeks before analysis. During this period the determined phosphate content does not decrease by more than 20%.

2.76 Phosphite

2.76.1 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.5

2.77 Polyphosphate

2.77.1 High performance liquid chromatography

Yaza *et al.* [238] analysed mixtures of monofluorophosphate, ortho-phosphate and polyphosphates by this technique using a photodiode array detector.

2.78 Polysulphide

2.78.1 Titration methods

Polysulphides can be determined in non saline waters by titration with mercury(II) solutions. Sulphides, thiosulphides, sulphites and thiols interfere in this procedure [663].

2.78.2 Flow injection analysis

Sonne and Dasgupta [664] have determined polysulphides, sulphate, sulphite and thiosulphate by simultaneous photometric flow injection analysis.

The application of this technique is discussed under multianion analysis in section 14.4.1.1.

2.79 Protocatechaute

2.79.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.80 Propionate

2.80.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.80.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.1.5 and 13.1.1.6.

2.81 Pseudohalides

2.81.1 Flow injection analysis

The application of this technique is discussed under multianion analysis in section 14.4.1.2.

2.82 Pyrenyl palmitate

2.82.1 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.6.

2.83 Pyrophosphate

2.83.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.84 Pyruvate

2.84.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.85 Quinate

2.85.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.86 Resorcyate

2.86.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.87 Salicylate

2.87.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.88 Selenate

In recent years, there has been increasing interest in the trace determination of selenium because of its dual role as an essential nutrient at low concentration levels and as a toxic substance at higher concentration levels. Selenium deficiency, for example, can be related to necrotic degeneration of the liver, pancreas, heart and kidney. High selenium concentrations can establish toxicity phenomena like inflammation of the feet, softening and loss of hoofs and horns in animals, or loss of hairs and nails and irritation of skin and eyes in humans. The narrow concentration range between the two contrary effects requires precise knowledge of the selenium content in the environment. The accurate determination of selenium, however, is still a major challenge for analysts.

Detailed information about the availability and mobility of an element in the environment and its behaviour in biological and geochemical systems, however, requires the additional knowledge of the different chemical forms in which the element exists. Species determination with respect to selenium, which can exist in different oxidation states (-2, selenide; 0, elemental selenium; +4, selenite; +6, selenate) and multiple chemical forms within the oxidation state -2 (eg organic and inorganic selenide), is especially important in aquatic systems, because the occurrence of selenium is mainly influenced by its chemical form. Therefore, analytical methods that can provide such information are receiving more attention.

2.88.1 Differential pulse polarography

Brimmer *et al.* [665] investigated the quantitative conversion of selenate in aqueous solution to selenite prior to determination by differential pulse polarography. Calibration curves of peak current against selenite concentrations of 2–15mg L⁻¹ with 0.12–3.0M hydrogen chloride solution as background electrolyte showed a good linear relationship which was consistent with results using standard solutions. Kinetic analysis indicated that the reaction was first order with respect to selenate and that the reaction rate increased with increasing hydrogen chloride concentration. The procedure was used to detect

selenite and selenate in drainage water samples and was effective over a wide range of concentrations, the lowest level of selenium was $35\mu\text{g L}^{-1}$.

2.88.2 Ion chromatography

Hoover and Jager [666] have discussed the determination of selenate together with other anions (selenite and arsenite) in potable and ground waters.

The application of this technique is also discussed under multianion analysis in sections 12.2.2 and 12.2.4.

2.88.3 Preconcentration

The preconcentration of selenate is discussed in section 15.1.9.

2.89 Selenite

2.89.1 Spectrophotometric methods

Bodini and Alzamora [667] used reaction of 4,5,6-triaminopyridine with selenite in acidic medium as the basis of Spectrophotometric method for estimating traces of the latter in non saline water. The reaction product is a piazselenol with an absorption maximum at 362nm. The precipitate is dissolved in 3.5M phosphoric acid in order to avoid interference from iron and chloride or tin(II). The calibration graph is linear up to 10mg L^{-1} selenium and the detection limit is 0.1mg L^{-1} . The relative standard deviation is 1.5% for pure solutions. The method is accurate and precise.

2.89.2 Spectrofluorometric methods

Takayanagi and Wong [668] give details of fluorometric procedure for the determination of tetravalent selenium in non saline waters. The optimal conditions for fluorometric determination of total selenium were also investigated.

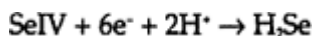
A method has been described [669] for the determination of selenite in non saline waters based on the formation of piazselenols by reaction with substituted 1,2-diaminobenzenes. The derivatives were extracted into solvents prior to analysis by fluorometry or gas chromatography with electron capture detection, according to published methods. The use of 1,2-diamino-3,5-dibromobenzene and 4-nitro,1,2-diaminobenzene enabled detection limits of 1ng L^{-1} and 6ng L^{-1} selenium in water to be achieved, respectively. Using diaminonaphthalene as a fluorometric reagent, a detection limit of 50ng L^{-1} could be obtained, although at the risk of severe interference from ferric iron, nitrite and nitrate. All organoselenium compounds could be decomposed by ultraviolet irradiation, with formation of selenite.

2.89.3 Polarography

Lin Ahmed *et al.* [670] determined selenite by a polarographic technique involving the

use of an acidic supporting electrolyte. Generally, hydrochloric or perchloric acids are used.

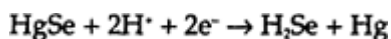
Christian *et al.* [671] reported that the polarographic reduction of selenite in hydrochloric acid exhibits two main waves corresponding to the following reactions.



at $E_{1/2} = -0.01\text{V}$ vs SCE, followed by depolarisation of mercury by the reduction product:



The second wave at $E_{1/2} = -0.54\text{V}$ vs SCE corresponds to the further reduction of the HgSe to hydrogen selenide.



The only elements and anions likely to interfere in the determination of selenite are arsenite, copper(II), iron(III), lead(II) and zinc(II). Arsenite and copper(II) strongly enhance the selenium peak, while iron(III) has a suppressant effect.

2.89.4 X-ray fluorescence spectroscopy

Robberecht and Van Grieken [672] determined $\mu\text{g L}^{-1}$ levels of total dissolved selenium and selenite in non saline waters by X-ray fluorescent spectrometry. Detection limits for tetravalent selenium and total selenium are 50ng L^{-1} and 60ng L^{-1} respectively. Coefficients of variation are 10% for tetravalent and hexavalent selenium at the $0.5\text{--}1\mu\text{g selenium L}^{-1}$ level.

2.89.5 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.2, 12.2.4 and 12.2.5.

2.89.6 Gas chromatography

Uchida *et al.* [673] have described a method for determination of selenium in river and sea water by gas chromatography with electron-capture detection. The specific reaction of 1, 2-diamino-3, 5-dibromo-benzene with selenium(IV) is used, the product (4, 6-dibromopiazselenol) being extracted into toluene and determined from its peak height in the gas chromatogram. Selenium (–II, 0) is oxidised to selenium(IV) by bromine

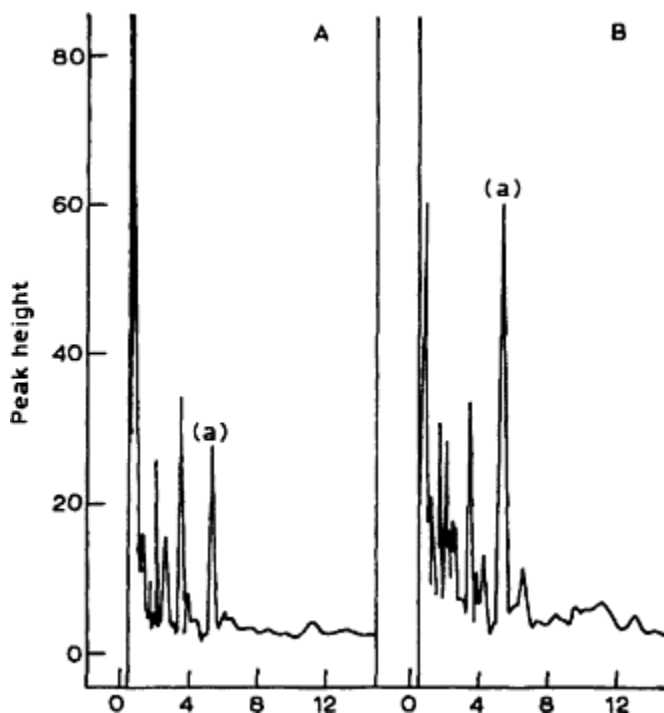


Fig. 2.45 Recorder tracings of selenium analysis of a river water sample: (A) Se(-II, 0) plus Se(IV) procedure 2; (B) total Se (procedure 2); (a) 4, 6-dibromopiazselenol

Source: Reproduced with permission from the American Chemical Society [673]

solution and selenium(VI) is reduced to the same state by bromine/ bromide redox buffer solution and determined as the piazselenol as above.

As an example, the gas chromatograms of selenium in river water are shown in A and B and Fig. 2.45 respectively. Selenium(VI) is calculated from the difference between the peak heights of 4, 6-dibromopiazselenol in A and B. The total amount of selenium in river water varied largely, eg from 16 to 230ng L⁻¹.

2.89.7 Miscellaneous

Brimmer *et al.* [665] have carried out an investigation of the quantitative reduction of selenate to selenite in aqueous solutions.

2.89.3 Preconcentration

The preconcentration of selenite is discussed in section 15.1.9.

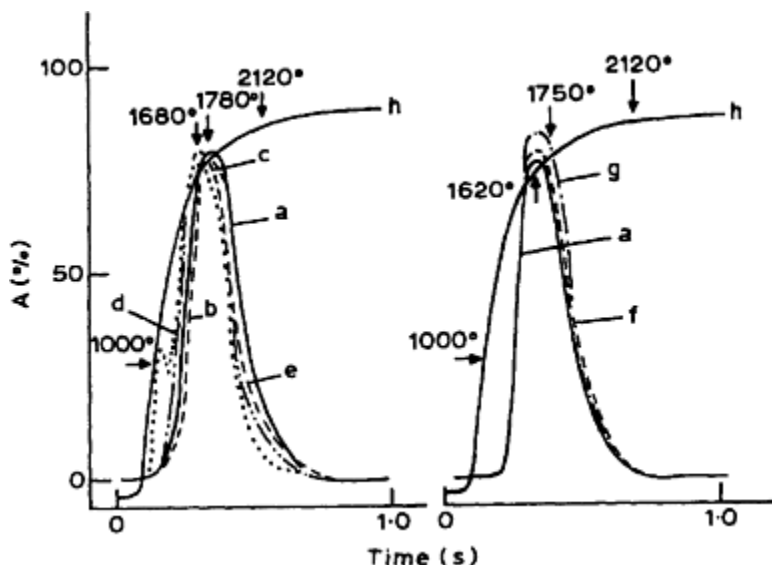


Fig.2.46 Memoriscope traces for effect of diverse elements; (a) 0.63ng Se(IV); (b) 0.63ng Se(IV) and 63ng Pb; (c) 0.63ng Se(IV), 63ng Pb and 63ng Cu; (d) 0.63ng Se(IV) and 63ng As; (e) 0.63ng Se(IV), 63ngAs and 63ng Cu; (f) 0.63ng Se(IV) and 63ng Te; (g) 0.63ng Se(IV), 63ng Te and 63mg Cu; (h) temperature increase. Gas flow rate 500ml Ar min⁻¹

Source: Reproduced with permission from American Chemical Society [674]

2.90 Selenate and selenite

2.90.1 Atomic absorption spectrometry

Ohta and Suzuki [674] using a molybdenum micro-tube atomiser have developed an atomisation technique for the determination of selenium in water samples. The highest absorption peak was achieved in pure oxygen, as was the lowest atomisation temperature, the analytical wavelength was 196.00nm. Extraction of selenium with diethyldithiocarbamate eliminated matrix interference and copper addition suppressed interference from co-extracted elements. No selenium(VI) was extractable from citrate buffered solutions containing EDTA, so that use of these reagents allowed separate determination of selenium(IV) and selenium(VI). Recoveries of 90–106% were achieved in analysis of water samples containing 30–130µg L⁻¹ selenium.

Most cations and anions have interferences on atomisation of selenium. The effects of 100-fold amounts of lead, arsenic and tellurium on atomisation of selenium are shown in Fig. 2.46. Samples were checked for background effects and reagent blank. Bismuth and antimony also depressed the selenium absorption.

Arsenic lowered somewhat the peak temperature in atomisation profile for selenium. Copper tends to suppress the interferences of diverse elements on atomisation of selenium. However, the interferences from large concentrations of diverse elements and matrices were not improved even in the presence of copper at the atomisation step. Therefore, the separation of selenium from matrices was recommended.

2.90.2 Polarography

AC polarography and differential pulse polarography [675] and anodic stripping voltammetry [676] have been used to determine selenium.

2.90.3 X-ray fluorescence spectroscopy

Robberecht and Van Grieken [677] determined $\mu\text{g L}^{-1}$ levels of total dissolved selenium and selenite in non saline waters by X-ray fluorescence spectrometry. Detection limits for tetravalent selenium and total selenium are 50ng L^{-1} and 60ng L^{-1} respectively. Coefficients of variation are 10% for tetravalent and hexavalent selenium at the $0.5\mu\text{g L}^{-1}$ selenium level.

2.90.4 Isotope dilution mass spectrometry

In order to clarify the species composition of selenium in environmental water samples, Tanzer and Henmann [678] developed analytical methods for the selective determination of different chemical forms of this element (selenite, selenate, and organic species including trimethylselenonium) using isotope dilution mass spectrometry. The species analysis was made possible by means of chromatographic separation procedures and an ^{82}Se -enriched selenate, selenite, and trimethylselenonium spike for the isotope dilution process. The total selenium concentration was determined after decomposition of organic compounds with nitric acid-perchloric acid mixture. Selenium was measured in the mass spectrometer by producing negative Se^- thermal ions for detection. Precise determination at the parts-per-trillion level was achieved. This new methodology was applied to different types of non saline water samples (groundwater, pond water, river water, moorland lake water) with total selenium concentrations in the range of 200pg g^{-1} to 15ng g^{-1} . Selenite and selenate have been the only detected species in most of the investigated samples, with selenate dominating all except one. In samples with high contents of dissolved organic carbon, however, different organoselenium compounds including trimethylselenonium ions were additionally quantified in the range of $10\text{--}95\text{pg g}^{-1}$. In these cases, the sum of all selenium species agreed well with the independently determined total element concentration.

2.90.5 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.2, 12.2.4 and 12.2.5.

2.90.6 High performance liquid chromatography

High performance ion exchange chromatography has been used [679] to separate selenite and selenate which were determined by post column derivatisation using 2, 3-diaminonaphthalene. Peak broadening was minimised by an air-segmented continuous flow autoanalyser. 2, 3-diaminonaphthalene reacted with selenium(IV) but not with selenium(VI). Selenium(VI) was determined after on-line reduction with hydrogen bromide (1.8N) at 100°C. Selenium(IV) was detected in potable water at $0.17\mu\text{g L}^{-1}$. Injection of larger volumes improved the detection limits. Samples of river or lake water were concentrated by column head techniques.

Cartoni and Coccioli [680] characterised mineral waters using high performance liquid chromatography. Filtered mineral water was pumped through a column packed with LiChrosorb RP-18. Traces of organic material dissolved in the water were adsorbed on to the first part of the column and were then desorbed using an acetonitrile gradient. The eluate was monitored with an ultraviolet variable wavelength detector.

2.90.7 Gas chromatography

Uchida *et al.* [673] have described a method for determination of selenium in rivers and sea water by gas chromatography with electron-capture detection. The specific reaction of 1, 2-diamino-3, 5-dibromobenzene with selenium(IV) is used, the product (4, 6-dibromopiazselenol) being extracted into toluene and determined from its peak height in the gas chromatogram. Selenium (–II, 0) is oxidised to selenium(IV) by bromine solution and selenium(VI) is reduced to the same state by bromine/ bromide redox buffer solution and determined as the piazselenol as above.

The gas chromatograph used in this study was equipped with ^{63}Ni electron capture detector and the column comprised 15% of SE-30 on 60–80 mesh Chromosorb W. The column and detector temperatures were maintained at 200 and 280°C respectively. The nitrogen flow rate was 28ml min^{-1} .

Procedure 1

In this method concentrated hydrochloric acid is added to the sample immediately after sampling (1ml L^{-1}). The solution is filtered by a membrane filter (pore size $0.45\mu\text{m}$) to remove suspended matter.

Se(IV) determination (procedure 1) is carried out as follows; to a 500ml separating funnel is added 500ml of the pretreated sample water and 20ml of concentrated hydrochloric acid. The solution is shaken vigorously with 25ml of toluene to saturate with toluene and to remove toluene soluble matter. The aqueous phase is transferred into another 500ml separating funnel after phase separation. To the solution is added 0.12% 1, 2-diamino-3, 5-dibromobenzene solution (10ml), and the solution left to stand for 2h, 1ml of toluene is added and the solution shaken vigorously for 5min and the 4, 6-dibromopiazselenol extracted. The extract is washed twice with 3ml of perchloric acid (2+1), and $2\mu\text{L}$ of the extract injected into the gas chromatograph and the peak height of 4, 6-dibromopiazselenol measured.

Procedure 2

Se(–II, 0, IV) determination is carried out as follows. To the pretreated sample solution (500ml) 25ml of concentrated hydrochloric acid and 2ml of bromine solution (3%) is added and the solution mixed for 5min at room temperature. By this treatment Se(–II, 0) is oxidised completely to the quadrivalent state but Se(VI) is not reduced. 2ml of hydroxylamine hydrochloride (1mol L^{-1}) is added to the solution to reduce the excess bromine to bromide. The solution is washed with 25ml of toluene. The solution is treated with 4, 6-dibromopiazaselenol and the analysis continued as above in procedure 1. Calculate selenium (–II, 0) from the difference between the peak heights of the piazaselenol by the two procedures 1 and 2.

Procedure 3

Se(–II, O, IV, VI) determination is carried out as follows. To the pretreated sample water (500ml) concentrated hydrochloric acid (50ml), 47% hydrobromic acid (25ml) and 3% bromine solution (0.5ml) is added, and the solution boiled gently for 15min. By this treatment Se(–II, O) is oxidised to Se(IV) and Se(VI) is reduced to Se(IV). Thus all selenium is now in the quadrivalent state. After the solution is cooled to room temperature, 2ml 1mol L^{-1} hydroxylamine hydrochloride is added to reduce the excess bromine. The solution is washed with 25ml of toluene and total selenium determined by the same method as procedure 1. Calculate selenium(VI) by deducting Se(–II, O, IV) from Se(–II, O, IV, VI).

Distilled water containing 4.6ng of Se 0, 4.8ng of Se(IV) and 5.9ng of Se(VI) were analysed by procedures 1, 2 and 3 and good recoveries were found (Table 2.45).

As an example, the gas chromatograms of selenium in river water by procedures 2 and 3 are shown in Fig. 2.47(a) (b) respectively. Selenium(VI)

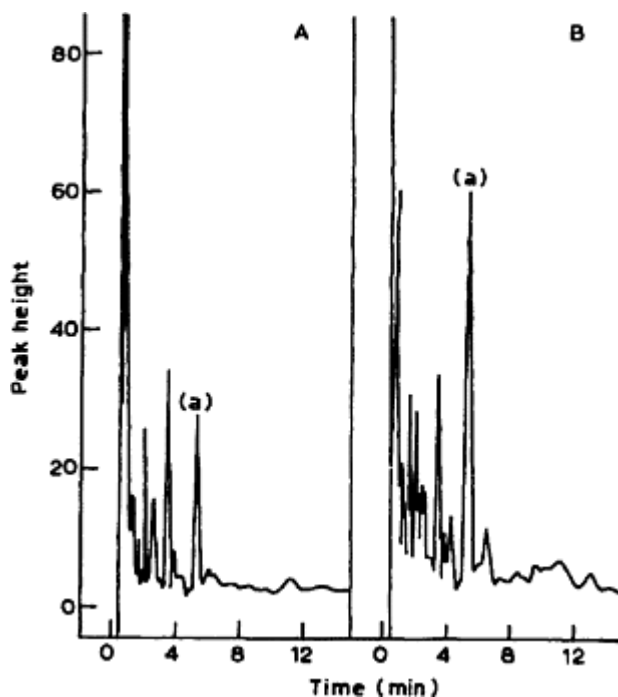


Fig. 2.47 Recorder tracings of selenium analysis of a river water sample: (a) analysis by procedure 2, (b) analysis by procedure 3 (see text)

Source: Reproduced with permission from the American Chemical Society [673]

Table 2.45 Analysis of simulated mixtures of 4.6ng of Se(O), 4.8ng of Se(IV) and 5.9ng of

	<i>Distilled water (500ml)</i>		
	<i>Peak height</i>	<i>Amount recovered ng</i>	<i>Recovery %</i>
Procedure 1	16.3	4.9	102
(Se(V))	15.0	4.5	94
Procedure 2	31.2	9.5	101
(Se(O)+Se(IV))	30.5	9.3	99
Procedure 3	51.9	15.9	104
(Total Se)	52.2	16.0	105

Source: Reproduced with permission from the American Chemical Society [673]

is calculated from the difference between the peak heights of 4, 6-dibromopiazselenol in these chromatograms. The amounts and oxidation states of selenium in river water in Japan are shown in Table 2.46. The total amount of selenium in river water varied greatly, eg from 16 to 230ng L⁻¹.

Table 2.46 Determination of selenium in river water

Sample ^a	ng L ⁻¹			
	Se(-II, O)	Se(IV)	Se(VI)	Total Se
Yoshii River, Okayama Pref. Feb 5, 1979	12	16	202	231
Takahashi River, Okayama Pref Feb 5, 1979	5	4	7	16
Asahi River, Okayama Pref Feb 5, 1979	11	<2	9	20
Asahi River, Okayama Pref Feb 17, 1979	11	2	3	16

^aSamples contained 1mL⁻¹ of concentrated hydrochloric acid

Source: Reproduced with permission from the American Chemical Society [673]

2.90.8 Sample preservation

Cheam and Agemian [681] studied the preservation and stability of inorganic selenium compounds at µg L⁻¹ levels in non saline water samples. They adopted the use of sulphuric acid as the preserving medium as this was found not to interfere with the hydride generation method they adopted for the determination of arsenite and arsenate. They found that the use of polyethylene sample containers and pH adjustment to 1.5 (with 0.2 vol% sulphuric acid) provided optimal conditions for the preservation of samples for periods of up to 125 days. Storage at 4°C also preserves samples effectively over the same time span.

2.90.9 Preconcentration

The application of preconcentration to selenate and selenite is discussed in sections 15.1.9 and 15.1.13.

2.91 Silicate

2.91.1 Spectrophotometric methods

Spectrophotometric methods for the determination of silicon in water are based on the

formation of silicomolybdenum blue. Reagents used for the reduction of β -silicomolybdic acid to methylene blue include sodium sulphite-4-amino-3-hydroxynaphthalene-1-sulphonic acid [682,683], sodium sulphite-metal [684] stannous chloride-glycerol [685] and stannic chloride-ascorbic acid-oxalic acid [684].

Pavlova *et al.* [685] extract the silicomolybdic acid into butanol or isoamyl alcohol prior to reduction to methylene blue in order to improve the sensitivity of the method.

Kasahara *et al.* [686] collect the methylene blue on a solvent soluble membrane filter which is then dissolved in N,N-dimethylformamide and determined spectrophotometrically. The detection limit of this method is $0.5\mu\text{g SiO}_2 \text{ L}^{-1}$.

Yoshimura *et al.* [687] determined silicic acid in non saline water at the $\mu\text{g L}^{-1}$ level or lower by gel-phase colorimetry based on the direct measurement of absorbance of molybdenum blue adsorbed on Sephadex gel.

Pakalns [688] studied the effect of surfactants on the spectrophotometric determination of silica. Three molybdenum blue methods using different reducing agents were used; 1-amino-2-naphthol-4-sulphonic acid [689], sodium sulphite [690] and ascorbic acid [691]. Pakalns [692] studied anionic, cationic and non-ionic detergents also sodium triphosphophosphate, and sodium pyrophosphate. Interferences were very large for the cationic and non-ionic detergents, but negligible for the biodegradable linear alkyl sulphate type detergents. The amino-naphthol-sulphonic acid method is recommended.

The National Water Council UK [693] has published two spectrophotometric methods for the determination of soluble molybdate reactive silicon (mainly monomeric and dimeric silicic acids and silicate); the first is based on the use of ascorbic acid for the reduction step, and the second is based on the use of 1-amino-2-naphthol-4-sulphonic acid to effect the reduction when analysing clean waters, especially those of low silicon content. In addition three alternative pretreatments are described for converting other forms to soluble molybdate-reactive silicon. The method with ascorbic acid as the reducing agent is particularly suited to a wide range of silicon concentrations up to 100mg L^{-1} measurements being made in 10mm cells at 700nm, but it is claimed to be easily modified for higher or low sensitivity.

Greenberg *et al.* [694] and Babulak and Gildenberg [695] determined silicate spectrophotometrically by means of the molybdenum blue method in which the extinction of the silicomolybdate complex is measured at 810nm. Ascorbic acid is added to reduce the silicomolybdic acid to the silicomolybdobblue complex. Phosphate interference is avoided by the addition of oxalic acid.

2.97.2 Spectrofluorometric method

A special and indirect method for the determination of silicon consists in the formation of molybdosilic acid, extraction with isoamyl alcohol, re-extraction with ammonia and determination of molybdenum by the formation of the molybdenum-carminic acid complex [696]. This method is used for the determination of silicon in hydrofluoric acid, ammonia, sodium hydrogen carbonate and ammonium molybdate.

2.91.3 Gas phase chemiluminescence analysis

Fujiwara *et al.* [697] described the application of gas phase chemi-luminescence analysis to the determination of silicate in non saline waters. Silicate is converted to silane using lithium aluminium hydride in a Teflon tube heated to 200°C. The silane is collected and mixed with ozone and analysed by chemiluminescence analyses. The detection limit is 0.5 µg silicon (absolute); phosphorus and arsenic interfere.

2.91.4 Flow injection analysis

Fogg and Blelsn [5] have studied the application of this technique to the determination of silicate.

Workers at Tecator Ltd UK [698,699] have developed flow injection methods for the determination of 0.03–1.2 mg L⁻¹ silicate (as SiO₂) in non saline waters. In these methods ammonium molybdate at pH of approximately 1.2 reacts with silica and also with any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molybdo-phosphoric acid but not the molybdosilicic acid. The yellow colour produced is reduced by means of stannous chloride to heteropoly blue. The blue colour is more intense than the yellow colour and is proportional to the 'molybdate-reactive' silica. The colour is measured at 695 nm.

The application of this technique is discussed under multianion analysis in sections 14.4.1.3 and 14.4.1.4.

2.91.5 Atomic absorption spectrometry

Two methods based on atomic absorption spectroscopy [700,701] have been discussed for the determination of silicate as silicon in water.

Simmons [700] described a digestion technique using a hydrofluoric/ nitric acid mixture in which the hydrofluoric acid decomposes silicates by the reaction of fluoride with silica to form silicon tetrafluoride. The organic matter including the cellulose nitrate filter is destroyed by the oxidising action of nitric acid. The excess hydrofluoric acid is complexed with boric acid and the resulting solution is sampled automatically and analysed for silicon by atomic absorption spectrophotometry using a nitrous oxide acetylene flame.

The detection limit of this method is 0.1 mg L⁻¹ SiO₂ and the reproducibility at the 1–150 mg L⁻¹ SiO₂ range is ±5%.

2.91.6 Ion chromatography

Okada and Kuwamoto [702] have described an ion chromatographic method for the determination of silicate in non saline waters.

The application of this technique is also discussed under multianion analysis in section 12.2.5.

2.91.7 High performance liquid chromatography

Silicate has been determined by high performance liquid chromatography [654].

2.91.8 Preconcentration

The application of preconcentration techniques in the determination of silicate is discussed in section 15.1.10.

2.92 Succinate

2.92.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.93 Sulphate

2.93.1 Titration methods

Various titration procedures have been described for the estimation of sulphate. These include reaction with excess barium ions and back titration of excess barium, direct titration of sulphate with barium ions, and direct titration of sulphate with lead ions.

2.93.1.1 Reaction with excess barium ions and back titration of unconsumed barium

In one method [703] for the determination of sulphate in non saline waters, the sample is passed through a strongly acidic cation-exchange resin (H^+ form), aerated to remove carbon dioxide, then titrated with 0.1N sodium hydroxide to the methyl orange end-point to obtain the sum of sulphate, chloride and nitrate.

The titrated solution is acidified with 0.2N nitric acid and excess of 0.05N barium nitrate and then ethanol is added to precipitate barium sulphate. The solution is neutralised with 0.1N sodium hydroxide, made alkaline with aqueous ammonia, and a solution of metalphthalein and naphthol green (CI Acid Green 1) added. Unconsumed barium ions are titrated with 0.05N EDTA to a green colour to obtain the content of sulphate. The solution acid is made with 0.2N nitric acid, a small amount of aluminium sulphate added then naphthol green solution and ethanolic diphenylcarbazone added. Titrate with 0.05N mercuric nitrate until the solution is violet. The amount of chloride and the amount of nitrate are obtained by difference. Correction factors are determined by analogously treating water (but omitting the addition of barium nitrate and aluminium sulphate).

Duvivier [704] has described a potentiometric method which can be used for the continuous determination of sulphate ions in non saline waters. It is based on the

precipitation of sulphate ions with barium and the complexation of excess barium with EDTA at pH 10.5. A calcium electrode was used to indicate the end-point to avoid ionic exchange. The electrode was regularly reconditioned in slightly alkaline calcium chloride. The principal interference came from phosphates, but they were seldom present at high enough concentrations to cause serious errors. The relative error was 3% for 0.0001N sulphate and 0.66% for 0.01N.

2.93.1.2 Direct titration of sulphate with barium ions

Sulphate in non saline waters has been determined [705] by direct titration with 0.01N barium cyanate in acetone-water medium to the carboxyarsenazo (if phosphates absent) or nitchromazo (if phosphates present) end-point. Cations contained in non saline water were found to interfere and must be removed by prior cation exchange of the sample. In another method [706], sulphate is separated from interfering ions by passing the sample through a column of KU-2 resin (H^+ form), then the column is washed with water, the eluate is neutralised to the yellow colour of 4-nitrophenol with hydrochloric acid and two drops of acid in excess are added. To this solution is added an equal volume of acetone and 10 drops of 0.05% aqueous orthonilic K (3-(2-carboxyphenylazo)-6-(2-sulphophenylazo) chromotropic acid), and sulphate is titrated with 0.02N barium chloride to a colour change from blue-violet to pale blue.

To overcome interference due to calcium ions in non saline water in the determination of sulphate, Akos-Szabo and Inczedy [707] first mixed the sample with a cation exchange resin (H^+ form). To an aliquot of the clear liquid was added an equal volume of 96% ethanol and 30mg solid barium chloride. Sulphate was then titrated with 10m mol L^{-1} barium acetate solution using a radio frequency titration technique.

Savvin *et al.* [708] titrated sulphate in non saline water with standard barium chloride using 3-(2-carboxyphenylazo)-6-(2-sulphophenylazo) chromotropic acid as metallochromic indicator. Cations are first removed using a cation exchange column (H^+ form) and the detection limit is 1mg L^{-1} .

A standard UK method [709] determines sulphate in waters by indirect titrimetry with disodium ethylene diamine tetraacetic acid. In this method cations are replaced by hydrogen ions. On passing the sample through a bed of a strong acid cation exchange resin in the hydrogen form sulphate ions in the eluate are precipitated with excess barium chloride. The pH is adjusted to 11–12 with ethanolamine and excess barium determined by titration with standard 0.01M ethylene diamine tetracetic acid solution using o-cresol phthalein screened with naphthol green as indicator. Down to 1.5mg L^{-1} sulphate can be determined using a 100ml sample. Phosphate and chromate interfere but compensation procedures are available. Standard deviations range from 0.36mg L^{-1} sulphate at the 19.6mg L^{-1} level to 0.68mg L^{-1} sulphate at the 98.4mg L^{-1} sulphate level.

2.93.1.3 Direct titration with lead ions

Duvivier [710] titrated sulphate with standard lead nitrate solution in methanol medium and monitored the reaction with a lead-selective electrode. There was a maximal error of 1% in measuring 19.2mg L^{-1} sulphate. Interference from carbonate ions could be

eliminated by lowering pH to 4–4.3 using nitric or perchloric acid. Interference from calcium ions could be removed by an ion exchange process followed by titration with sodium hydroxide in the presence of methanol to pH 5.0.

Pakalns and Farrer [711] investigated the effect of several surfactants (cationic, anionic and non-ionic) and detergent builders (phosphates and nitriloacetic acid) in the method described by Duvivier [710].

The method can tolerate quite high concentrations (up to 2500mg L^{-1}) of all surfactants, particularly anionics, tripolyphosphates and soaps. Interference by high concentrations of metals can be eliminated by passing the acidified sample (pH 1.5) through a strongly basic cation-exchange column prior to titration of sulphate with lead nitrate. Chloride concentrations up to 400mg L^{-1} did not interfere.

Archer [712] titrated sulphate with standard lead nitrate using dithizone as indicator. Pakalns and Farrer [711] investigated the effect of several surfactants (cationic, anionic and non-ionic) and detergent builders (phosphates and nitriloacetic acid) in this method.

The method can tolerate quite high concentrations (up to 2500mg L^{-1}) of all surfactants, particularly anionics, tripolyphosphates and soaps. Interference by high concentrations of metals can be eliminated by passing the acidified sample (pH 1.5) through a strongly basic cation exchange column prior to titration of sulphate with lead nitrate. Chloride concentrations up to 400mg L^{-1} did not interfere. Pakalns and Farrer [711] also titrated sulphate with 0.01mol L^{-1} lead acetate in 1:1 acetone:water medium to determine sulphate in the range 0 to $50\mu\text{g}$. The extinction is measured at 430nm after 20min standing.

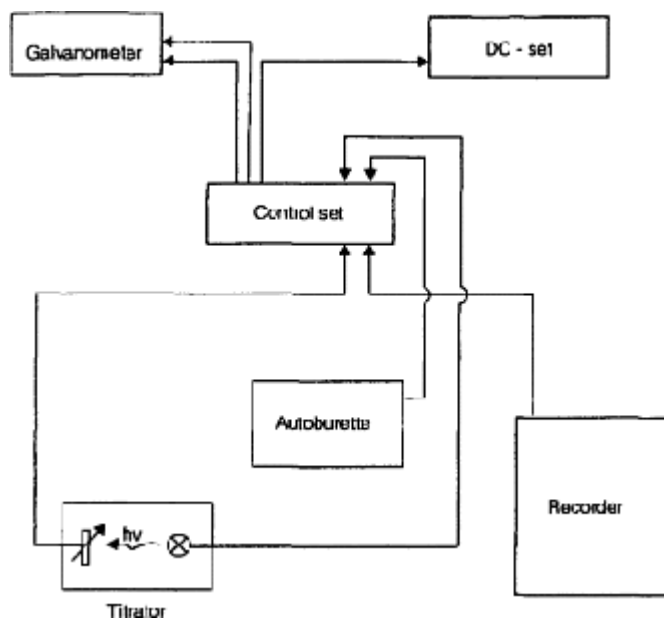


Fig. 2.48 Block diagram

Source: Reproduced with permission from the Swedish Water and Air

2.93.1.4 Spectrophotometric titration

Askne [713] has described a photometric titration procedure for determining low concentrations (2×10^{-5} – $20 \times 10^{-5} \text{ mol L}^{-1}$) of sulphate in non saline waters by measuring the intensity of the orange-coloured complex formed between thorin and excess barium ions from a solution of barium perchlorate.

The thorin method is based on the fact that sulphate ions in the sample solution are precipitated as barium sulphate through the addition of barium perchlorate via a burette. After the whole amount of sulphate is precipitated, further additions of barium ions form an orange-coloured complex with added thorin, the absorbance of which is measured at 520nm.

The titration is carried out in a medium comprising aqueous sample (20% by volume)-acetone (80% by volume). By addition of perchloric acid, the pH is adjusted to between 2.5 and 4. The sample should be cation exchanged (Dowex 50W×850–100 mesh) before titration to prevent cations from interfering by forming coloured complexes with thorin.

The titration can be carried out either manually using a microburette or automatically using an autotitrator unit linked to the spectrophotometer (Fig. 2.48).

Table 2.47 Chromogenic reagent, for the spectrophotometric determination of sulphate

Chromophore	λ max nm	Interferences	Limit of detection	Ref.
Excess 2-amino perimadine HCl added, unused reagent estimated	305	Slight with 500 mg L^{-1} acetate Cl, Br, I and 100 mg L^{-1} of PO_4 , NO_3 , F, Interference by IO_3 , SO_3 , SeO_4	$4\text{--}120 \text{ mg L}^{-1}$	[715]
Molybdosulphate complex micro 6(- <i>p</i> -acetyl-phenylazol)				[716]
–2-amino perimadine FeSO_4^+ Complex	325– 360		0.1nm	[717]
Thorin-thymolblue	–	Interference by humic acid	–	[718]
Thorin and thorium (measure decrease in extinction)	410	–	$0.2\text{--}0.5 \text{ mg L}^{-1}$	[719]
Thorn	520	All cations interfere, HBO_3 , As, ClO_4 , NO_3 , Cl, F, CN, PO_4 , S do not interfere	$0\text{--}8 \text{ mg L}^{-1}$	[720, 721]
Barium dimethyl Sulphonzo(III)	654	No interference – $\text{Cl} < 2 \times 10^{-2} \text{ mol L}^{-1}$ $\text{NO}_3 < 3 \times 10^{-2} \text{ mol L}^{-1}$ $\text{PO}_4 <$	–	[722]

$$1.5 \times 10^{-2} \text{ mol L}^{-1}$$

Reduction of SO_4 to sulphite by HCl -
acetic anhydric and
spectrophotometric determin-ation of
sulphide as Fe(III) phenanthroline
complex

510 –

[723]

Source: Own files

The automatic equipment consists of a control unit connected to the titrator. This contains a photocell, the resistance of which is 2 and 250k, respectively, in the directions forward-backward. The cell is connected via a switch either to the mirror galvanometer ($R_i=420\text{M}\Omega$, current for maximum scale deflection= $0.57\mu\text{A}$) (manual titration), or to a follower ($R_i=400\text{M}\Omega$) with an accompanying linear amplifier in the control unit (automatic titration). The follower and the linear amplifier are built from operational amplifiers.

The current from the photocell gives a voltage drop over the input of the follower which is amplified in the subsequent step. The amplified signal may be somewhat unstable and an RC-step is therefore used as an attenuation circuit.

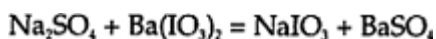
Table 2.48 Results of analyses of pure sulphate solutions

<i>Sulphate concn. given, $\mu\text{mol L}^{-1}$</i>	<i>Sulphate concn. found</i>	<i>Stand, dev $\mu\text{mol L}^{-1}$</i>	<i>% rel</i>
1.0	1.3	0.7	54
2.0	2.3	0.7	30
3.0	3.2	0.5	16
5.0	4.5	0.4	9
7.5	7.4	0.4	5
10.0	9.8	0.4	4
20.0	19.2	0.6	3
40.0	39.8	0.9	2.3
50.0	50.0	1.0	2.0
60.0	60.4	1.4	2.3

^aCalculated from six determinations

Source: Reproduced with permission from Springer Verlag [722]

Ion exchange with barium iodate achieved by passing the sample through a column of homologously precipitated barium iodate, leads to the following reaction [714]



Reaction of sodium iodate in the percolate with sodium iodide in hydrochloric acid medium leads to the production of an amount of iodine equivalent to the sulphate content of the sample. Iodine is titrated with 0.05N sodium thiosulphate to the starch end-point. In the determination of 250mg L⁻¹ sulphate in non saline water by this method, 250mg L⁻¹ of sodium, potassium, calcium, chloride or nitrate did not interfere. Phosphate (100mg L⁻¹) or bicarbonate (200mg L⁻¹) caused an error of +10%.

Some of the chromophoric reagents that have been used to estimate sulphate are reviewed in Table 2.47.

Reijnders *et al.* [722] have described the following batchwise photometric method for the determination of sulphate in water. In this method metal ions are removed from the sample by ion exchange and the sulphate reacts with the barium complex of dimethylsulphonazo(III) in an ethanolic medium. The optical absorbance of the complex indicates the sulphate concentration.

The results of determinations of pure sulphate solutions, containing 1–60μmol L⁻¹ sulphate are presented in Table 2.48. Table 2.49 shows the effect of different amounts of interfering substances on the results of sulphate standards. The lower limit of determination, defined as the concentration at which the coefficient of variance is 24%, was 2.6μmol L⁻¹

Table 2.49 Effect of different amounts of interfering substances on the results of sulphate standards

<i>Sulphate given</i> μmol L ⁻¹	<i>Interference</i>	<i>Sulphate found</i> μmol L ⁻¹
0	1	2.6
0	2	4
0	3	8
50	1	51
50	2	53
50	3	53
100	1	100
100	2	100
100	3	102

Key to interference:

1 No interferences

2 Sulphate and interference as specified in 3 in 1:1 dilution

3 Sulphate and 0.01mol L⁻¹ NaCl, 0.00 15mol KCl, 0.01mol L⁻¹ L⁻¹ NaHCO₃, 0.05mol L⁻¹ I Fe (NO₃)₃, 0.01mol L⁻¹ Ca(NO₃)₂

Source: Reproduced with permission from Springer Verlag [722]

of sulphate. Chloride, nitrate and phosphate do not interfere below concentrations of 2.10^{-2} , 3.10^{-2} and $1.5.10^{-3}\text{mol L}^{-1}$ respectively.

McKeller *et al.* [724] determined sulphate in non saline water indirectly by spectrophotometric titration of excess barium ions with ethylene-diaminetetraacetate. Parts per million of sulphate could be determined with a precision of $\pm 3\%$.

2.93.1.5 Automated titration procedures

Fishmann and Pascoe [725] studied the application of various automated titrimetric procedures to the determination of sulphate in non saline waters.

Henrikksen and Paulsen [720] have described an automated procedure for the determination of sulphate in natural salt water which involves precipitation of sulphate with barium perchlorate dissolved in isopropanol, and determination of excess barium by its complex with thorin. Cations are removed by an acidic cation exchange resin. The precision of the method is $\pm 0.05\text{mg L}^{-1}$ of sulphate over the range 0–8mg L⁻¹.

All cations interfere in this method. The following anions do not interfere below the concentrations (mg L⁻¹) given in parenthesis: H_3BO_3 (1000, acetate (1000), ClO_4^- (60), NO_3^- (60), Cl^- (25), F^- (10), HCN (1), PO_4^{3-} (1), HS^- (1). The interference from cations is eliminated by incorporating a strong acidic cation exchange column in the analytical system.

Airey *et al.* [414] have described a method for removing sulphide prior to the determination of sulphate anions in anoxic estuarine waters. Mercury(II) chloride, was used to precipitate free sulphide from samples of anoxic water. The sulphide-free supernatant was used to estimate sulphide by measuring the concentration of unreacted mercury(II), as well as to determine sulphate by a spectrophotometric method in which sulphide interferes. Sulphide concentrations in the range 0.5–180,000 $\mu\text{g L}^{-1}$ sulphur could be measured, while the lower limits for sulphate was 0.024 $\mu\text{g L}^{-1}$.

2.93.2 Spectrophotometric methods

Bjarnborg and Korhonen [718] tested manual spectrophotometric methods for sulphate using thorin and thymol blue and found that the former had a very narrow working range, and the latter was too sensitive to interference from humic substances. When a titrimetric method based on thorin was tested, the technique was acceptable even with highly coloured waters. When interference by humic substances was monitored, the titrimetric and automatic calorimetric thorin methods performed best, followed by a nephelometric method.

Toei *et al.* [716] carried out a spectrophotometric determination of micro amounts of sulphate in river waters using 6-(p-acetylphenylazol)-2-aminoperimidine.

Honjo and Hayashi [726] described precipitation and indirect spectrophotometric methods for the determination of sulphate in fresh water with lead nitrate and tetraphenylporphine trisulphonic acid. The method is based on the formation of insoluble

lead sulphate at pH 2.0–3.5 in the presence of ethanol. Excess lead(II) ions were determined with tetraphenylporphine trisulphonic acid in alkaline solution by measuring the absorbance at 464nm.

A method for determining sulphate in non saline waters based on measuring the excess barium ions following precipitation of barium sulphate was reported by Yin and Zhang [727]. In this case the excess barium ions was determined by titration with sodium tetraphenylborate. The method had a relative standard deviation of <1.4% based on 7 to 11 measurements of sulphate at 17.6–28.5ppm levels.

An indirect spectrophotometric method for determining sulphate in non saline waters has been developed by Kamaya and Murakami [728]. The sulphate reacts with barium nitranilate to form barium sulphate and displace the coloured anion which has a constant absorptivity at 300nm over the pH range of 2–9. The ions phosphate, thiosulphate, arsenite, arsenate, chromate, sulphite, oxalate, calcium and strontium all interfere.

Honjo *et al.* [726] discuss a spectrophotometric method for determining trace (6–10ppm) concentrations of sulphate in fresh waters based on precipitating sulphate as lead sulphate at pH 2–3.5 in the presence of 50–70% ethanol. The excess lead ions are reacted with tetraphenylpor-phinetrisulphonic acid at pH 10.9 and the absorbance is measured at 464nm.

Cheam and Chau [729] discuss the correction of historical colorimetric data for determining sulphate in coloured waters, and Bosch Serrat [730] discusses methods for minimising errors in the titrimetric determination of sulphate.

Greenberg *et al.* [731] and Colovas [732] have described a method for determining 0–60mg L⁻¹ sulphate in which cations are removed on an ion exchange resin and sulphate determined by the methyl thymal blue method at a wavelength of 460nm.

In a standard UK method [733] capable of determining down to 4mg L⁻¹ sulphate the sulphate is precipitated at pH 3.5 to 4.5 by 2-aminoperimidine and the precipitate isolated by centrifugation. The excess precipitant in the supernatant phase is determined by either direct uv absorbance measurements at 305nm or treatment with nitrous acid and alkali to give a red colour which is evaluated spectrophotometrically at 525nm.

2.93.3 Spectrofluorometric methods

Fluorometric methods for determining sulphate are mainly based on the ability of this anion to react with thorium ion to liberate an organic reagent that initially forms a complex with thorium. These methods are subject to interference from ions such as phosphate and fluoride. The method using thorium-salicylfluorone [734,735] is the most sensitive (0–2µg).

This thorium-morin system has been amply utilised to determine sulphate. Fletcher and Milkey [736,737] studied the thorium-morin system in a dilute acid medium and noted the serious interference of sulphate in the formation of the complex caused by the formation of sulphate complexes with thorium. Based on these interactions, a determination of sulphate has been developed by Guyon and Lorah [738]. This method is more sensitive than most existing methods, is rapid, manipulatively simple and adaptable to the determination of large numbers of samples. Vlasov *et al.* [739,740] have used this method to determine sulphate in weakly mineralised waters, and Nasu [741] to analyse

snow and river waters.

Nasu *et al.* [742] have also studied the determination of sulphate with the thorium-flavonol system. They have used it to analyse lake, river and mine waters in snow.

Thorium forms a light red non-fluorescent complex with salicyl-fluorone [9-(*o*-hydroxyphenyl)trihydroxyfluorone] in a weakly acidic medium, whereas free salicylfluorone in ultraviolet light gives a clear greenish yellow illumination [743]. If thorium is added to a solution of sulphate, followed by the reagent, part of the thorium becomes bound in the sulphate complex and part is liberated. The sensitivity of the reaction depends on the ratio of thorium to salicylfluorone and it increases when the concentration of thorium exceeds that of salicylfluorone.

A method has been proposed for determining sulphate in distilled water [735] based on the reaction with salicylfluorone [*a*-(*o*-hydroxy-phenyl)trihydroxyfluorone].

Hems *et al.* [311] studied the interference of zirconium with Calcein Blue(XV) and verified the positive interference that sulphate and fluoride ions produce on the fluorescence intensity of the complex. Based on this fact, Har and West [313] proposed two methods for the determination of both anions.

Nasu *et al.* [744] used the hydroxyflavone-thorium complex. The extinction at the absorption maximum at 390nm of the 1:1 complex decreases in the presence of sulphate owing to the formation of the sulphate complex of thorium. The blue fluorescence of the hydroxyflavone thorium complex at 470nm also decreases on addition of sulphate. The calibration graphs are almost rectilinear, and reproducible for 0.2–4.0 and 0.02–0.8mg L⁻¹ of sulphate in 30% aqueous ethanol at pH 2.4–2.7 and pH 2.5–3.0 by the spectrophotometric and fluorometric method, respectively. Interference is caused by iron (III), aluminium, zirconium, barium, fluoride and phosphate, organic anions, and other oxy-anions of sulphur.

A further fluorescence method [745] is based on the quenching by sulphate of the fluorescence of the thorin-thorin complex. Interfering ions are first removed by ion exchange. Down to 25µg sulphate can be determined.

2.93.4 Turbidimetric methods

Coleman *et al.* [746] compared barium chloride and 4-amino-4'-chlorobiphenyl hydrochloride as precipitants in the turbidimetric determination of sulphate at 430nm with barium chloride. Good results (coefficient of variation 1–4%) were obtained 30s after mixing. The performance with 4-amino-4'-chlorobiphenyl hydrochloride for measurements 20s after mixing was better (coefficient of variation 0.33 and 1.0% for 18 and 4µg mL⁻¹ of sulphate respectively); internal calibration for each run is recommended. In this method the reagent is stable for at least 1 month and there is no interference from up to 500mg L⁻¹ of phosphate.

Bonda *et al.* [747] described a column turbidimetric method for determining sulphate. The method uses solid barium chloride in crystals of 0.3–0.6mm diameter. The method is precise and reproducibility is good. The advantage of the method is the stability of the reagents and the speed, economy and simplicity of performance. Photometric determination is carried out over the range 460–540nm and the method may be used to

Table 2.50 The effect of surfactants on turbidimetric sulphate determination at various sulphate concentrations

Surfactant	mg L ⁻¹	% Recovery		
		5mg L ⁻¹ SO ₄	10mg L ⁻¹ SO ₄	20mg L ⁻¹ SO ₄
Cationic detergent 1000		101	103	104
Linear alkyl	0.2	99	103	100
Sulphate	0.5	107	103	100
	2.0	144	120	110
Non-ionic detergent	30	112	107	104
Formulated detergent	5	109	105	102
Mixed detergent	5	106	102	100
	20	120	118	105
Sodium pyrophosphate	100	103	107	110
Sodium tripolyphosphate	2	100	105	101
	5	101	106	108
Soap	2	112	110	103
NTA	500	100	99	103

Source: Reproduced with permission from Vodni Hospodorstri [747]

determine sulphate in the range 30–150mg L⁻¹ with a correlation coefficient of 0.99.

Cationic, anionic and non-ionic surfactants, polyphosphates and nitriloacetic acid are without interference in barium-based turbidimetric methods for the determination of sulphate (Table 2.50).

Krug *et al.* [748] have used continuous flow injection turbidimetry for the rapid determination of sulphate in non saline waters.

Slanina *et al.* [749] and Van Raaphorst *et al.* [750] claim a detection limit of 0.5mg L⁻¹ with a relative accuracy of 5% in the turbidimetric determination of sulphate in rain water.

Okawara and Kadota [751] compared the turbidimetric determination of sulphate in non saline waters by using 2-aminoperimidine and barium sulphate as precipitating reagents in the presence of glycerin and sodium chloride. The calibration plots were linear over the range of 0–10mg of sulphate L⁻¹. Use of 2-aminoperimidine gave the more sensitive method because of the smaller particle sizes formed. The coefficient of variation ($n=5$) was 1.4% when 2-amino-perimidine was used and 7.8% when barium sulphate was used for sulphate concentrations of 2mg L⁻¹.

2.93.5 Nephelometry

2-aminoperimidine hydrochloride yields a microcrystalline precipitate of the corresponding sulphate with solutions containing down to 0.05mg L^{-1} sulphate [752]. For the determination of sulphate, 0.5% aqueous reagent is added to the test solution, the mixture is diluted and a nephelometer reading is made after 5 to 10min and compared with the readings obtained with use of standard potassium sulphate solution. Many other anions also yield precipitates but, with the exception of iodide, fluoride, silicofluoride and phosphate, at least 10-fold amounts of most common anions are tolerated.

2.93.6 Flow injection analysis

Sulphate determination is one of the routine analyses encountered frequently in analytical laboratories. Besides the technique of ion chromatography [753,754] methods applicable to the analysis of sulphate are indirect. The analytical procedures usually include the precipitation of sulphate ions with barium or lead ions, followed by the turbidimetric, spectrophotometric or potentiometric determination of the precipitates formed or the remaining barium or lead ions in solution [755–768]. Among these methods, the potentiometric method has attracted continuous attention due to its convenience and ease of operation. Recently, the flow injection technique has been coupled with the lead ion selective electrode and used for the determination of sulphate (see section 2.93.6).

Kondo *et al.* [769] determined sulphate ion in river water by flow injection analysis at a rate of 30 samples per h. The method was applied to samples whose sulphate contents were typically less than 30mg L^{-1} . The reagent solution contains dimethylsulphonazo(II), barium chloride, potassium nitrate and chloroacetate buffer in 70% (v/v) ethanol, and is saturated with barium sulphate. The aqueous carrier stream is also saturated with barium sulphate. The sample is filtered and treated with Amberlite IR120 B cation exchanger before injection into the carrier stream, and the decoloration of the barium-dimethylsulphonazo(III) complex by sulphate is measured at 662nm. The calibration graph is linear over the range $0\text{--}30\text{mg L}^{-1}$ for sulphate in water.

A diagram of the flow system is shown in Fig. 2.49.

The absorption spectra of DMSA-III and its barium chelate are shown in Fig. 2.50. The absorption maxima are 586nm and 660nm for DMSA-III and its chelate, respectively. Measurement at 662nm provides the largest difference for the sulphate determination.

Maximum constant absorbance is achieved between pH 3.5 and 5.5, so the monochloroacetate buffer (pH 4.2) is again appropriate.

A calibration run obtained with 0mg L^{-1} sulphate standards had good reproducibility. Linear calibration graphs can be obtained up to 30mg L^{-1} sulphate, with a correlation coefficient of 0.999.

The effects of coexisting ions are listed in Table 2.51. Calcium ion in river water interferes with the determination. To prevent this, samples are

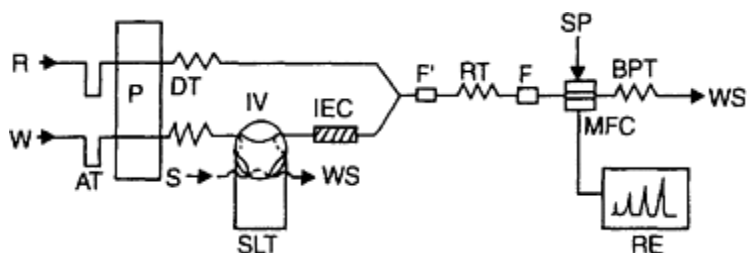


Fig. 2.49 Schematic flow diagram. R, reagent solution (dimethylsulphonazo (III)) 5.6ml of 10^{-2} mol L $^{-1}$ dimethylsulphonazo(III) solution, 5ml of 1mol L $^{-1}$ potassium nitrate, 3.9ml of 10^{-2} mol L $^{-1}$ barium chloride, 20ml of 1mol L $^{-1}$ chloroacetic acid-sodium chloroacetate buffer (pH 2.8) and 700ml of ethanol into a 1L volumetric flask and dilute to the mark with distilled water. Saturate the solution with barium sulphate in an ultrasonic bath and filter it through a Millipore filter (pore size 0.45 μ m). W, water saturated with BaSO $_4$; P, double plunger micro pump (2.0ml min $^{-1}$); AT, air trap; DT, damping coil (0.5mm $\times$ 20m); IV, injection valve; SLT, sample injector (1.0mm tubing 80 μ L); F, fine filter; RT, reaction coil 1mm $\times$ 5m); MFC, micro flow cell (1mm $\times$ 10mm); BPT, back pressure coil (0.5mm $\times$ 10m); W, waste; SP, spectrophotometer; R, recorder

Source: Reproduced with permission from Elsevier Science [769]

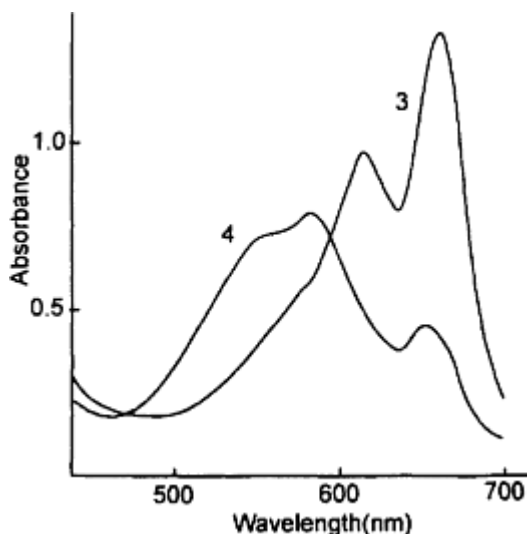


Fig. 2.50 Absorption spectra measured in 50 vol.% ethanolic solution against a water reference: (3) 2.5×10^{-5} mol L $^{-1}$ barium-dimethylsulphonazo-III; (4) 2.5×10^{-5} mol L $^{-1}$ dimethylsulphonazo(III)

Source: Reproduced with permission from Elsevier Science [769]

first passed through a column of cation exchange resin. The first 20ml of effluent is discarded and the next portion is used.

Table 2.51 Effect of co-existing ions

Ion	Added as	Conc. (mg L ⁻¹)	Found SO ₄ ²⁻ (mg L ⁻¹)	Ion	Added as	Conc. (mg L ⁻¹)	Found SO ₄ ²⁻ (mg L ⁻¹)
None	—	—	5.0	K ⁺	KCl	5×10 ⁻⁴	5.1
Cl ⁻	KCl	5×10 ⁻⁴	5.1	Na ⁺	NaCl	1×10 ⁻³	5.0
HCO ₃ ⁻	KHCO ₃	1×10 ⁻⁴	5.0	NH ₄ ⁺	NH ₄ Cl	5×10 ⁻⁴	5.0
NO ₃ ⁻	KNO ₃	1×10 ⁻⁴	5.0	Mg ²⁺	MgCl ₂ .6H ₂ O	1×10 ⁻⁴	5.0
H ₂ P ₄ ⁻	KH ₂ PO ₄	1×10 ⁻⁴	5.1	Ca ²⁺	CaCl ₂ .2H ₂ O	5×10 ⁻⁵	4.9
SiO ₃ ²⁻	Na ₂ SiO ₃	5×10 ⁻⁴	0.0	Fe ³⁺	FeCl ₃ .6H ₂ O	5×10 ⁻⁴	5.0

Source: Reproduced with permission from Elsevier Science [769]

Van Staden [770] has also described an automated turbidimetric determination of sulphate in non saline waters by flow injection analysis. One sampling loop of a two-position sampling valve is used to sample an alkaline buffer/EDTA solution, while the other loop is used alternately to sample water, thus avoiding acidification of water samples and lessening baseline drift. Residual precipitate is redissolved from the walls of the flow cell. The coefficient of variation for standard sulphate solutions and for water samples, containing 50–140mg L⁻¹ sulphate, is less than 0.95%. The procedure is suitable for carrying out 60 analyses per h.

A typical representative strip-chart recorder output obtained by this method at a sampling rate of 60 actual water samples per h is illustrated in Fig. 2.51. The negative peaks between samples are due to the alternate sampling of alkaline buffer-EDTA solution. Carry-over from one sample to another is negligible. No baseline drift was experienced.

Krug *et al.* [771] have used flow injection analysis for the turbidimetric determination of sulphate in non saline waters. They give details of equipment and procedures for a flow injection system with automated alternating streams of reagents for the turbidimetric determination of sulphate. The method is suitable for 120 samples per h with a relative standard deviation less than 1% for sulphate concentrations in the range 1–30mg L⁻¹.

Samples are injected into an inert carrier stream which is mixed with barium chloride to form a barium sulphate suspension. The range of the method can be extended to low concentrations by continuously adding sulphate to the sample carrier stream. System performance is improved by automatic alternate pumping of the reagent stream and an alkaline EDTA solution at high flow rate. All operations are controlled by an electronically-operated proportional injector-commutator.

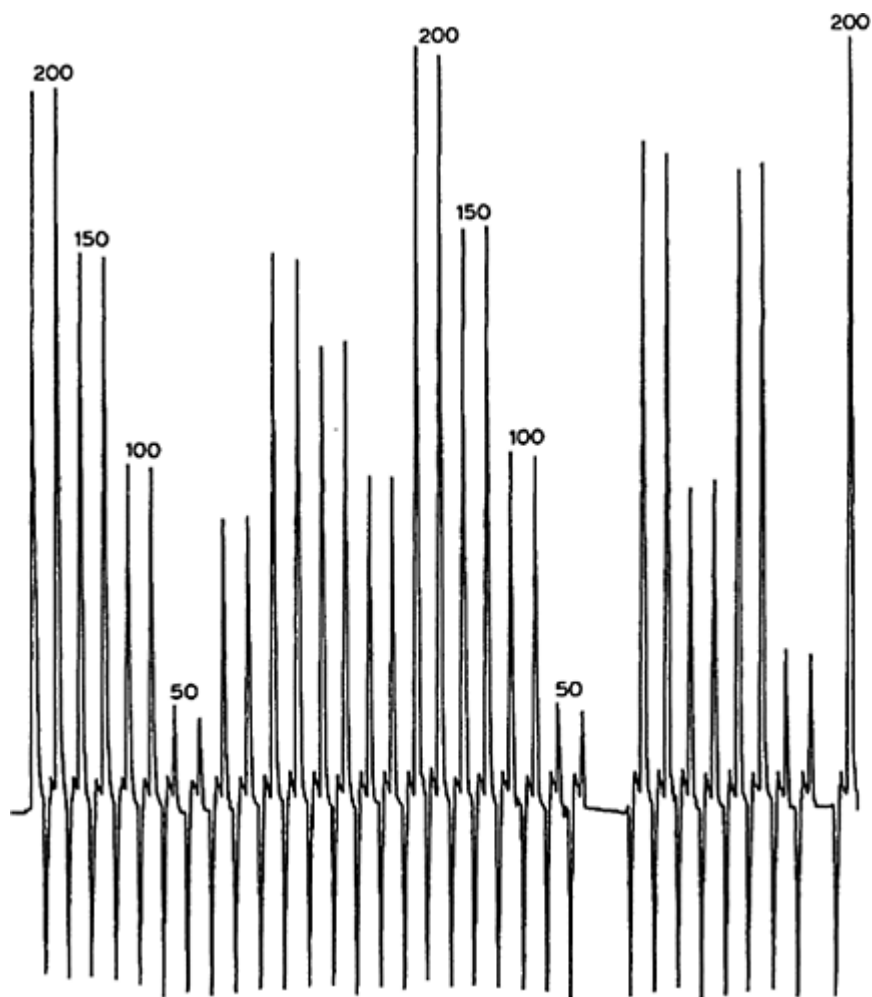


Fig. 2.51 Recorder tracing for the flow injection determination of sulphate in water. Recorder paper speed 30 cm h^{-1} . Recorder range 500 mV . Sulphate concentration in mg L^{-1} . Negative peaks due to alkaline buffer EDTA solution sampled

Source: Reproduced with permission from Springer Verlag [770]

After 1200 determinations, no baseline drift was noticed and changes in the slope of the calibration curves were very small (less than 5%), indicating good long-term stability. Also, relative standard deviations of measurements were in general about 0.5% when the sulphate content exceeded 10 mg L^{-1} .

Table 2.52 Comparison of procedures for the determination of sulphate in plant digests and non saline waters

<i>Plant</i>	<i>% S (dry matter)</i>		<i>Water sample</i>	<i>mg L⁻¹ SO₄²⁻</i>	
<i>Sample</i>	<i>Flow injection analysis</i>	<i>Manual gravimetric method</i>		<i>Flow injection analysis</i>	<i>Manual turbidimetric method</i>
01	0.30	0.25	109	11	10
12	0.25	0.24	114	18	18
16	0.32	0.29	122	25	23
22	0.30	0.27	125	21	23
36	0.26	0.26	134	16	15
79	0.46	0.46	192	32	29

Source: Reproduced with permission from Elsevier Science [771]

When 500mg L⁻¹ of calcium (as calcium chloride), hydrogen carbonate (as sodium hydrogen carbonate) or magnesium (as magnesium chloride) was added to the sulphate standards, no interference was detected for the water analysis systems. Also, recoveries ranging from 97 to 102% were assessed for the water system; interference from organic matter thus seems unlikely. It can be seen from Table 2.52 that the results obtained by the proposed methods compare well with those obtained by the standard turbidimetric procedure for water samples [772]. Colour interference can be corrected by running blanks, if necessary; this is easily done in the flow injection system by withdrawing the barium chloride from the R, reagent.

Non-turbidimetric flow injection analysis has also been used to determine sulphate in water. One such system employs dimethylsulph-onazo(III) as the reagent [773].

A diagram of the analytical system is shown in Fig. 2.52. It was not necessary to saturate the reagent solution with barium sulphate. However, it was necessary to saturate the carrier solution with barium sulphate to obtain high sensitivity and good reproducibility. Moreover, when not in use, it was necessary to fill the reaction coil with ethanol and water (1:1) to obtain high sensitivity.

Calcium interference was a serious problem when this method was applied to waters. This was overcome by passing the samples through a cation exchange resin, located just after the sample injection valve. The suppressive effect of calcium ion was almost eliminated by inserting the cation exchange column. Columns either 8 or 15cm in length showed almost similar effects. For the determination of 10mg L⁻¹ sulphate, other ions did not interfere within 5% negative errors up to the following concentrations: 30mg L⁻¹ of magnesium and ammonium, 50mg L⁻¹ of

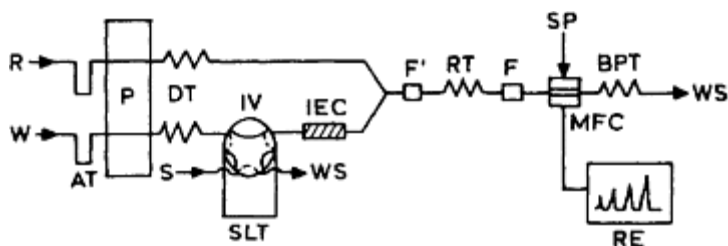


Fig. 2.52 Schematic flow diagram. R, reagent solution; W, water saturated with BaSO_4 ; AT, air trap; P, double plunger micro pump; DT, damping coil; IV, injection valve; S, sample injection; SLT, sample injector (1.0mm tubing 130 μL); WS, waste; IEC, cation exchange resin column; F, line filter; RT, reaction coil; SP, spectrophotometer; MFC, micro flow cell; BPT, back pressure soil; RE, recorder
Source: Reproduced with permission from Springer Verlag [773]

sodium, 80mg L^{-1} of potassium and 100mg L^{-1} (maximum concentrations tested) of chloride, nitrate, phosphate, hydrogen carbonate and silicate. These ions therefore did not interfere with sulphate determination at levels which are normally present in non saline waters. The lifetime of the cation exchange resin column was found to be at least two months when regularly used.

Calibration graphs were linear over the sulphate range 0–14mg L^{-1} and slightly curved over the range 14–32mg L^{-1} . The relative standard deviations of 20 analyses of solutions containing 6 and 10mg L^{-1} of sulphate were 0.94 and 1.2% respectively. The detection limit was found to be about 0.2mg L^{-1} of sulphate ion. The sampling rate was 20–30 samples per h.

Sonne and Dasgupta [774] carried out a simultaneous photometric flow injection determination of sulphate, sulphide, polysulphide, sulphite and thiosulphate.

Eremina *et al.* [775] used flow injection spectrophotometry to determine sulphate at concentrations of 0.5–20mg L^{-1} ; the sulphate in non saline waters masked the reaction of barium with Orthanilic K.

Van Staden [776] presented a procedure for the on-line automated monitoring of sulphate in effluent streams by reversed flow injection. The sampling capacity was 60 sulphate determinations per h, with alternate sampling of the barium chloride reagent and the buffer EDTA solution. Results compared favourably with those of normal flow injection and a standard automated segmented method.

Tang and Huang [777] have described a method for determining sulphate based on a potentiometry-based linear calibration graph. These workers point out that although various potentiometric procedures have been developed, a non-linear or semi-linear plot is usually obtained and used as the calibration graph, or the equilibrium constant for the reaction of sulphate with lead has to be known or determined in order to linearise the calibration graph [766–768]. This introduces either unpredictable uncertainties or tedious procedures. In order to overcome these drawbacks, the derived equations based on the behaviour of the lead ion electrode and the interaction between a sulphate-containing

solution and solid lead sulphate were derived and applied them to the potentiometric determination of sulphate in solutions. With this procedure, a linear calibration graph can be obtained from a plot of measured potential-related variables vs the concentration of sulphate in solutions. Similarly, by following the same procedures, a standard addition method can also be applied to the potentiometric determination of sulphate.

In this work, based on the behaviour of lead ion selective electrode and the interaction between a sulphate-containing solution and solid lead sulphate, equations describing the explicit linear relationships between the measured potential of lead in selective electrode and the sulphate concentration in sample solutions were derived and applied to the determination of sulphate by the flow injection analysis technique. These proposed procedures improved the sensitivity of the potentiometric method and the reliability of the analytical results. With a mixed solvent system (35 vol% methanol) a detection limit as low as $1.0 \times 10^{-3} \text{M}$ can be obtained optimistically.

The application of this technique is discussed under multianion analysis in sections 14.4.1.1, 14.4.1.4 and 14.4.1.6.

2.93.7 Atomic absorption spectrometry

In an indirect flow photometric method [778], sulphate is precipitated in hydrochloric acid medium by addition of a known amount of aqueous barium chloride, followed by flame photometric determination of excess barium in the filtrate at 493nm. Atomic absorption spectrophotometry has also been used to determine sulphate. Little *et al.* [779] precipitated sulphate as lead sulphate from 40% ethanol medium and unconsumed lead was determined by atomic absorption spectrometry. Siemer *et al.* [780] precipitated sulphate as lead sulphate. The precipitate was filtered off on a porous graphite cup which was then placed in a constant temperature Woodruff furnace for analysis of lead by non-resonance line atomic absorption spectrometry. Calcium and chloride had no effect on the determination but high phosphate levels enhance the lead signal. Non saline waters were analysed by this method and results compared well with those obtained by turbidimetric and gravimetric methods.

Montiel [781] reacted sulphate in a buffered medium with excess standard barium chloride. Unreacted barium was then determined by atomic absorption spectrometry at 553.55nm and the concentration of sulphate in the sample calculated. Errors due to the presence of alkali and alkaline earth metals are corrected by the incorporation of calcium in the standard solution and by the presence of sodium in the buffer solution.

Kokkenonen *et al.* [782] have carried out the indirect determination of sulphate (and sulphite) in non saline waters by flame atomic absorption spectrometry.

Englmaier [783] determined sulphate concentrations in non saline water by addition of barium ions, centrifugation of the precipitate, and atomic absorption spectrophotometric determination of the excess barium ions at 553.6nm, using cesium as a radiation buffer. The method gave a detection limit of 0.0352mg of sulphate L^{-1} and a reproducibility of 1.5% at sulphate concentrations of 0.5–20mg L^{-1} .

A standard UK procedure [784] is based on the addition of excess barium chloride solution to the sample and after precipitation of barium sulphate the excess barium is determined using atomic absorption spectrometry with an air-acetylene flame. This

method is capable of determining down to 5mg L^{-1} sulphate with a standard deviation ranging from 1.2mg L^{-1} at the 20mg L^{-1} sulphate level to 1.6mg L^{-1} at the 175mg L^{-1} sulphate level.

2.93.8 Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma atomic emission spectrometry has also been used to determine sulphate directly in non saline waters [785].

By monitoring the 180.73nm sulphur line, it was possible to detect 0.08mg L^{-1} sulphate with a precision of 0.8% RID at the 200mg L^{-1} sulphate level.

Cox *et al.* [786] have developed a rapid and sensitive method for determining sulphate in non saline waters based on flow injection inductively coupled plasma atomic emission spectrometry. A microcolumn of activated alumina in the acidic form was used in the flow injection manifold to preconcentrate sulphate before inductively coupled plasma atomic emission spectrometry determination at 180.73nm . The calibration curve was linear over the concentration range of $0\text{--}1000\mu\text{g L}^{-1}$, and the limit of detection (based on 2mL sampling volumes) was $2.8\mu\text{g L}^{-1}$. Relative standard deviation at 10 and $1000\mu\text{g L}^{-1}$ were 7.0 and 0.8% respectively.

2.93.9 Capillary coupling isotachoelectrophoresis

Bocek *et al.* [787] determined sulphate (and chloride) in mineral waters by this technique and Zelinski *et al.* [788] applied the technique to the determination of 0.02 to 0.1mg L^{-1} quantities of sulphate, chloride, fluoride, nitrate, nitrite and phosphate in river waters.

The application of this technique is discussed under multianion analysis in section 14.6.1.1.

2.93.10 Ion selective electrodes

In an indirect method [789], excess ferric ions are added to the sample to complex the sulphate. The solution is then titrated with barium chloride and liberated ferric iron detected with an iron-selective electrode. In another method [762], sulphate is titrated directly with 0.01mol L^{-1} lead perchlorate in the presence of 50% dioxan, the end-point being detected with a lead-selective electrode. The indirect method is subject to several interference effects. The direct method is subject to interference effects by metal ions and phosphate. Hulanicki *et al.* [790] eliminated ionic interferences in the determination of sulphates using a lead sensitised ion selective electrode. Jones *et al.* [791] studied interferences of a barium ion selective electrode used in the potentiometric titration of sulphate.

Hara *et al.* [767] have applied a continuous flow method using a lead-selective electrode for the determination of sulphate.

A solid state lead selective electrode has been used to estimate sulphate in mineral waters [792]. The sample is passed through two columns of strong cation-exchange resins, the first in the Ag^+ form (to remove chloride) and the second in the H^+ form (to remove bicarbonate). After adjustment of the pH of the effluent to between 5 and 6 ,

measure a volume, dilute with an equal volume of 1, 4-dioxan and titrate with, eg 5mmol L⁻¹ lead nitrate, using the lead-selective electrode to indicate the end-point. Down to 10mg L⁻¹ sulphate could be determined in the presence of up to a 10-fold excess of chloride. Phosphate interferes in the procedure.

Lukianets *et al.* [793] described a rapid method for the determination of sulphate in river water by potentiometry with a lead selective electrode using a hard membrane of lead sulphide and silver sulphide. The titrant was lead(II) perchlorate. Acetone was the most effective solvent for accelerating the precipitation process. Adsorption of sulphate ions on to the precipitant was prevented by addition of crystal violet solution. The method was unaffected by pH in the range 2–8. Calcium, magnesium, sodium and chloride did not interfere with sulphate determination. Carbonate interference was eliminated by adding acetic, perchloric and nitric acid. Analysis of river water using the method compared well with analysis by high frequency titration with barium acetate.

Workers at Orion Research Inc US [794] have described an ion selective electrode method using their Orion 960 lead electrode and Autochemistry system. This system determines the end-point of a lead perchlorate titration and calculates the concentration of sulphate in the sample. The standard deviation of this procedure is 0.87% at the 59mg L⁻¹ sulphate level.

2.93.11 Ion chromatography

Singh *et al.* [795] determined sulphate in deep sub surface waters by suppressed ion chromatography.

Conboy *et al.* [796] employed ion chromatography mass spectrometry to determine sulphate and ammonium compounds in non saline waters.

The ion spray liquid chromatography/mass spectrometry interface is coupled via a post-suppressor split with an ion chromatography system. The micromembrane suppressor selectively removes over 99.9% of the ion-pair agents required for ion chromatography from the eluent. The resulting solution consists of analyte, organic modifier, and water, which is compatible with ion evaporation mass spectrometry. A flow rate of 0.8 or 1.0mL/min from the column was split after suppression such that approximately 10–20µL/min was directed to the ion spray liquid chromatography/mass spectrometry interface, which was coupled to an atmospheric pressure ionisation mass spectrometer. This system provided a convenient way to effect isocratic and gradient separations of organic ions under chromatographic conditions incompatible with most forms of mass spectrometric ionisation. This work describes the separation and positive ion detection of quaternary ammonium drugs and tetraalkylammonium compounds of industrial importance using both single and tandem mass spectrometric detection (eg ion chromatography/mass spectrometry and ion chromatography/mass spectrometry/mass spectrometry). The former easily provided the molecular weights of these compounds while the latter gave some structural information. The limit of detection of 40pg injected on-column for tetra-propylammonium cation is a factor of 10 better than that obtained with the conventional ion chromatography detector. The separation, detection, and identification of some alkyl sulphates and sulphonates are also shown with negative ion

detection. Again, ion chromatography/mass spectrometry readily produced the molecular weights of these compounds while ion chromatography/mass spectro-metry/mass spectrometry provided some structural information.

The application of this technique is discussed under multianion analysis in sections 12.2.1, 12.2.4, 12.2.5 and 12.2.6.

2.93.12 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.1.1 and 13.1.1.4.

2.93.13 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.3.

2.93.14 Ion exchange chromatography

Stainton [797] has described an automated method for the determination of sulphate and chloride in non saline waters. An ion exchange resin is used to convert the sulphates and chlorides to their free acids. Detection is achieved by electrical conductance. The use of silver-saturated cation exchange resin to precipitate chloride permits distinction between chloride and sulphate. High levels of nitrate, orthophosphate and fluoride give positive interference for sulphate; bromide and iodide similarly interfere with chloride estimates.

2.93.15 Miscellaneous

A contribution to the classical gravimetric barium precipitation method for the determination of sulphate is that of Ferns and Torrades [798]. These workers showed that the detection limit of the method could be extended below the usually accepted levels. They achieved a detection limit of 1mg L^{-1} using 200ml water samples. It was essential to use a large excess of barium chloride to achieve these detection limits.

Meehan and Tariq [799] determined sulphate in the range 0.05 to 1.0mg L^{-1} by infrared spectroscopy by the KBr-pellet technique. Spectra were scanned from 1000 to 400cm^{-1} and the extinction at 619cm^{-1} was measured. Nitrate and nitrite do not absorb significantly between 800 and 600cm^{-1} , and sulphate could be determined with a coefficient of variation of 5% in the presence of 400- and 60-fold molar excesses of nitrate and nitrite respectively

Five different methods have been compared for the determination of sulphate in river waters [800]. These are a gravimetric method involving barium sulphate precipitation, two titrimetric methods involving either indirect titrimetry with EDTA or direct barium titrimetry, a method employing indirect atomic absorption spectrometry, and a method using excess 2-aminoperimidine to precipitate sulphate, with two possible variants for estimation of the excess reagent. Details of the range of application, possible interferences and sensitivity of the method are given in each case.

Krug *et al.* [748] have used continuous flow injection turbidimetry for the rapid determination of sulphate in non saline waters.

Bonda *et al.* [747] described a column turbidimetric method for determining sulphate. The method uses solid barium chloride in crystals of 0.3–0.6mm diameter. The method is precise and reproducibility is good. The advantage of the method is the stability of the reagents and the speed, economy and simplicity of performance. Photometric determination is carried out over the range 460–540nm and the method may be used to determine sulphate in the range 30–150mg L⁻¹ with a correlation coefficient of 0.99.

Titration with 0.01M lead acetate in 1:1 acetone: water medium has been used [875] to determine sulphate in the range 0–50µg. The extinction is measured at 430nm after 20min standing.

Cationic, anionic and non-ionic surfactants, also polyphosphates and nitriloacetic acid are without interference in barium and lead based turbidimetric methods for the determination of sulphate.

Cronan [801] has discussed the determination of sulphate in organically coloured water samples.

A piezoelectric crystal has been used to determine sulphate in non saline waters at concentrations of 0.5–10mg L⁻¹ [802]. The sulphate was precipitated as barium sulphate on the crystal, and the oscillation frequency of the crystal was inversely proportional to the mass of precipitate. Barium sulphate was removed from the crystal with EDTA.

2.94 Sulphide

2.94.1 Titration methods

Wronski [803] determined µg L⁻¹ levels of sulphide in non saline waters by thiomercurimetric titration. The procedure consists of separation of hydrogen sulphide as bis (triethyl-lead) sulphide by precipitation with triethyl-lead chloride in hexanol followed either by direct titration with o-hydroxymercuribenzoic acid in the presence of dithizone or by fluorometric titration in hexanol-ethanol with tetramercurated fluorescein (excitation at 520nm). The fluorometric procedure is applicable to concentrations of hydrogen sulphide of greater than 0.01 µg L⁻¹ and the direct titration which determines thiols and sulphide is applicable to concentrations above 2µg L⁻¹. For the direct titration, thiols are removed with acrylonitrile and hydrogen cyanide with formaldehyde. Thiols, cyanide, xanthates and dithiocarbamates do not affect the end-point of the fluorometric titration. Neither method is affected by the common ions present in non saline water samples.

Dyrssen and Wedborg [804] determined sulphide (polysulphides, thiosulphates, sulphites and thiols interfere) in non saline water by titration with mercury(II) solutions. The stoichiometry of the titrations were calculated using selected values of relevant stability constants. Mathematical functions for the evaluation of the titrimetric equivalence points were derived. The presence of halide ions interfered only in the titration of sulphite by the formation of halide complexes.

Sulphide has been determined [805] in non saline water by potentiometric or visual

titration with standard solutions of caesium octacyano-molybdate ($\text{Cs}_3 \text{Mo} (\text{CN})_8$) or caesium octacyanotungstate ($\text{Cs}_3 \text{W} (\text{CN})_8$) ions. With the former titrant, the reaction is carried out in 0.05mol L^{-1} borate buffer at pH 9.5. With the latter titrant the reaction is carried out in 0.05mol L^{-1} phosphate buffer at pH 11.5. Methylene blue is used as indicator in the visual titration procedure. In the determination of 1–40mg of sulphide the average error was $\pm 0.14\%$. Dithionite and sulphite also react but there is no interference from sulphate or thiosulphate ions.

A standard UK method [806] describes the determination of sulphide hydrogen sulphide liberated from the sample by acidification and carried by a stream of carbon dioxide into zinc acetate solution. Standard 0.01417M potassium iodate-iodine is added and excess iodine titrated with 0.0125M or 0.25M sodium thiosulphate. Down to 0.26mg L^{-1} sulphide can be determined with a standard deviation ranging from 0.19mg L^{-1} at the 4.75mg L^{-1} sulphide level to 0.7mg L^{-1} at the 26.4mg L^{-1} sulphide level.

2.94.2 Spectrophotometric methods

Spectrophotometric methods for sulphide have been developed based on the use of the following chromogenic reagents; NN-dimethyl-p-phenylene diamine (methylene blue methods) [807,808] sodium nitro-prusside [809,810], 1, 10-phenanthroline-ferric chloride [811], methylene blue [812,876], bis-2,9-dimethyl-1, 10-phenanthroline copper ion [813], and copper quinolin-8-olate [814]. The latter two methods are based on solvent extraction of the coloured produced formed with sulphide followed by spectrophotometry.

Caspiery *et al.* [810] automated the nitroprusside procedure using an AutoAnalyser. The samples are treated in a reproducible manner, and the colour is measured after a definite time from addition of the reagents. The inclusion of a distillation step increases the selectivity of the procedure and eliminates the necessity for filtration. The precision is satisfactory in the concentration range $1\text{--}10 \mu\text{g L}^{-1}$ of sulphide and is slightly better than that for the manual procedure. The coefficient of variation at the 10mg L^{-1} level for the AutoAnalyzer and manual procedures are 4.2% and 3.6%, respectively. If high selectivity is not required, the distillation of hydrogen sulphide may be omitted. At a sampling rate of 40 per h, 250 samples can be analysed daily.

Bethea and Bethea [809] overcame some of the problems encountered in this method by lengthening the mixing coils and alternating reagent flow rates. A detection limit of 0.05mg L^{-1} sulphide was achieved.

In the methylene blue procedure [808] ferric chloride and NN-dimethylphenylene diamine is added to the sample to form methylene blue. After 20min the extinction is measured at 670nm. The method is applicable to waters containing between 0.03 and 32mg L^{-1} of sulphide. Within this range, Beer's law is obeyed and the method is free from salt effects and temperature dependence. The precision is $\pm 2\%$ at the 95% confidence level.

Grasshoff and Chau [807] automated the methylene blue procedure using an AutoAnalyser.

Ceba *et al.* [815] developed a method which is claimed to be a simple, rapid, sensitive and selective means of determining microgram levels of sulphide in water. The technique involves the use of chloroform solutions of copper quinolin-8-olate, which are re-

extracted by aqueous solutions of sulphide, for the indirect spectrophotometric determination of sulphide. The effects of variables on the decolouration of the coloured complex by the aqueous sulphide were established, and the presence of other sulphur anions (sulphite, thiosulphate, and thiocyanate) did not interfere. Results compared favourably with those from the methylene blue method.

A study of the effect of other ions was carried out by preparing a series of synthetic samples containing 40.0 µg of sulphide and variable amounts of foreign ions. The results obtained for binary mixtures are summarised below.

Relative amount tolerated	Ion tested sulphide mg L ⁻¹
Na, K, Cl, NO ₃ , SO ₄ , Ca, Mg, Ba, Sr	25–400
NO ₂ , S ₂ O ₃ , CNS, SO ₃	100–125
tartrate, citrate, PO ₄ , F, BO ₃	25–50
Al, EDTA, CN	1–8

As can be seen, the procedure is highly selective and some results, especially for the sulphide mixtures with thiosulphate, have analytical interest, eg the relative amount of thiosulphate tolerated is greater than that in the methylene blue method.

The recommended method was tested by applying it to the determination of sulphide in water samples. A sample was prepared by adding a known amount of sodium sulphide to a sample of Guadiana River water. The decrease in the sulphide concentration in this sample was studied as a function of time in order to establish the evolution of a possible accidental spill. The results obtained are given in Table 2.53 together with those obtained by using the methylene blue method. These results agree for concentrations of sulphide in the range 0.5–1.0 mg L⁻¹ whereas for sulphide concentrations greater than 1.0 mg L⁻¹ the methylene blue method gives values higher than the method described by Ceba *et al.* [815]. To confirm the above results, two synthetic samples of water were prepared with the following composition: 5 mg L⁻¹ of aluminium, 10 mg L⁻¹ of sodium, 10 mg L⁻¹ of potassium, 30 mg L⁻¹ of magnesium, 30 mg L⁻¹ of calcium, 185 mg L⁻¹ of chloride, and 1.25 or 0.9 mg L⁻¹ of sulphide. The results obtained as a function of time are given in Table 2.54.

Broderius and Smith [816] have developed a procedure for the determination of traces of sulphide in non saline waters in which compressed nitrogen is bubbled through the sample to displace hydrogen sulphide which is collected in a glass bead column and measured colorimetrically.

Table 2.53 Evolution of the sulphide concentration in a sample of Guadiana river water

Time/min	Re-extraction method		Methylene blue method	
	Decoloration value	S ²⁻ found/ mg L ⁻¹	Absorbance	S ²⁻ found/ mg L ⁻¹
10	0.853	1.15	0.605	1.28

30	0.831	1.11	0.571	1.20
60	0.722	0.98	0.456	0.98
90	0.679	0.92	0.448	0.95
120	0.613	0.82	0.395	0.84
150	0.561	0.76	0.361	0.77
200	0.419	0.58	0.280	0.60
240	0.328	0.44	0.230	0.48

Source: Reproduced with permission from the Royal Society of Chemistry [815]

2.94.3 Spectrofluorometric methods

A rapid and sensitive method has been developed for the determination of microgram amounts of sulphide and cyanide [262]. This method depends on the demasking of quinolin-8-ol-5-sulphonic (1) acid by sulphide from the non-fluorescent potassium bis(5-sulphoxino)-palladium (2). The liberated quinolin-8-ol-5-sulphonic acid then coordinates with the magnesium ion present to form a fluorescent chelate (3), which is a measure of the amount of cyanide or sulphide present. The reactions are shown below.

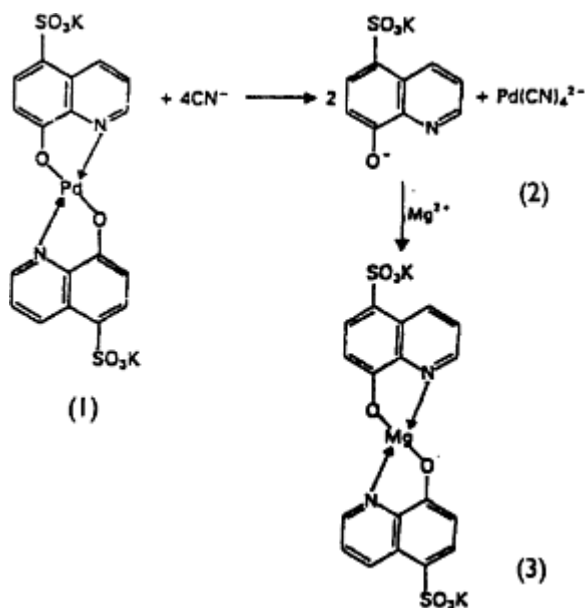


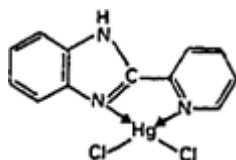
Table 2.54 Comparison of re-extraction spectrophotometric and methylene blue methods for the determination of sulphide

Time/min	Re-extraction method				Methylene blue method			
	Decoloration value		S^{2-} found/mg L ⁻¹		Absorbance		S^{2-} found/mg L ⁻¹	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
10	0.830	0.602	1.12	0.81	0.562	0.383	1.20	0.81
30	0.828	0.600	1.12	0.81	0.568	0.381	1.20	0.81
60	0.808	0.593	1.10	0.80	0.550	0.385	1.16	0.82
90	0.781	0.575	1.05	0.78	0.525	0.375	1.10	0.80
120	0.753	0.542	1.02	0.73	0.508	0.347	1.07	0.73

Source: Reproduced with permission from the Royal Society of Chemistry [815]

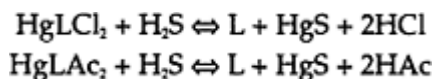
The oxidation of thiamine to thiochrome by oxidants such as permanganate is subject to interference by sulphides in the medium [817] because of the involvement of two competing reactions with permanganate, that of oxidation of thiamine and that of sulphide. A quenching method to determine sulphide has been proposed, with excellent reproducibility, but diverse ions can interfere by reacting with sulphide, thiamine or permanganate.

Bark and Rixon [818] described the determination of trace amounts of sulphide with mercury(II)-2,2'-pyridylbenzimidazole. This chelate, with the probable structure (4), is non-fluorescent and the free reagent is very



(4)

fluorescent. If the sulphide ion is added to the system containing the mercury(II) complex, mercury(II) sulphide is formed and an equivalent amount of the fluorescent organic ligand is released. Thus the fluorescence intensity of the system is increased. When a large excess of acetate buffer is added to the system, some of the chloride may be replaced by acetate and the authors suggested the following reactions for release of the ligand:



where L represents ligand and Ac represents CH_3COO^- .

Sulphide can be determined by its inhibitory action over the enzymatic activity of the

hyaluronidase enzymatic system [229].

A method [782,818] based on mercury(II) 2-(2-pyridyl) benzimidole is very sensitive, being capable of determining down to $0.3\mu\text{g L}^{-1}$ sulphate. The sample is acidified with acetic acid and the hydrogen sulphide formed is swept into the reagent buffered to pH 6.2–7.3. The fluorescence produced due to sulphide is measured at 381nm (excitation 311nm).

A simple and sensitive fluorometric method for determining sulphide in non saline waters is based on the blue fluorescence($\lambda_{\text{ex}} = 338\text{nm}$ and $\lambda_{\text{em}} = 450\text{nm}$) after alkylation with methyl p-toluenesulphonate and successive condensation reactions with taurine and o-phthalaldehyde at pH 8.0 [819]. Sulphide can be determined in the range of 0.03–5nmol/100 μL with relative standard deviations ($n=10$) of 1.6% at 0.2nmol and 2.7% and 3nmol. A 100-fold molar excess of each of the common anions did not interfere, except for cyanide, thiosulphate, sulphite and carbonate, the tolerance ratios of which were 5, 10, 30 and 50 respectively. Interferences due to metal ions such as calcium, magnesium and zinc can be masked by addition of EDTA, copper(II) and manganese(II) must be absent.

2.94.4 Flow injection analysis

A flow-injection method for determining sulphide has been reported by Aoki *et al.* [820]. A non saline water sample containing sulphide was mixed with sulphuric acid and injected into the outer tube of a microporous Teflon membrane separator. The generated hydrogen sulphide permeated through the membrane and gave a chemiluminescent reaction with the flowing luminol reagent solution in the inner tube of the separator. Chemiluminescent intensity was measured with a photomultiplier. The detection limit was $2.6\mu\text{g L}^{-1}$ and the relative standard deviation was 0.7%. Cobalt, copper and chromium ions did not interfere, and carbonate and nitrite had a negligible interference.

Milosavljevic *et al.* [821] have reported a preconcentrating gas diffusion flow injection analysis method with amperometric detection for selective determination of sulphide. The method has based on using the acceptor stream of the diffusion unit in a closed-loop, mobile (recirculating) mode for the accumulation of the analyte. In the analysis step the contents of the acceptor loop are injected into a sodium carbonate stream and are carried to the amperometric detector. The various flow patterns required for this method are regulated by a single eight-port rotary valve. The method developed has very low detection limits of $0.15\mu\text{g L}^{-1}$. The relative standard deviation for a $1\mu\text{g L}^{-1}$ standard is 4%, and of the potential interferences tested, only cyanide had an effect.

Sonne and Dasgupta [774] have carried out a simultaneous determination of sulphide, polysulphide, sulphate, sulphite and thiosulphate.

Kuban *et al.* [822] have described nitroprusside and methylene blue methods for silicone membrane differential flow injection determination of sulphide in water and wastewater. Hydrogen sulphide evolved from the acidified sample is collected in an alkaline acceptor. Down to $2\mu\text{g L}^{-1}$ sulphide can be determined.

The application of this technique is also discussed under multianion analysis in sections 14.4.1.1 and 14.4.1.4.

2.94.5 Polarography

Differential pulse polarography has been used [823] to determine sulphide in non saline waters. Java *et al.* [824] preconcentrated sulphide at concentrations ranging from 0 to $40\mu\text{g L}^{-1}$ on to a silver electrode. The electrode was preconditioned at a constant negative potential of 1.2V. The open circuit mode of the potentiostat was selected and the sample stirred for 10min, after which the current measurement mode was selected immediately. Peak currents or charges passing were compared with those obtained from standard solutions. The procedure was precise and reliable with a similar sensitivity to and better selectivity than conventional cathodic-stripping voltammetry. Sulphide at $\mu\text{g L}^{-1}$ levels was determined in non saline water samples, with a precision of 2%.

2.94.6 Ion selective electrodes

Studies on sulphide selective electrodes have been reported by various workers [825–832].

Al Hitti *et al.* [827] carried out direct potentiometric titration of sulphide sulphur in non saline water using standard cadmium sulphate solution as titrant and an electrode comprising silver deposited on to a carbon reed. The sensitivity of this procedure is 2mg L^{-1} sulphide.

Guterman and Ben-Yaakov [829] determined total dissolved sulphide in the pH range 7.5–11.5 by ion selective electrodes. Their instruments combine a sulphide ion activity electrode and pH glass electrode to produce a pH-independent output voltage that is proportional to total dissolved sulphide concentration.

Gulens [830] developed a portable monitor for measurement of total dissolved sulphide in non saline water based on the glass/sulphide electrode couple.

Tse *et al.* [831] used an electrode coated with electrochemically deposited N, N^I, N^{II}, N^{III} tetramethyl tetra 3, 4 pyridimoporphydazino cobalt(I) for the determination of sulphide ions.

2.94.7 Ion chromatography

Bond *et al.* [280] used ion chromatography to determine sulphide and cyanide in non saline waters. Peschet and Tinet [281] used this procedure to co-determine sulphide, hypochlorite and cyanide in ground waters.

Goodwin *et al.* [833] determined traces of sulphide in turbid waters by gas dialysis ion chromatography. Sulphide quantitation was achieved in zinc preserved samples by this technique with a $1.9\mu\text{g L}^{-1}$ detection limit, a precision of $0.64\mu\text{g L}^{-1}$ and a recovery of 98–101%.

Haddad and Heckenberg [834] converted trace levels of sulphide in environmental samples to a stable product by reaction with *N,N'*-dimethyl-*p*-phenylenediamine to form methylene blue, thus avoiding the major problems normally associated with ion exchange methods. Optimal chromatographic conditions were selected and the effects of various analytical parameters and interferences established. Ferrocyanide and ferricyanide at 10mg L^{-1} levels, which normally presented a major problem for spectrophotometric

methods, did not interfere with this chromatographic method. Calibration was linear for $1\text{--}2000\mu\text{g L}^{-1}$ sulphide and at $10\mu\text{g L}^{-1}$ the relative standard deviation was 3.7%.

The application of this technique is also discussed under multianion analysis in section 12.2.5.

2.94.8 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.1.

2.94.9 Micelle chromatography

The application of this technique is discussed under multianion analysis in section 13.5.1.1.

2.94.10 Gas chromatography

Radford-Knoery and Cutter [835] determined carbonyl sulphide and hydrogen sulphide species in non saline waters using specialised collection procedures and gas chromatography with flame photometric detection uncomplexed species. H_2Saq , HS^- , S^{2-} and particulate metal sulphides were determined. The procedure involved helium stripping of 300ml sample and liquid nitrogen trapping of the evolved gas followed by gas chromatography. The detection limit was 0.2p mole L^{-1} total dissolved sulphide.

Yamamoto and Tsuji [836] describe a variation of head-space gas chromatographic analysis for determining sulphide in non saline waters. Water samples ($10\text{--}100\mu\text{L}$) were injected into a chamber containing sulphuric acid and sodium sulphate. The generated hydrogen sulphide was stripped with nitrogen carrier gas and introduced into a gas chromatograph with a flame photometric detector. The method is suitable for analysis of small samples of water without pretreatment, allowing 0.02ppm of hydrogen sulphide in $100\mu\text{L}$ of water to be measured.

Lech and Bagander [837] determined sulphide in aqueous solutions using gas chromatography with a flame detector.

2.94.11 Preconcentration

The preconcentration of sulphide in non saline waters is discussed in section 15.1.11.

2.94.12 Miscellaneous

Garber *et al.* [838] compared various methods for the determination of sulphide in waters. These included methylene blue spectrophotometric procedures, iodimetric titration, automated analysis and coulometric procedures.

Zakhayavko *et al.* [839] compared various methods of determining sulphide in waters. Various volumetric photometric, spectroscopic and potentiometric methods were examined. The characteristics of these are tabulated. A potentiometric method having high selectivity and sensitivity (0.01mg L^{-1}) and suitable for the analysis of coloured

solutions had clear advantages for the determination of sulphide sulphur up to 500mg L⁻¹.

Khan *et al.* [840] reported a detection limit of 0.01µg mL⁻¹ for determination of sulphide in river water and wastewater based on staining lead acetate paper with hydrogen sulphide evolved from the samples.

Landers *et al.* [841] have discussed various methods for the determination of sulphides in non saline waters.

2.95 Sulphite

2.95.1 Titration methods

Bruno *et al.* [842] have described a procedure for the titration of sulphite in non saline water using standard cerium(IV) as titrant.

Sulphites can be determined in non saline waters by titration with mercury(II) solutions [663]. Sulphides, polysulphides, sulphates, thio-sulphates, halide ions and thiols interfere in this procedure.

Sulphite has been determined in water [843] by a process involving acidifying the sample with 6N hydrochloric acid and purging with nitrogen to strip out sulphur dioxide, which is then absorbed in a solution containing ferric iron (0.01mol L⁻¹) and 1,10-phenanthroline (0.03mole L⁻¹). The ferric iron is reduced to the ferrous state by the sulphur dioxide, and an orange tris-(1,10-phenanthroline)iron complex is formed, which can be quantified spectrophotometrically at 510nm after removal of excess ferric iron with 5% ammonium bifluoride. The effects of temperature and the removal of interferences are described. The detection limit is 0.01mg L⁻¹ sulphite.

The apparatus (shown in Fig. 2.53) consisted of a nitrogen gas source, stopcock or valve, 21min⁻¹ flow meter, 250ml gas washing bottle to purge the sample and a 100ml Nessler tube with a 50ml mark to absorb the sulphur dioxide liberated from the sample. The gas washing bottle had a coarse porosity 12mm diameter fritted cylinder gas dispersion tube. A similar gas dispersion tube was used in the Nessler tube. Polyethylene tubing was used for all connections with quick-disconnect tubing connectors on both sides of the gas washing bottle. It was found convenient to run several gas trains in parallel, since samples and standards could then be run at the same time and temperature.

The colour complex was quite stable after the addition of ammonium bifluoride. The absorbances vs distilled water were read at 510nm using either a 5cm cell for a range of 0–40µg sulphite per aliquot or a 1cm cell for a range of 0–120µg sulphite. A pipette was used to transfer the clear lower portion of the absorbing solution to the calorimetric cell after

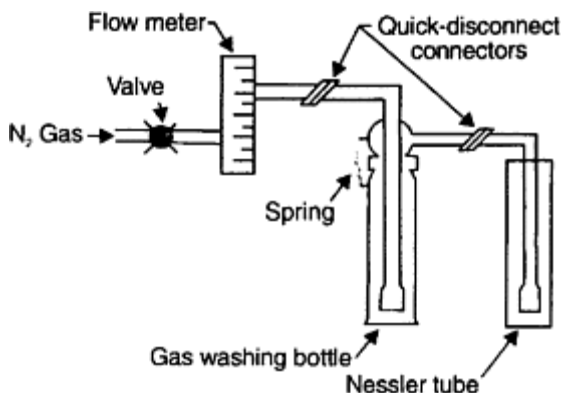


Fig. 2.53 Gas train apparatus for evolution and adsorption of sulphite

Source: Reproduced with permission from Elsevier Science [843]

allowing the octyl alcohol to rise to the surface. The concentration of sulphite ion was calculated from a calibration curve obtained by analysing a procedure blank and several stabilised sulphite standards.

Good agreement was obtained between results obtained by this procedure and those obtained by the standard iodometric procedure [844].

2.95.2 Spectrophotometric methods

Sulphite has been determined in water [843] by a process involving acidifying the sample and purging with nitrogen to strip out sulphur dioxide, which is then absorbed in a solution containing ferric iron and 1,10-phenanthroline; the ferric iron is reduced to the ferrous state by the sulphur dioxide, and an orange tris-(1,10-phenanthroline)iron complex is formed, which can be quantified spectrophotometrically at 510nm after removal of excess ferric iron with ammonium bifluoride. The effects of temperature and the removal of interferences are described. The detection limit is 0.01mg L^{-1} sulphite.

Good agreement was obtained between results produced by this procedure and those by the standard iodometric procedure [844].

Williams [845] and West and Gaebe [846] determined sulphite spectrophotometrically by the *p*-rosaniline method. Sulphate reacts with mercuric chloride to form a dichlorosulphurmercurate complex. After the addition of formaldehyde and *p*-rosaniline the coloured *p*-rosaniline-methyl sulphonic acid is formed and this is evaluated spectrophotometrically at 560nm.

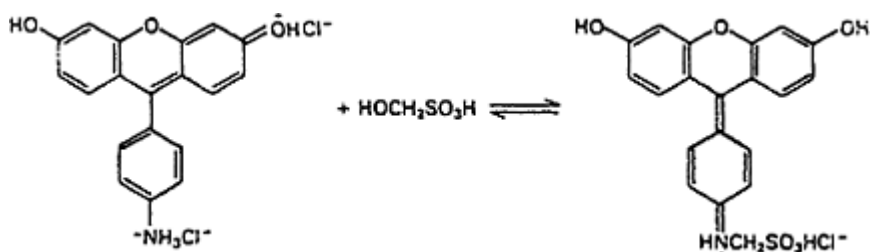
Sulphite, sulphate and dithionate have been determined spectrophotometrically in the presence of each other [293].

The sulphur(IV) catalysis of the oxidation of cobalt(II) by dissolved oxygen forms the basis of a spectrophotometric method for determining sulphite in aqueous solutions in non saline waters [847]. The cobalt(III) produced is reacted with azide to form a complex having a strong absorption at 365nm. A working range of 5×10^{-7} to $5 \times 10^{-5}\text{mol}$ of

sulphite L^{-1} is reported, and ways to avoid the only two relevant interferences, ferric iron and formaldehyde, are discussed.

2.95.3 Spectrofluorometric methods

A method for the determination of sulphur dioxide as sulphite by reaction with formaldehyde and 5-aminofluorescein has been proposed [848]. The simulated samples of trapped sulphur dioxide were made by dioxide dissolution of $\text{Na}_2\text{S}_2\text{O}_5$ in a solution with Na_2HgCl_4 and later reaction with formaldehyde. The aldehyde-bisulphite complex formed oxidises 5-aminofluorescein to a non-fluorescent product.



The probable result of the Schiff reaction is the formation of a quinoid structure. This structure shifts the double bond on the central (pyran) carbon atom so that the quinone in the upper ring is no longer the dominant structure, and the resulting compound is no longer fluorescent.

2.95.4 Chemiluminescence method

Al-Tamrah *et al.* [849] have described a flow injection chemiluminescence method for the determination of sulphite in water.

Takeuchi [850] describes a technique for determining trace amounts of sulphite in non saline waters based upon the chemiluminescent oxidation of nitrite. Various oxidising agents were evaluated and the special advantages of ferric sulphate are discussed as well as specially designed reaction cells. A detection limit of 0.08ng of sulphate L^{-1} was reported.

2.95.5 Continuous flow analysis

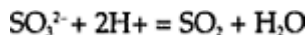
Continuous flow chemiluminescence analysis has been applied to the determination of sulphite and sulphur dioxide in water [851].

2.95.6 Flow injection analysis

Sonne and Dasgupta [774] carried out a simultaneous photometric flow injection analysis determination of sulphites, sulphate, sulphide, polysulphide and thiosulphate.

Workers at Tecator Ltd UK [852] have described a method for the determination of sulphite based on the injection of the aqueous sample into a carrier stream which is

merged with an acid stream. Sulphur dioxide is formed in the resulting stream.



This stream is diffused through a gas permeable membrane into a reagent stream containing formaldehyde which is then merged with a stream of *p*-rosaniline to form a red-purple complex which is measured at 560nm.

The application of this technique is also discussed under multianion analysis in section 14.4.1.1.

2.95.7 Ion selective electrodes

Sulphite (and thiosulphate) can be titrated potentiometrically with mercuric ions using a sulphide ion selective electrode as indicator electrode in 0.1N sodium hydroxide medium. Sulphide and polysulphides interfere in this procedure [853].

2.95.8 Enzymatic assay

Guilbault *et al.* [229] have shown that sulphite can be determined by its inhibitory action over the enzymatic activity of the hyaluronidase enzymatic system.

2.95.9 Ion chromatography

Ion chromatography has been applied to the determination of sulphite and arsenate [854], and sulphite and selenite [855] in non saline waters.

Grados *et al.* [856] have described an ion chromatographic method for the determination of sulphite in non saline waters in the presence of other anions. The application of this technique is also discussed under multianion analysis in section 12.2.5.

2.95.10 High performance liquid chromatography

A sensitive method for sulphite is based on high performance liquid chromatography followed by detection using inductively coupled plasma atomic emission spectroscopy [857].

2.95.11 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.1.

2.95.12 Micelle chromatography

The application of this technique is discussed under multianion analysis in section 13.5.1.1.

2.95.13 Miscellaneous

Bruno *et al.* [842] have described a procedure for the titration of sulphite in non saline water using standard cerium(IV) as titrant.

Gonzalez *et al.* [858] have described a method of kinetic multicomponent analysis based on miscellar analysis for the determination of sulphite and thiocyanate. The method is based on reaction with 5, 5'-dithiobis (2 nitrobenzoic acid) in aqueous cetyltrimethyl ammonium bromide miscelles. Down to $0.2\text{--}1.5 \times 10^{-4} \text{ mol L}^{-1}$ sulphite can be determined with a relative error of less than 5%.

2.96 Sulphonates

2.96.1 Column chromatography

This technique has been applied to the determination of sulphonates [161].

2.97 Tartrate

2.97.1 Spectrofluorometric method

Bishop [236] has proposed a spectrofluorometric method for the determination of tartrate.

2.97.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.97.3 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.1.4.

2.98 Tungstate

2.98.1 Atomic absorption spectrometry

This technique has been used to determine tungstate as the benzoin oxime complex in methyl isobutyl ketone extracts of non saline waters [859].

2.98.2 Inductively coupled plasma atomic emission spectrometry

Hall *et al.* [860] preconcentrated tungsten and molybdenum from natural spring water onto activated charcoal prior to analysis by inductively coupled plasma atomic emission

spectrometry and inductively coupled plasma mass spectrometry. The detection limit for both elements by inductively coupled plasma atomic mass spectrometry was $0.06\mu\text{g L}^{-1}$ and by inductively coupled plasma atomic emission spectrometry the detection limits were 1.2 and $0.4\mu\text{g L}^{-1}$, respectively, for tungsten and molybdenum.

2.98.3 Preconcentration

The preconcentration of tungstate is discussed in section 15.1.13.

2.99 Tellurate

2.99.1 Spectrophotometric methods

A spectrophotometric method utilising tetramethyl thiourea as chromogenic reagent has been described for the determination of tellurate in water [861].

2.100 Thiocyanate

2.100.1 Spectrophotometric methods

The spectrophotometric method for the determination of free cyanide in non saline waters described by Nagashima and Ozawa [862] has also been applied to the determination of thiocyanate.

A spectrophotometric method has been described for the determination of thiocyanate (and simple and complex cyanides) in water in which the sample is reacted with acid cuprous chloride and the released hydrogen cyanide absorbed in sodium hydroxide solution. The alkali is then acidified and reacted with chloramine-T to produce cyanogen chloride. A pyridine-pyrazolone reagent is added and the absorbance of the resulting blue dye is evaluated at 620nm [863].

Thiocyanate, after complexation with mercury(II) and *n*-phenylbenzo hydroxamic acid, has been determined spectrophotometrically [864].

2.100.2 Ion selective electrodes

Thiocyanate has been determined using a liquid membrane electrode [865].

2.100.3 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.100.4 High performance liquid chromatography

Stetzenbach and Thompson [138] employed high performance liquid chromatography on anion exchange columns to determine thiocyanate in admixture with chloride, bromide,

iodide and nitrate in non saline water.

The application of this technique is also discussed under multianion analysis in sections 13.1.1.2 and 13.1.1.4.

2.100.5 Micelle chromatography

The application of this technique is discussed under multianion analysis in section 13.5.1.3.

2.100.6 Gas chromatography

Nota *et al.* [866] have described a gas chromatographic headspace analysis technique for the determination of 0.01–100mg L⁻¹ thiocyanate (and cyanide) in coke oven effluents.

2.100.7 Miscellaneous

Gonzalez *et al.* [867] described the miscellar determination of mixtures of thiocyanate and sulphite. The method is based on reaction with 5,5'-dithiobis-(2-nitrobenzoic acid) in aqueous cetyltrimethyl ammonium bromide miscelles. Down to 0.5–1.5×10⁻⁴mol L⁻¹ concentrations of thiocyanate can be determined with a relative error of less than 5%.

Thieleman [868] attempted the separation of thiocyanate, cyanate and cyanide ions by thin layer and paper chromatography. Thin layer chromatography was not successful but these three ions were successfully separated by paper chromatography with the solvent methanol:pyridine:dioxan (7:2:1) in 7–8h. Cyanide and cyanate were identified by means of bromocresol purple and thiocyanate by 15% ferric chloride solution, as spray reagent. Carbonate ions have the same R_F value as cyanide and cyanate.

2.101 Thiosulphate

2.101.1 Titration methods

Thiosulphate (and sulphate) can be titrated potentiometrically with mercuric ions using a sulphide ion selective electrode in 0.1N sodium hydroxide medium [853]. Sulphite can be decomposed with formaldehyde and, consequently, thiosulphate can be titrated alone. Polysulphide and sulphide can be converted to thiosulphate and titrated. Thiosulphates can be determined in non saline waters by titration with mercury(II) solutions. Sulphides, polysulphides and sulphites interfere in this procedure [663].

2.101.2 Flow injection analysis

The application of this technique is discussed under multianion analysis in section 14.4.1.1.

2.101.3 Anodic stripping voltammetry

Differential pulse anodic stripping voltammetry has been used [869] to detect thiosulphate, a potential substrate for sulphuric acid forming thiobacilli. The method was selective for thiosulphate in the presence of hydrogen sulphide, sulphite, polysulphide and elemental sulphur. Reproducible results were obtained for thiosulphate concentrations of 3–5mg L⁻¹.

2.101.4 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.5.

2.101.5 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.1.3.

2.101.6 Micelle chromatography

The application of this technique is discussed under multianion analysis in section 13.5.1.3.

2.101.7 Preconcentration

The application of preconcentration is discussed in section 15.1.12.

2.102 Titanate

2.102.1 Spectrophotometric methods

Titanates have been determined spectrophotometrically in water extracts by a method based on reaction with *N*-*p*-methoxyphenyl-2 furo-hydroxamic acid which forms a golden yellow colour with an absorption maximum at 385nm with titanium(V). In this method [870] the titanate is reduced to titanium(III) with stannous chloride and then extracted with *N*-*p*-methoxy-phenyl-1–2-furohydroxamic acid in chloroform. The chloroform extract was then evaluated spectrophotometrically. Beer's law is obeyed over the range 0.5–10mg L⁻¹ titanate and 1.7mg L⁻¹ of titanium could be detected.

The following ions did not interfere when present at 50 times the concentration of titanate: Cu²⁺, Co²⁺, Zn²⁺, Hg²⁺, Ag⁺, Cd²⁺, UO₂²⁺, V⁴⁺, Fe²⁺, Fe³⁺, Al³⁺, La³⁺, Sc³⁺, Ga³⁺, Th⁴⁺, halides, acetate, carbonate, nitrate, oxalate.

2.103 Transaconitate

2.103.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.104 Trifluoroacetate

2.104.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.105 Triphosphate

2.105.1 Flow injection analysis

The application of this technique is discussed under multianion analysis in section 14.4.1.6.

2.106 Total alkalinity

See section 2.14.

2.107 Uranate

2.107.1 Spectrophotometric method

Kuroda *et al.* [871] observed that uranium is strongly absorbed from acidified saline solutions by a strongly basic ion exchange resin in the presence of azide ions. The distribution coefficient of uranium with 0.5mol L^{-1} sodium chloride increased rapidly with an increase in azide concentration, and was much higher than the coefficient obtained with hydrazoic acid alone. The sorbed uranium was easily eluted with 1mol L^{-1} , hydrochloric acid, and was determined spectrophotometrically. Recoveries of 98.3–99.6% uranium were obtained from artificial sea water containing $3.4\mu\text{g L}^{-1}$ uranium.

2.108 Valerate

2.108.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.2.4.

2.109 Vanadate

2.109.1 Spectrophotometric methods

Murthy *et al.* [872] determined vanadium(IV) and vanadium(V) in water by solvent extraction of the complexes with 2-hydroxy-acetophenone oxime followed by spectrophotometry.

Mori [873] described a spectrophotometric method for the determination of vanadate ion in non saline water which utilised *o*-hydroxyhydroquinonephthalein as the complexing agent. Hexadecyltri-methylammonium chloride and L-ascorbic acid serve as a reducing agent. The method was applied to the determination of total vanadium in the range of 0–8µg.

2.109.2 Spectrofluorometric method

Bishop [236] has discussed the fluorometric methods for the determination of vanadate.

2.109.3 Chemiluminescence method

Zhang [874] applied chemiluminescence analysis to the determination of vanadium in non saline waters. Oxidation of thiosulphate by hydrogen peroxide is catalysed by vanadate (VO_3^-) and is coupled to the chemiluminescent redox reaction of luminol and hydrogen peroxide. The detection limit is reported as 4.3×10^{-7} µg of vanadium L^{-1} with a relative standard deviation of 3.2% at 2µg L^{-1} vanadium.

2.109.4 Preconcentration

The preconcentration of vanadate is discussed in section 15.1.13.

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Chapter 3

Anions in seawater

3.1 Acetate

3.1.1 Ion chromatography

The application of this technique is discussed in section 12.3.1.

3.2 Acrylate

3.2.1 Ion chromatography

The application of this technique is discussed in section 12.3.1.

3.3 Alkalinity

3.3.1 Titration method

Among the possible analytical methods for alkalinity determination, Gran-type potentiometric titration [1] combined with a curve-fitting algorithm is considered a suitable method in seawaters because it does not require *a priori* knowledge of thermodynamic parameters such as activity coefficients and dissociation constants which must be known when other analytical methods for alkalinity determination are applied [2–5].

Alkalinity determination in hypersaline solutions by the Gran-type titration is subject to a number of errors which can usually be neglected in lower ionic strength solutions. For example, the pH readings along the titration path may be inaccurate due to the marked difference between the ionic strength and composition of the sample and the standard buffers used to calibrate the glass and reference electrode pair [6].

Ben Yaakov and Lorch [7] identified the possible error sources encountered during an alkalinity determination in brines by a Gran-type titration and analysed the possible effects of these errors on the accuracy of the measured alkalinity. Special attention was paid to errors due to possible non-ideal behaviour of the glass-reference electrode pair in brine. The conclusions of the theoretical error analysis were then used to develop a titration procedure and an associated algorithm which may simplify alkalinity determination in highly saline solutions by overcoming problems due to non-ideal behaviour and instability of commercial pH electrodes.

The titration procedure used was that described by Ben Yaakov *et al.* [8] in which

100ml seawater or brine sample is titrated in 30–50 burette increments with 3–5ml standard 0.1M hydrochloric acid using a pH electrode.

The accuracy of the method was tested experimentally by running duplicate titrations on distilled water, artificial seawater with and without sulphate and artificial Dead Sea waters. For each run, alkalinity was calculated by two methods:

- (1) by the conventional Gran plot which presumes that the glass electrode is properly calibrated and
- (2) by the method that applies the titration data for *in situ* calibration of the glass electrode by the slope correction algorithm.

The precision of the latter method when applied in the distilled water runs was found to be significantly better than the conventional method. This should be attributed to the non-stability of the glass electrode which is corrected for by the proposed algorithm.

3.3.2 Spectrophotometric methods

Various workers have discussed the determination of total alkalinity and carbonate [9–11] and the carbonate-bicarbonate ratio [11] in seawater. A typical method utilises an autoanalyser. Total alkalinity (T m-equiv. per litre) is found by adding a known (excess) amount of hydrochloric acid and titrating back with sodium hydroxide solution; a pH meter that records directly and after differentiation is used to indicate the end-point. Total carbon dioxide (C m-equiv. of HCO_3^- per litre) is determined by mixing the sample with dilute sulphuric acid and segmenting it with carbon dioxide free air, so that the carbon dioxide in the sample is expelled into the air segments; the air is then separated from the sample and passed into buffered phenolphthalein solution, thereby lowering the pH and diminishing the colour of the phenolphthalein. The reduction in colour is measured colorimetrically (540nm). The concentration of carbonate is given by $2(T - C)$ m-equiv. L^{-1} , and the concentration of bicarbonate is $2C - T$ m-equiv. L^{-1} .

A computer program has been used to calculate the magnitude of systematic errors incurred in the evaluation of equivalence points in hydrochloric acid titrations of total alkalinity and carbonate in seawater by means of Gran plots. Hansson [12] devised a modification of the Gran procedure that gives improved accuracy and precision. The procedure requires approximate knowledge of all stability constants in the titration.

3.4 Arsenate

3.4.1 Spectrophotometric method

Haywood and Riley [13] have described a spectrophotometric method for the determination of arsenic in seawater. Adsorption colloid flotation has been employed to separate phosphate and arsenate from seawater [14]. These two anions, in 500ml filtered seawater, are brought to the surface in less than 5min, by use of ferric hydroxide (added as 0.1M FeCl_2 , (2ml) as collector, at pH 4, in the presence of sodium dodecyl sulphate (added as 0.05% ethanolic solution (4ml)) and a stream of nitrogen (15ml min^{-1}). The

foam is then removed and phosphate and arsenate are determined spectrophotometrically [15]. Recoveries of arsenate and arsenite exceeding 90% were obtained by this procedure.

The application of this technique to the determination of arsenate is also discussed under multianion analysis in section 3.32.1.

3.5 Arsenite

3.5.1 Spectrophotometric method

See section 3.4.1 above, also multianion analysis in section 3.32.1.

3.6 Benzoate

3.6.1 Ion chromatography

The application of this technique is discussed in section 12.3.1.

3.7 Butyrate

3.7.1 Ion chromatography

The application of this technique is discussed in section 12.3.1.

3.8 Borate

3.8.1 Spectrophotometric method

Sato [16] has examined several α -hydroxy acids as complexing agents for the extraction-spectrophotometric determination of boron. Mandelic acid is the most useful. The boron-complex anion obtained is extracted into benzene with malachite green in a single extraction; boron is determined indirectly by measuring the absorbance of malachite green in the extract at 633nm. The calibration graph is linear over the range 7.50×10^{-7} – 1.50×10^{-5} mol L⁻¹ boron; the apparent molar absorptivity is

Table 3.1 The reagent blank and the apparent molar absorptivity (ϵ) with selected solvents and dyes

Solvent	Note	<i>Ethyl violet</i>	<i>Crystal violet</i>	<i>Malachite green</i>	<i>Methylene blue</i>
Chlorobenzene	blank	— ^a	0.46	0.10	0.17
		2200	17400	52000	

	£				
Benzene	blank	_ ^a	0.25	0.10	0.20
	£		19000	65200	15000
Toluene	blank	0.13	0.15	0.23	0.08
	£	4500	12000	13000	5000
Carbon tetrachloride	blank	0.18	_ ^b	_ ^b	_ ^b
	£	12000			

^aThe absorbance of the reagent blank was very high

^bThe ion-pair formed between the boron-complex anion and the dye was not extracted

Source: Reproduced with permission from Elsevier Science [16]

$6.52 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The method is applied to the determination of micro amounts of boron in waters with satisfactory results.

Various solvents and dyes were examined by Sato [16] to achieve the best determination of boron. The solvents examined were 4-methyl-2-pentanone, 1, 2-dichloroethane, dichloromethane, o-dichlorobenzene, chloroform, toluene, carbon tetrachloride, benzene, n-hexane and cyclohexane: the dyes tested were ethyl violet, crystal violet, malachite green and methylene blue.

The solvents can be classified into three groups:

- (1) the cationic dye itself is easily extracted without mandelic acid (4-methyl-2-pentanone, 1,2-dichloroethane, dichloromethane, chloroform and o-dichlorobenzene);
- (2) the ion-pair formed between the boron-complex anion and the dye is extracted (chlorobenzene, benzene and toluene);
- (3) the ion-pair formed between the boron-complex anion and the dye is not extracted (carbon tetrachloride except for the ethyl violet system, n-hexane and cyclohexane).

Accordingly, the group (2) solvents and carbon tetrachloride were examined further. Table 3.1 shows the practical results obtained by using these solvents. It is clear that the method based on malachite green and benzene should be the most suitable for the determination of boron. The method recommended in the experimental part was therefore worked out.

The absorption spectra of the reagent blank and the ion-pair formed between the boron complex and malachite green in benzene are shown in

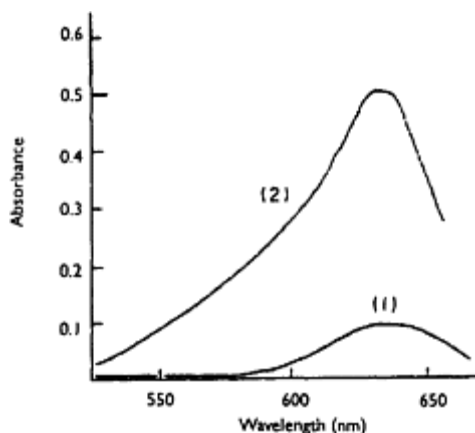


Fig. 3.1 Absorption spectra: (1) reagent blank; (2) $6.25 \times 10^{-6} \text{ mol L}^{-1}$ boric acid. Conditions: $2.5 \times 10^{-4} \text{ mol L}^{-1}$ malachite green, $2.5 \times 10^{-2} \text{ mol L}^{-1}$ mandelic acid, pH 3.0; benzene as reference

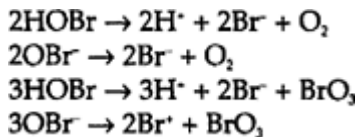
Source: Reproduced with permission from Elsevier Science [16]

Fig. 3.1. Malachite green itself was not extracted into benzene irrespective of the presence or absence of boron, when mandelic acid was absent. The wavelength of maximum absorption of each spectrum occurs at 633nm.

3.9 Bromate

3.9.1 Spectrophotometric titration and differential pulse polarography

Chlorinated waters are being discharged to estuaries and coastal waters in increasing quantities. In such systems the chlorine reacts with the natural bromide and ammonia at pH 8 to produce the highly toxic hypobromous acid, hypobromite ion and haloamines. For normal seawater of pH 8, the initial products of chlorination are a mixture of hypobromous acid and hypobromite ion. Both of these compounds are unstable with respect to decomposition and disproportionation.



Macalady *et al.* [17] report experiments in which chlorinated sea water was exposed to sunlight at various intensities, to simulate different periods of the day. The results of subsequent analyses for bromates and residual oxidants show that the rate and extent of bromate formation depend on the intensity of the sunlight, with none found in samples

kept

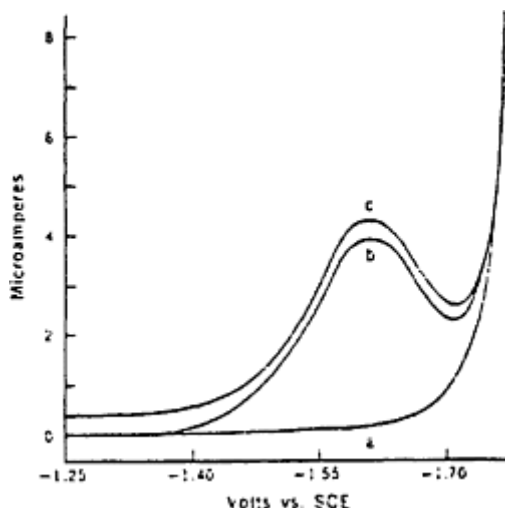


Fig. 3.2 Differential pulse polarographic verification of sunlight-induced bromate production in chlorinated seawater. Curve (a) polarogram from untreated seawater, seawater immediately after chlorination to 4.9ppm, or chlorinated seawater kept in the dark for 4h at 40°C. Curve (b) polarogram from chlorinated seawater exposed to full sunlight for 70min. Curve (c) standard: 1.0×10^{-6} M sodium bromate in seawater, offset with respect to curves (a) and (b). Polarograms were recorded at 25°C and pH 8.35; SCE, saturated calomel electrode
Source: Reproduced with permission from Springer-Verlag [18]

in the dark for 24h at 40°C It would appear that large amounts of bromate have already been produced in estuarine and coastal waters with unknown effects, as little information is available on the direct toxicity of the bromate ion.

Details of the chlorination experiment referred to above are now discussed in more detail.

After chlorination, beakers were removed from the sunlight at regular (usually 30min) intervals, placed in a dark box, and analysed for bromate and residual oxidants without delay. Residual oxidants analyses were performed by the I_3^- spectrophotometric titration procedure described by Carpenter [18] with a pH of 2 and a potassium iodide concentration of $4g L^{-1}$. Bromate analyses were made by differential pulse polarography at 25°C and a pH of 8.35 (after oxygen stripping with nitrogen), using a Princeton Applied Research model 174A polarographic analyser.

A typical polarographic recording is shown in Fig. 3.2 curve (a) is the polarogram obtained for chlorinated seawater analysed immediately after chlorination. Identical traces were observed for non-chlorinated seawater and for chlorinated seawater kept in the dark for periods up to 24h at temperatures up to 40°C, which indicates a lack of bromate formation under these conditions ($BrO_3^- \leq 10^{-7}M$, less than 0.5%

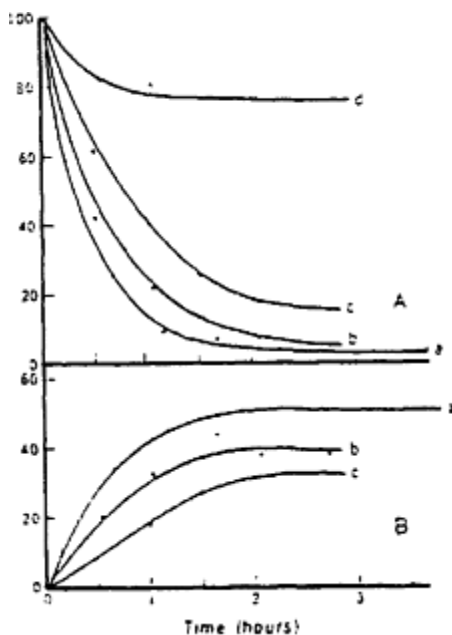


Fig. 3.3 (a) Disappearance with time of residual oxidants and (b) concomitant appearance of bromate (equation (2) above) in chlorinated seawater (4.2 to 4.9ppm of Cl_2) as a function of exposure to sunlight. The conditions were: Curve (a) full midday sunlight, Curve (b) 65% of full sunlight, and curve (c) overcast, 20% of full sunlight. Curve (d) shows residual oxidant disappearance in the dark at 40°C . no bromate production was observed in the dark.

Source: Reproduced with permission from Springer-Verlag [18]

conversion of chlorine). Addition of copper sulphate to give a cupric ion concentration in the seawater of 100 parts per billion did not induce measurable bromate production in the dark. Curve (b) was obtained from a chlorinated (4.9mg L^{-1}) seawater solution that was exposed to full sunlight for 70min. Curve (c), which is offset by $0.4\mu\text{a}$ with respect to curves (a) and (b), shows $1.0 \times 10^{-5}\text{M}$ sodium bromate in seawater.

Fig. 3.3 illustrates kinetic data for the appearance of bromate (Fig 3.3(a)) and disappearance of residual oxidants (Fig. 3.3(b)) in chlorinated seawater exposed to sunlight. Curves (a) were obtained from solutions exposed to full midday sunlight for the duration of the experiment: curves (b) are for exposure to partial sunlight (the average light intensity was approximately 65% of full sunlight); and curves (c) are for overcast conditions (average light intensity, 20% of full sunlight). Curve (d) in Fig. 3.3(a) shows the disappearance of residual oxidants with time at 40°C in the dark. The ordinates are calibrated as the percentage of the added chlorine recovered as residual oxidants (Fig. 3.3 (a)) or as bromate formed according to equation (2) above (Fig. 3.3(b)).

The lack of observable bromate production in the dark is not inconsistent with the

report of Lewin and Avrahami [19] that substantial bromate was formed in their 0.05M hypobromide solutions. The solutions used by Macalady *et al.* [17] which correspond to current chlorine use, were 1000 times more dilute. Using their rate constants, they calculated in their solutions a conversion to bromate of less than 1% after 24h.

The loss of residual oxidants does not correspond exclusively to bromate formation, and other reactions, including oxidation of organic matter and perhaps those in equation (1) above, also take place. The rate and extent of bromate formation depend on the intensity of sunlight.

Solutions of 10^{-5} M sodium bromate in sea water were also titrated by using the residual oxidants procedure. The results show that only about 5% of the added bromate appears as residual oxidants. Thus, the apparent residual oxidants remaining after exposure to sunlight could be completely due to bromate.

3.10 Bromide

3.10.1 Titration method

Bromide in seawater can be determined by the procedure described below which is capable of determining down to 0.1mgL^{-1} bromide.

The sample is acidified with sulphuric acid. The bromide content is then determined by the volumetric procedure described by Kolthoff and Yutzy [20]. In this procedure the buffered sample is treated with excess sodium hypochlorite to oxidise bromide to bromate. Excess hypochlorite is then destroyed by addition of sodium formate. Acidification of the test solution with sulphuric acid followed by addition of excess potassium iodide liberates an amount of iodine equivalent to the bromate (ie the original bromide) content of the sample. The liberated iodine is titrated with standard sodium thiosulphate.

3.10.2 Segmented flow analysis

Basel *et al.* [21] have described methods for compensation for chloride, ammonia and bicarbonate interferences in determining bromide in saline waters with an automated segmented flow analyser utilising the phenol red method.

3.10.3

Isotachoelectrophoresis

Fukushi and Hiro [22] have described a capillary-type isotacho-electrophoretic method for the determination of bromide in seawater.

3.10.4 Solid state membrane electrodes

Walters [23] has examined the effect of chloride on the use of bromide and iodide solid state membrane electrodes and he calculated selectivity constants. Multiple linear

regression analysis was used to determine the concentrations of bromide, fluoride and iodide in geothermal brines and indicated high interferences at high salt concentrations. The standard curve method was preferred to the multiple standard addition method because of:

- (1) The deviation from linearity at high salt concentrations of the bromide electrode.
- (2) The loss of accuracy due to increase in sample volume by using volume increments.
- (3) The limitations in reading from the Orion meter (0.1mV).
- (4) The fact that bromide, fluoride and iodide were present at relatively low concentrations (where the electrode exhibited non-linear behaviour).

3.10.5 X-ray fluorescence spectroscopy

Sichère *et al.* [24] determined bromine concentrations in the 0.06–120mg L⁻¹ range in brines directly by X-ray fluorescence using selenium as an internal standard to eliminate interference effects. Lower concentrations of bromine must be concentrated on filter paper containing an ion exchange resin. The same concentrations of chlorine can be determined with the addition of barium to reduce the interferences from carbonates and sulphates. Relative standard deviation was better than 1%.

In this method barium is added to reduce interference by carbonates and sulphates. The interference of some other ions, eg calcium, potassium, magnesium, sodium, strontium and iron was examined.

3.10.6 X-ray emission spectrometry

Rose and Cuttita [25] proposed a graphical method for evaluating the background when determining traces of bromide by X-ray emission spectrography (carried out on cellulose pellets containing the residue from evaporation of the sample in the presence of standard bromide solution). Based on this work a graphical method is proposed which provides a value (m_B) of the amount of bromide equivalent to the background, which is substituted into the equation: counts per sec = $k(m + m_s + m_B)$, where k is a factor depending on the sample, m is the bromide content of the original solution and m_s is the amount of bromide added as 'spike'. Results obtained by both methods agree satisfactorily but it is stressed that both methods are approximations.

3.10.7 Electrostatic ion chromatography

The application of this technique is discussed under multianion analysis in section 3.32.2.

3.10.8 Miscellaneous

Foti [26] has studied the feasibility of concentrating traces of radioactive bromide ions by passing the seawater sample through a column of inactive silver bromide (to effect isotopic exchanges). The effects of column height and of flow rate, volume and/or residence time of the seawater on the extent of exchange were examined; each of these variables had significant effect.

3.1.1 Carboxylic acids

3.11.1 Ion chromatography

The application of this technique is discussed in section 12.3.1.

3.12 Chloride

3.12.1 Titration method

Chloride at the percentage level, as occurs in sea water, is usually determined by classical titration procedures using standard silver nitrate as the titrant and potassium chromate indicator or alternatively by the mercuric thiocyanate procedure using dithizone as indicator. As large dilutions of the original sample are involved in these analyses it is essential to use grade A glassware and take all other suitable precautions, such as temperature control in these analyses.

Chloride can also be estimated by potentiometric titration using standard silver nitrate [27]. The results are recorded directly on punched tape and by teletyper and evaluated by means of a computer program based on the Gran extrapolation method. The determinations have a precision of $\pm 0.02\%$ and since many samples can be titrated simultaneously, the time for a single determination including evaluation and editing of titration data can be reduced to less than 5min.

Jagnuer [28] has also described a semi-automatic titration for the precision determination of chloride in seawater. This titrator supplies pre-set increments of titrants, and has a direct teletyped read-out system on punched tape suitable for subsequent computer treatment of the titration curve. It has been used for the potentiometric determination of total halides (silver electrode), and of alkalinity (glass electrode) and for the photometric titration of total alkaline-earth metals, in seawater. Several titrations can be effected simultaneously.

Grasshoff and Wenck [29] have described a version of the Mohr-Knudsen silver nitrate titration procedure for the determination of the chlorinity of sea water. In this method, which overcomes the disadvantages of conventional burettes, use is made of a motor-driven piston burette of 20ml capacity, which is sufficient for the range of chlorinities 0 to 45 per thousand. The accuracy is the same as for conventional titration. The apparatus is compact and portable.

Several autoanalyser procedures are available for the determination of chloride.

3.12.2 Ion selective electrodes

Noborn [30] has studied the dynamic properties of chloride selective electrodes and their application to sea water concentrates. An Orion 94-17 electrode was used in these studies.

In the presence of bromide ions the electrode was subject to a drop in potential (eg 1.5

to 5.7mV at a molar ratio of Br^- to Cl^- of 2000:3) and to delayed response. A considerable hysteresis effect is also observed in concentrated solutions of chloride when the electrode is used in a 1M chloride solution and then dipped in one that is 0.02M in chloride. Equilibrium is reached only after 10min. The junction potential is minimised by diluting the test solution with the salt-bridge solution (10% aq. potassium nitrate).

3.12.3 Chronopotentiometry

Chronopotentiometry has also been used to determine chloride ions in seawater [31]. The chloride in the solution containing an inert electrolyte was deposited on a silver electrode (1.1cm²) by the passage of an anodic current. The cell comprised a silver disc as working electrode, a symmetrical platinum-disc counter-electrode and a silver—AgCl reference—electrode to monitor the potential of the working electrode. This potential was displayed on a one channel of a two-channel recorder, and its derivative was displayed on the other channel. The chronopotentiometric constant was determined over the chloride concentration range 0.5 to 10mM and the concentration of the unknown solution was determined by altering the value of the impressed current until the observed transition time was about equal to that used for the standard solution.

3.12.4 Miscellaneous

Wilson [32] has described a portable flow-cell membrane salinometer. Although test solutions are normally passed through the cell, the

Table 3.2 Chromium species in saline waters, $\mu\text{g L}^{-1}$

Source of sample	Salinity %	Labile Cr(VI)	Labile Cr(III)	Total Cr
Cronulla Point, Australia	35	0.13	0.08	0.25
Woronora River, Australia	21	0.20	0.03	0.31
Georges River, Australia	35	0.68	0.22	1.25

Source: Reproduced with permission from the American Chemical Society [33]

electrodes can be connected to a remote membrane sensor head by means of salt bridges for measurement of the salinity of estuarine muds *in situ*. The error is within $\pm 1\%$ over the salinity range 1 to 40%.

3.13 Chromate and dichromate

3.13.1 Atomic absorption spectrometry

A method has been developed for differentiating hexavalent from trivalent chromium [33]. The metal is electrodeposited with mercury on pyrolytic graphite-coated tubular furnaces in the temperature range 1000–3000°C, using a flow-through assembly. Both the hexa- and trivalent forms are deposited as the metal at pH 4.7 and a potential at -1.8V against the standard calomel electrode, while at pH 4.7, but -0.3V , the hexavalent form is selectively reduced to the trivalent form and accumulated by adsorption. This method was applied to the analysis of chromium species in samples of different salinity, in conjunction with atomic absorption spectrophotometry. The limit of detection was $0.05\mu\text{g chromium L}^{-1}$ and relative standard deviation from replicate measurements of $0.4\mu\text{g chromium(VI)}$ was 13%. Matrix interference was largely overcome in this procedure.

Results for the analyses of some saline waters are shown in Table 3.32.

Various workers have discussed the separate determination of Cr(III) and Cr(VI) in seawater [34–38].

Cranston and Murray [35,36] took samples in polyethylene bottles that had been pre-cleaned at 20°C for 4 days with 1% distilled hydrochloric acid. Total chromium (Cr(VI) + Cr(III) + Cr_p) (particularly chromium) was co-precipitated with iron(II) hydroxide and reduced chromium (Cr(III) + Cr_p) was co-precipitated with iron(III) hydroxide. These co-precipitation steps were completed within minutes of sample collection to minimise storage problems. The iron hydroxide precipitates were filtered through $0.4\mu\text{m}$ Nucleopore filters and stored in polyethylene vials for later analyses in the laboratory. Participate chromium was also obtained by filtering unaltered samples through 0.4μ filters. In the laboratory the iron hydroxide co-precipitates were dissolved in 6N distilled hydrochloric acid and analysed by flameless atomic absorption. The limit of detection of this method is about 0.1 to 0.2nM . Precision is about 5%.

3.13.2 Organic forms of chromium

In the determination of the two oxidation states of chromium the calculation of one oxidation state by difference presupposes that the two oxidation states in question were statistically the only contributors to the total concentration. Because of this, contributions from other possible species such as organic complexes were generally not considered. It has been suggested [39] however, that this presumption may not be warranted and that contributions from organically bound chromium should be considered. This arises from the reported presence of dissolved organic species in non saline waters which form stable soluble complexes with chromium and which may not readily be amenable to determination by procedures commonly in use. The results of research into the valency of chromium present in seawater has not always been consistent. For instance, Grimaud and Michard [40] reported that chromium(III) predominates in the equatorial region of the Pacific Ocean, whereas Cranston and Murray [35] found that practically all chromium is in the hexavalent state in the north-east Pacific. Organic chromium(III) complexes may

be formed under the conditions prevailing in seawater as well as inorganic chromium(III) and chromium(VI) forms. Inconsistencies in earlier research may therefore, be at least partly due to the fact that the possibility of organic chromium species was ignored [41,42].

Nakayama *et al.* [38] have described a method for the determination of chromium(III), chromium(VI) and organically bound chromium in seawater. They found that seawater in the sea of Japan contained about $9 \times 10^{-9} \text{M}$ dissolved chromium. This is shown to be divided as ca. 15% inorganic chromium(III), ca. 25% inorganic chromium(VI) and ca. 60% organically-bound chromium.

These workers studied the co-precipitation behaviours of chromium species with hydrated iron(III) and bismuth oxides.

The collection behaviour of chromium species was examined as follows. Seawater (400ml) spiked with 10^{-8}M chromium(III), chromium (VI) and chromium(III) organic complexes labelled with ^{51}Cr was adjusted to the desired pH by hydrochloric acid or sodium hydroxide. An appropriate amount of hydrated iron(III) or bismuth oxide was added; the oxide precipitates were prepared separately and washed thoroughly with distilled water before use [43]. After about 24 h, the samples were filtered on $0.4 \mu\text{m}$ Nuclepore filters. The separated precipitates were dissolved with hydrochloric acid and the solutions thus obtained were used for γ -activity measurements. In the examination of solvent extraction, chromium was measured by using ^{51}Cr , while iron and bismuth were measured by electrothermal atomic absorption spectrometry. The decomposition of organic complexes and other procedures were also examined by electrothermal atomic absorption spectrometry.

3.13.2.1 Collection of chromium(III) and chromium(VI) with hydrated iron (III) or bismuth oxide

Only chromium(III) co-precipitates quantitatively with hydrated iron(III) oxide at the pH of seawater, around 8. In order to collect chromium(VI) directly without pretreatment, eg reduction to chromium(III), hydrated bismuth oxide, which forms an insoluble compound with chromium(VI) was used. Chromium(III) is collected with hydrated bismuth oxide (50mg per 400mL seawater) to collect chromium(VI) in seawater is collected at about pH 4 and chromium(VI) is collected below pH 10. Both chromium(III) and chromium(VI) are thus collected quantitatively the pH of seawater around 8.

3.13.2.2 Collection of chromium(III) organic complexes with hydrated iron (III) or bismuth oxide

The percentage collection of chromium(III) with hydrated iron(III) oxide may decrease considerably in the neutral pH range when organic materials capable of combining with chromium(III) such as citric acid and certain amino acids, are added to the seawater [41]. Moreover, synthesised organic chromium(III) complexes are scarcely collected with hydrated iron(III) oxide over a wide pH range [41].

As it was not known what kind of organic matter acts as the major ligand for chromium in seawater Nakayama *et al.* [38] used EDTA and 8-quinolinol-4-sulphuric

acid to examine the collection and decomposition of organic chromium species, because these ligands form quite stable water-soluble complexes with chromium(III) although they are not actually present in seawater. Both these chromium(III) chelates are stable in seawater at pH 8.1 and are hardly collected with either of the hydrated oxides. The organic chromium species were then decomposed to inorganic chromium(III) and chromium(VI) species by boiling with 1g ammonium persulphate per 400mL–1 seawater acidified to 0.1M with hydrochloric acid. Iron and bismuth, which would interfere in atomic absorption spectrometry, were 99.9% removed by extraction from 2M hydrochloric acid solution with a *p*-xylene solution of 5% tri-iso-

Table 3.3 Vertical distribution of chromium species in the Sea of Japan and in the Pacific Ocean

Depth (m)	Cr(III) ^a ($\times 10^{-9}$ M)	Cr(VI) ($\times 10^{-9}$ M)	Org. Cr ($\times 10^{-9}$ M)	Total Cr ($\times 10^{-9}$ M)
Japan Sea (44° 11.9'N 138°56.4'E; depth 3447m)				
0	1.3	2.1	4.9	8.3
10	1.4	1.7	5.9	9.0
51	1.6	1.8	4.3	7.7
102	1.2	1.7	5.3	8.2
152	1.3	1.8	4.2	7.3
203	1.2	1.8	4.6	7.6
403	1.4	2.9	5.0	9.3
602	1.1	2.3	3.7	7.1
1000	1.5	2.4	3.5	7.4
1427	1.1	3.0	4.2	8.3
1920	1.8	1.7	6.2	9.7
2417	1.1	2.1	4.6	7.8
2916	1.2	—	—	9.1
3165	1.4	1.7	5.0	8.1
Av.	1.3	2.1	4.8	8.2
Max.	1.8	3.0	6.2	9.7
Min	1.1	1.7	3.5	7.1
Pacific Ocean (32°19.3'N 137°33.5'E; depth 4079m)				
0	1.4	2.0	5.0	8.4
10	1.4	—	—	8.1
49	1.3	2.5	4.7	8.5

98	0.96	2.4	—	—
143	1.0	2.8	4.1	7.9
197	1.2	2.1	5.5	8.8
394	1.2	2.6	4.9	8.7
591	1.5	2.4	5.0	8.9
985	1.1	3.6	5.9	10.6
1477	1.1	3.3	6.2	10.6
1804	1.2	4.5	6.0	11.7
2299	1.4	4.0	5.4	10.8
2803	1.2	3.7	5.2	10.1
3303	1.5	3.4	—	—
3801	1.0	3.3	5.3	9.6
4050	1.1	3.7	5.8	10.6
Av.	1.2	3.1	5.2	9.5
Max.	1.5	4.5	6.2	11.7
Min.	0.96	2.0	4.1	7.9

^aInorganic

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octylamine. Chromium(III) remained almost quantitatively in the aqueous phase in the concentration range 10^{-9} – 10^{-6} M, whether or not iron or bismuth was present. However, as about 95% of chromium(VI) was extracted by the same method, samples which may contain chromium(VI) should be treated with ascorbic acid before extraction so as to reduce chromium(VI) to chromium(III).

When the residue obtained by the evaporation of the aqueous phase after the extraction was dissolved in 0.1M nitric acid and the resulting solution was used for electrothermal atomic absorption spectrometry, a negative interference, which was seemingly due to residual organic matter, was observed. This interference was successfully removed by digesting the residue on a hot plate with 1mL concentrated hydrochloric acid and 3mL of concentrated nitric acid. This process had the advantage that the interference of chloride in the atomic absorption spectrometry, was eliminated during the heating with nitric acid. Table 3.3 shows examples of the vertical distribution of each chromium species in the Japan Sea and the Pacific Ocean samples which were collected during the summer of 1979.

For comparison, some of the results reported by other workers for chromium concentrations in seawater are listed in Table 3.4. In most of these methods, co-precipitation with hydrated iron(III) oxide was used to separate chromium(III) from chromium(VI) and the chromium(VI) concentration was subsequently determined by suitable reduction of chromium(VI) to chromium(III) before a further co-precipitation. In

others, hydrated iron(II) oxide served as both reductant and carrier. Ishibashi and Shigematsu [44] used co-precipitation with aluminium hydroxide and did not employ reduction, so that the value reported most likely corresponds to inorganic chromium(III) alone; in fact, the present value for inorganic chromium(III) is in remarkable agreement.

In Chuecas and Riley's study [45] the samples were stored for a long time under acidic conditions before analysis, so that chromium(VI) could have been reduced to chromium(III) and any organic chromium dissociated with the result that all chromium species would have been determined as chromium(III). When a sample is reduced under acidic conditions, organic chromium is likely to dissociate partly, initially increasing the apparent concentration of chromium(VI). When the analytical procedure described earlier [46,47] was re-examined the value for chromium(III) was found actually to be the sum of chromium(III) and chromium(VI) while the value for chromium(VI) was partly organic chromium. For the same reason the chromium(VI) values determined by Fukai [48], Fukai and Vas [49] and Yamamoto *et al.* [50] probably include organic chromium species. When an iron(II) precipitate is used, there seems to be little chance of determining the organic chromium species as chromium(VI). The value for chromium(VI) reported by Cranston and

Table 3.4 Literature data on the chromium contents of seawater

Ref.	Date	Locations	Methods	Concentration $\mu\text{g L}^{-1}$
Ishibashi and Shigematsu [44]	1950	Japanese coastal	$\text{Al}(\text{OH})_3$ co ppt	Cr(III), 0.01
Chuecas and Riley [45]	1966	British coastal	$\text{Fe}(\text{OH})_3$ co ppt acidic reduction	Cr(III) 0.46 Cr(VI) 0.01
Fukai [48,49]	1967	Mediterranean	$\text{Fe}(\text{OH})_3$ co ppt acidic reduction	Cr(III) 0.02–0.25 Cr(VI) 0.05–0.38
Kuwamoto and Murai [46]	1970	Pacific Ocean	$\text{BiOH}(\text{NO}_3)_2$ co ppt acidic reduction	Cr(III)? Cr(III) ⁺ Cr(IV) 0.1 3–0.90 Cr(VI)? OrgCr 0.07–0.27
Grimaud and Michard [47]	1974	Pacific Ocean	$\text{Fe}(\text{OH})_3$ co ppt $\text{Fe}(\text{OH})_3$ reduction	Cr(III) 0.24–0.52 Cr(VI) 0.03–0.11
Yamamoto <i>et al.</i> [50]	1974	Pacific Ocean	$\text{Al}(\text{OH})_3$ co ppt acidic reduction	Total 0.06–0.96 Cr(III) 17–99%
Cranston and Murray [35]	1978	Pacific Ocean	$\text{Fe}(\text{OH})_3$ co ppt	$\text{Fe}(\text{OH})_3$ reduction Cr(III) 0.005 Cr(VI) 0.15
Nakayama <i>et al.</i> [38]	1981	Pacific Ocean and Japan Sea		Cr(III) 0.06 Cr(IV) 0.14 OrgCr 0.26

Source: Reproduced with permission from Elsevier Science [38]

Murray [35] agrees quite well with the value for chromium(VI) reported by them although the value for chromium(III) is lower. The results obtained by Grimaud and Michard [40] for chromium(III) differ considerably but the discrepancies cannot be discussed because details of the analytical procedure were not given. It seems reasonable to conclude that the inconsistency of past results concerning the dominant chromium species and the total chromium concentration in seawater can be attributed, at least partly, to the fact that the presence of organic chromium species was not considered properly.

Mullins [37] has described a procedure for determining the concentrations of dissolved chromium species in seawater. Chromium(III) and chromium(VI) separated by co-precipitation with hydrated iron(III) oxide and total dissolved chromium are determined separately by conversion to chromium(VI), extraction with ammonium pyrrolidine diethyl dithiocarbamate into methyl isobutyl ketone and determination by atomic absorption spectrometry. The detection limit is 40ng L⁻¹ chromium. The dissolved chromium not amenable to separation and direct extraction is calculated by difference. In the waters

Table 3.5 Determination of dissolved chromium species in some seawaters

Location	Chromium found ^a (µg L ⁻¹)			
	Cr(III)	Cr(VI)	Cr bound	Cr total
Port Hacking	0.27±0.02	0.49±0.03	0.56±0.07	1.32±0.05
Georges River	0.42±0.04	0.89±0.04	0.42±0.08	1.72±0.06
Drummoyne Bay	0.32±0.03	0.95±0.04	0.69±0.10	1.96±0.07
Botany Bay	0.45± 0.04	1.26±0.06	0.71±0.04	2.41±0.09
Cooks River	0.51±0.04	2.98±0.11	0.88±0.10	4.37± 0.06
Parramatta River	0.88 ± 0.02	3.1 7 ±0.06	0.82 ± 0.09	4.87 ±0.11

^aAll results are the mean (±s.d.) of three measurements; s.d. calculated as in Table 3.3

Source: Reproduced with permission from Elsevier Science [37]

investigated, total concentrations were relatively high (1–5µg L⁻¹) with chromium(VI) the predominant species in all areas sampled with one exception, where organically bound chromium was the major species.

A standard contact time of 4h found to be necessary for the quantitative co-precipitation of chromium on ferric oxide. The results of triplicate determinations of samples taken from six locations in the Sydney area are listed in Table 3.5. The rsd values for the determinations of chromium(III), chromium(VI) and total dissolved

chromium were generally 10.0%, 5.0% and 5.0% respectively. From these results, the rsd for the calculated concentration of the bound species was 20%.

Ahern *et al.* [51] have discussed the speciation of chromium in seawater. The method involved co-precipitation of trivalent and hexavalent chromium, separately, from samples of surface seawater and determination of the chromium in the precipitates and particulate matter by thin-film X-ray fluorescence spectrometry. An ultraviolet irradiation procedure was used to release bound metal. The ratios of labile trivalent chromium to total chromium were in the range 0.4–0.6 and the totals of labile tri- and hexavalent chromium were in the range 0.3–0.5 $\mu\text{g L}^{-1}$. Bound chromium ranged from 0 to 3 μg per litre, and represented 0–90% of total dissolved chromium. Acidification of the samples in the usual manner for the determination of trace metals altered the proportion of trivalent to hexavalent chromium.

3.14 Fluoride

3.14.1 Spectrophotometric method

Fletsch and Richards [52] determined fluoride in seawater spectrophotometrically as the cerium alizarin complex. The cerium alizarin complexan chelate was formed in 20% aqueous acetone at pH 4.35 (sodium acetate buffer) and, after 20–60min, the extinction measured at 625nm (2.5cm cell) against water. The calibration graph was rectilinear for 8–200 $\mu\text{g L}^{-1}$ fluoride; the mean standard deviation was $\pm 10 \mu\text{g L}^{-1}$ at a concentration of 1100 $\mu\text{g L}^{-1}$ fluoride.

Spectrophotometric procedures based on the lanthanum-alizarin complex are also described [53].

3.14.2 Photoactivation analysis

Photoactivation analysis has also been used to determine fluoride in seawater [54]. In this method a sample and simulated seawater standards containing known amounts of fluoride are freeze-dried, and then irradiated simultaneously and identically, for 20min, with high-energy photons. The half-life of ^{18}F (110min) allows sufficient time for radio-chemical separation from the seawater matrix before counting. The specific activities of sample and standards being the same, the amount of fluoride in the unknown may be calculated. The limit of detection is 7ng fluoride, and the precision is sufficient to permit detection of variations in the fluoride content of oceans. The method can be adapted for the simultaneous determination of fluorine, bromine and iodine.

3.14.3 Ion selective electrodes

Ion selective electrodes are emerging as the method of preference for the determination of fluoride in seawater [55–60].

Anfalt and Jagner [59] measured total fluoride ion concentration by means of a single-crystal fluoride selective electrode (Orion, model 94–09). Samples of seawater were

adjusted to pH 6.6 with hydrochloric acid and were titrated with 0.01M sodium fluoride with use of the semi-automatic titrator described by Jaguer [61]. Equations for the graphical or computer treatment of the results are given. Calibration of the electrode for single-point potentiometric measurements at different seawater salinities is discussed.

Rix *et al.* [60] have commented that earlier published potentiometric methods for determining fluoride in seawater appear to be unnecessarily complicated in several respects. Reagents, such as a total ionic strength adjustment buffer, TISAB, are added to the sample at high concentrations to set the pH and ionic strength and to liberate the majority of fluoride bound in metal complexes. The possibility of introducing solution contamination when using high concentrations of TISAB is always a potential hazard and, if this step can be avoided, this will obviously be advantageous. Furthermore, a significant drawback with most earlier methods was the difficulty of establishing an acceptable or representative matrix in which to prepare standards, as the actual matrix is often unknown in non saline waters. This aspect of fluoride determination in seawater has received considerable attention, and extensive and elaborate procedures have been used to match the sample and standard matrices [55].

The method of standard additions is frequently employed in environmental analysis for samples of variable matrix [62]. The method of data treatment used by Rix *et al.* [60] is similar to that originally described by Gran [1] for the exact determination of potentiometric end-points. Brand and Rechnitz [63], Baumann [64] and Craggs *et al.* [65] have described procedures employing the method of standard additions to selective ion electrode potentiometry, but no data are available for non saline waters using this direct method except for the work of Liberti and Mascini [66] who determined fluoride in mineral waters. The procedure used by Rix *et al.* [60] is exceedingly simple, and the method of data treatment provides a linear plot, the slope and intercept of which give independent measures of the original concentration of fluoride in the sample. Total fluoride concentration is determined despite the fact that the activity of the fluoride ion is the parameter monitored by the fluoride selective ion electrode.

The concentration of fluoride in seawater is approximately 1.4ppm or $7 \times 10^{-5} \text{ mol L}^{-1}$ and the fluoride electrode has been shown to give a Nernstian response at this level and indeed three orders of magnitude lower [67].

It has been well established that the fluoride electrode is highly selective in its response to the activity of fluoride with the only common interferant being hydroxide [68]. Nevertheless, although seawater has a uniform pH of 8, possible hydroxide interference was shown not to be a problem as indicated by the results presented in Table 3.6.

Complexation of fluoride by metal ions in seawater has previously been overcome by the addition of TISAB solution. This reagent is presumed to release the bound fluoride by preferential complexation of the metal ions with EDTA type ligands present in the TISAB. Examination of the metal ions present in seawater [69,70] suggests that magnesium is the major species forming fluoride complexes. Theoretical calculations for the simple case when only MgF^+fa , Mg^{2+}fa and F^- are considered demonstrate that even this species is unlikely to interfere.

Results for seawater of 35.21 ‰ salinity are presented in Table 3.6, and the average value of $1.35 \pm 0.05 \text{ mg L}^{-1}$ is in excellent agreement with previously published data [55,56,69,71,72].

The first result in Table 3.6 is the value found directly. The next set of three results shows that recovery of fluoride after deliberate addition to the spiked samples is excellent. The fifth result is that obtained on an acidified sample. The sixth, seventh, eighth and ninth sets of data show that the expected fluoride concentration is still obtained after deliberate

Table 3.6 Determination of fluoride in seawater under a variety of conditions to demonstrate the reliability of the method

Sample		{F} found (mg L ⁻¹)	Conditions
Point Lonsdale, Victoria, Australia	1	1.40±0.05 1.35±0.05*	pH=8
	2	1.30±0.05	1.5ppm spike added. [F] _T determined=2.80±0.05ppm
	3	1.40±0.05	4.0ppm spike added. [F] _T determined=5.40±0.05ppm
	4	1.30±0.05	8.6ppm spike added. [F] _T determined=9.90±0.05ppm
	5	1.28±0.05	pH 5.50 (HCl added)
	6	1.36±0.05	5mg potassium alum added/100 ml seawater≈2.7ppm Al ³⁺
	7	1.43±0.10	50mg potassium alum added/100ml seawater≈27ppm Al ³⁺ . Equilibration time of electrode very long
	8	1.39±0.05 1.37±0.05*	50mg potassium alum and 3g ammonium citrate added/100ml seawater
	9	1.30±0.05	37mg ferric alum added to 100ml seawater and pH adjusted to 3 by adding few drops of glacial acetic acid. Soln≈40ppn Fe ³⁺
	10	1.37±0.05	50ml TISAB added/100ml seawater
	11	1.28±0.10	Calculated via addition of TISAB and calibration vs. synthetic seawater
Synthetic		0.0068±0.0008 0.0053±0.0008	pH5.8 pH4.3

*This determination was performed approximately three weeks after the first
Source: Reproduced with permission from the American Chemical Society [60]

addition of aluminium or iron in the form of their alums. Aluminium(III) and iron(III) form very strong fluoride complexes [73] and, provided that sufficient time is allowed for equilibration (as also noted by Baumann [67] for very low fluoride concentrations), total fluoride could still be determined accurately by the method of standard additions even though the artificial concentration levels of aluminium and iron were three orders of

magnitude greater than those normally occurring in seawater [69]. This observation is noteworthy, since the work of Liberti and Mascini [66] suggests that the direct method cannot be used for fluoride in the presence of high relative concentrations of aluminium (III) or iron(III) aquo species.

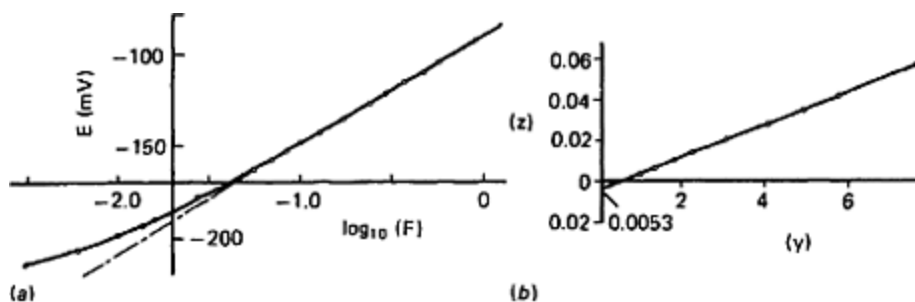


Fig. 3.4 (a) Plot of emf versus $\log(F^-)$ for data obtained from synthetic seawater sample. (b) Plot of z versus y for data in (a) showing the linear extrapolation

Source: Reproduced with permission from the American Chemical Society [60]

This complication is probably avoided in seawater (even with relatively high concentrations of aluminium(III) and iron(III)) by the large excess of chloride ions which partially complex with any aluminium(III) or iron(III) present to produce chloro-complexes of the metals, thus sequestering their influence on the fluoride concentration. Data obtained after addition of TISAB to release bound fluoride and using the calibration method further confirm the validity of the direct method. The data in Table 3.6 demonstrate the absence of hydroxide ion interference caused by metal ion complexation and indicate that total rather than free fluoride is determined by the method of standard additions. Fig. 3.4(a) shows a plot of potential versus the logarithm of the concentration of added fluoride in synthetic seawater. The slope of the linear portion of the graph was 58.8mV per decade change in fluoride ion concentration, and this value was used in the calculations of fluoride concentration in seawater. At lower levels of fluoride ($<10^{-6}\text{mol L}^{-1}$), it might be assumed that the electrode behaves in a non-Nernstian fashion. However, calculations of the kind suggested by Rix *et al.* [60] reveal that the deviation from linearity can satisfactorily be attributed to residual fluoride resulting either from reagent contamination or from the electrode itself at a concentration of about $3 \times 10^{-7}\text{mol L}^{-1}$.

The level of fluoride in seawater is at least two orders of magnitude higher than this residual level, hence contamination does not significantly influence the results.

When handling large numbers of samples, computerised rather than graphical analysis is considered to be substantially superior. The precision of the data reported in Table 3.6 is largely limited by the accuracy of the potential measurement ($\pm 1\text{mV}$). Using instrumentation capable of measuring 0.1mV and with least-square fitting of data, average deviations on replicate determinations were routinely found to be 2%.

Ke and Regier [74] have described a direct potentiometric determination of fluoride in seawater after extraction with 8-hydroxyquinoline. This procedure was applied to samples of seawater, fluoridated tap-water, well-water and effluent from a phosphate reduction plant. Interfering metals, eg calcium, magnesium, iron and aluminium were removed by extraction into a solution of 8-hydroxyquinoline in 2-butoxyethanol-chloroform after addition of glycine-sodium hydroxide buffer solution (pH 10.5 to 10.8). A buffer solution (sodium nitrate-1,2-diamino-cyclohexane-NNN'N'-tetra-acetic acid-acetic acid) (pH 5.5) was then added to adjust the total ionic strength and the fluoride ions were determined by means of a solid membrane fluoride-selective electrode (Orion, model 94-09). Results were in close agreement with, and more reproducible than those obtained after distillation [75]. Omission of the extraction led to lower results. Four determinations can be made in 1h.

3.15 Formate

There is considerable interest in the role of formic acid and other volatile fatty acids in the early diagenesis of organic matter in lacustrine and marine sediments. Formic acid is an important fermentation product or substrate for many aerobic and anaerobic bacteria and for some yeasts. In the atmosphere, formic acid is an important product in the photochemical oxidation of organic matter.

Despite its potential importance, formic acid has proven difficult to quantify at submicromolar levels in non saline water samples. Formidable analytical difficulties are associated with its detection in highly saline samples. Ion exclusion, anion exchange, and reversed-phase high performance liquid chromatography techniques based on the direct detection of formic acid in aqueous samples are prone to interferences (especially from inorganic salts) that ultimately limit the sensitivity of these methods.

A potentially more sensitive and selective approach involves reaction of formic acid with a reagent to form a chromophore or fluorophore, followed by chromatographic analysis. A wide variety of alkylating and silylating reagents have been used for this purpose. Two serious drawbacks to this approach are that inorganic salts and/or water interfere with the derivatisation reaction, and these reactions are generally not specific for formic acid or other carboxylic acids. These techniques are prone to errors from adsorption losses, contamination and decomposition of the components of interest. Enzymatic techniques, in contrast, are ideal for the analysis of non saline water samples, since they are compatible with aqueous media and involve little or no chemical or physical alterations of this sample (eg pH, temperature).

3.15.1 High performance liquid chromatography

As a consequence of the above considerations Kieber *et al.* [76] have developed an enzymatic method to quantify formic acid in non saline water samples at sub-micromolar concentrations. The method is based on the oxidation of formate by formate dehydrogenase with corresponding reduction of β -nicotinamide adenine dinucleotide (β -NAD⁺) to reduced β -NAD⁺ (β -NADH); β -NADH is quantified by reversed-phase high

performance liquid chromatography with fluorometric detection. An important feature of this method is that the enzymatic reaction occurs directly in aqueous media, even seawater, and does not require sample pre-treatment other than simple filtration. The reaction proceeds at room temperature at a slightly alkaline pH (7.5–8.5) and is specific for formate with a detection limit of $0.5\mu\text{M}$ ($S/N=4$) for a $200\mu\text{L}$ injection. The precision of the method was 4.6% relative standard deviation ($n=6$) for a $0.6\mu\text{M}$ standard addition of formate to Sargasso seawater. Average recoveries of $2\mu\text{M}$ additions of formate to seawater were 103%. Intercalibration with a Dionex ion chromatographic system showed an excellent agreement of 98%. Concentrations of formate present in natural samples ranged from 0.2 to $0.8\mu\text{M}$ for Biscayne Bay seawater.

3.16 Hypochlorite

3.16.1 Spectrophotometric method

Williams and Robertson [77] have described a simple inexpensive method for determining reactive chlorine in non saline waters. It involves addition of bromine, which is oxidised by the reactive chlorine in the sample, and which in turn brominates fluorescein to give a pink derivative; this can be measured visually or spectrophotometrically, or the decrease in fluorescein can be measured fluorometrically. Potential applications of the method are indicated.

The basis of this method is that when normal seawater is chlorinated at the usual levels of 1 to 10mg/L to chloride, the bromide in seawater ($8.1 \times 10^{-4}\text{M}$, 65mg L^{-1} at salinity=35 ‰) is rapidly and quantitatively oxidised to BrO^- and HBrO . If 50mg L^{-1} of bromide is added to distilled or fresh waters containing HClO plus ClO^- , then HBrO plus BrO^- are both formed. The HBrO plus BrO^- , in turn, will rapidly brominate fluorescein (9-[*o*-carboxyphenyl]-6-hydroxy-3-isoxanthenone) to give the pink tetrabromo derivative eosin yellow (2,4,5,7-tetrabromo-9-[*o*-carboxyphenyl]-6-hydroxy-3-isoxanthenone), provided the molar ratio of bromide to fluorescein is 4:1. The resultant increase in eosin can be measured visually or spectrophotometrically, and the decrease in fluorescein measured fluorometrically. If the molar ratio of bromide to fluorescein is $<4:1$, then the mono-, di- and tri-bromo derivatives are formed reproducibly. These derivatives have extinction coefficients close to eosin and are accounted for in the standardisation.

3.17 Iodate

3.17.1 Spectrophotometric method

Truesdale [78] has described autoanalyser procedures for the determination of iodate and total-iodine in seawater. The total iodine content of seawater (approximately $50\text{--}60\mu\text{g L}^{-1}$) is believed to be composed of iodate- ($30\text{--}60\mu\text{g L}^{-1}\text{I}$) and iodine-iodine ($0\text{--}20\mu\text{g L}^{-1}$) with perhaps a few $\mu\text{g L}^{-1}$ of organically bound iodine. In both of the methods, the iodine species of interest are first converted to iodate. Then the iodate is reacted with acid

and excess iodide to give iodonium ions, I_3^- , which are detected spectrophotometrically at 350nm. In the total-iodine procedure a pre-oxidation step is therefore required; here bromine-water was chosen. Interference from nitrite ions, which in acid also oxidise iodide to iodonium ions, is suppressed by sulphamic acid which destroys the nitrite ions.

Originally the objective of this work was only the automatic iodate-iodine procedure. This was needed to give the extra precision called for in an earlier study [79] which suggested that most of the observed variation in iodate-iodine results for the deeper waters (>200m) of the oceans is due to analytical imprecision. However, in addition to the original objective the procedure for total-iodine has developed. This development stemmed from the need to test the likelihood of iodonium ions, produced in the iodate procedure, being reduced by substances occurring naturally in seawater. This problem was defined when Truesdale [80] showed that molecular iodine is reduced rapidly in some seawaters; he found that the oxidising capacity of $260\mu\text{g L}^{-1}$ of iodine-iodine added to a filtered coastal seawater disappeared within 30min. The effect of such a process on the iodate method would be to lower the observed iodate concentrations. Further, the effect, if it occurred, would be expected to have its maximum effect in coastal and oceanic surface waters where primary productivity is highest; these waters also appear to contain the lowest recorded iodate concentrations. To test for the iodonium-ion reduction, a pre-oxidation step including iodine-iodine was incorporated in the analytical method for iodate-iodine. Having accomplished the iodine-water pre-oxidation step successfully, it was logical to attempt the bromine-water pre-oxidation and thereby produce the total-iodine method.

Methods for the following three determinations were described by Truesdale [78].

(1) *Determination of iodate without pre-oxidation*

Iodate in the buffered sample is reacted with sulphamic acid (to destroy nitrite) and potassium iodide to produce the iodonium ion I_3^- which is determined spectrophotometrically at 350nm.

(2) *Determination of iodate with pre-oxidation*

Iodine water is added to an acetic acid sodium acetate buffered sample to reoxidise to iodate any iodine-containing substances produced by reduction of iodate by naturally occurring reducing substances present in the sample. Total iodate (ie iodate present in the original sample as iodate plus additional iodate produced by iodine water treatment) is then reacted with phenol solution at pH 5.4 to destroy excess free iodine and then with sulphamic acid and potassium iodide to produce the iodonium ion which is estimated spectrophotometrically at 350nm.

This determination will test for the presence of naturally occurring reducing agents in seawater which by their action on iodonium ions could lead to an underestimate in iodate concentration. (The use of the method on anoxic waters containing sulphide is a prime example of when this precaution should be taken.)

(3) *Determination of total iodine with pre-oxidation*

This procedure is the same as that described under (2) except that the iodine water is replaced by bromine water, and the buffer contains added sodium bromide (ie sodium bromide-acetic acid-sodium acetate instead of the acetic acid-sodium acetate buffer used in method (1)).

In all three methods a blank is obtained. To ascertain the blank excess sodium thiosulphate is added to the potassium iodide reagent at a concentration of $4.0 \times 10^{-14} \text{ mol L}^{-1}$. Samples were reanalysed and the appropriate blank subtracted from the sample signal.

Variations in the salinity of the sample have very little effect on the accuracy of the results obtained in all three methods provided that the difference in salinity between the samples and the standards does not exceed 2.5 ‰.

Determinations of iodate without pre-oxidation in Pacific seawater by the above method gave a mean result of $583 \mu\text{g L}^{-1}$ with a standard deviation of $0.23 \mu\text{g L}^{-1}$. For samples containing between 40 and $60 \mu\text{g L}^{-1}$ standard deviations of $0.19 \mu\text{g L}^{-1}$ (iodate method with pre-oxidation), $0.12 \mu\text{g L}^{-1}$ (iodate method without pre-oxidation) and $0.43 \mu\text{g L}^{-1}$ (total iodine method) were obtained.

A set of Pacific open-ocean samples were analysed for iodate-iodine using both the procedure which incorporates pre-oxidation with iodine-water and that which does not. Also, in a similar exercise total-iodine was determined using both the method that incorporates pre-

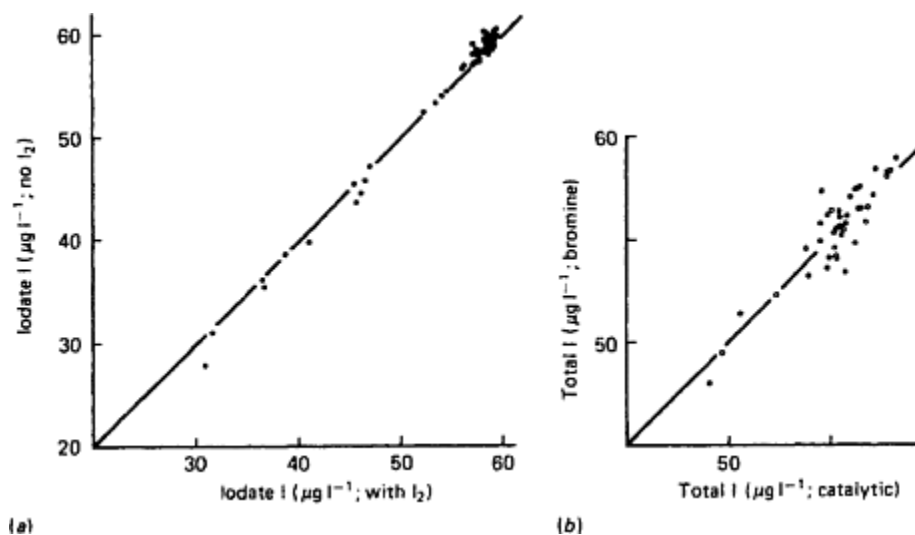


Fig. 3.5 The distribution of sample concentrations (means) encountered in the comparison of methods exercised (a) for iodate-iodine with and without iodine-water pre-oxidation; (b) for total iodine using the bromination procedure and older catalytic procedure. The analysis of variance has shown that in both exercises there was no significant difference between methods; any apparent bias is not significant when the variance due to sample replication is included. For convenience the line of unit gradient is shown. Note that an expanded scale has been used in the plot for total-iodine results

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oxidation with bromine water and the catalytic method using the reaction between Ce(IV) and As(III) [82]. Variance tests showed that differences between either replicates or methods was not significant (Fig. 3.5).

Truesdale and Smith [81] also carried out a comparative study of the determination of iodate in open ocean, inshore Irish seawaters and waters from the Menai Straits, using the spectrophotometric method (with and without pre-oxidation using iodine water) and also by a polarographic method [83].

Fig. 3.6 shows the results obtained in a comparison of these methods on a range of deep-sea and offshore samples. The line of gradient 1.0 on each diagram shows the result which would have occurred had agreement been obtained. The Students t-test (Table 3.7) showed that in both exercises the colorimetric method with iodine-water treatment yielded higher values than that without iodine-water treatment, and the polarographic method yielded, on average, a concentration lower than that obtained by the colorimetric procedure without iodine-water.

Schnepfe [84] has described yet another procedure for the determination of iodate and total iodine in seawater. To determine total iodine, 1ml 1% aqueous sulphamic acid is added to 10ml seawater which, if necessary, is filtered and then adjusted to a pH of less than 2.0. After

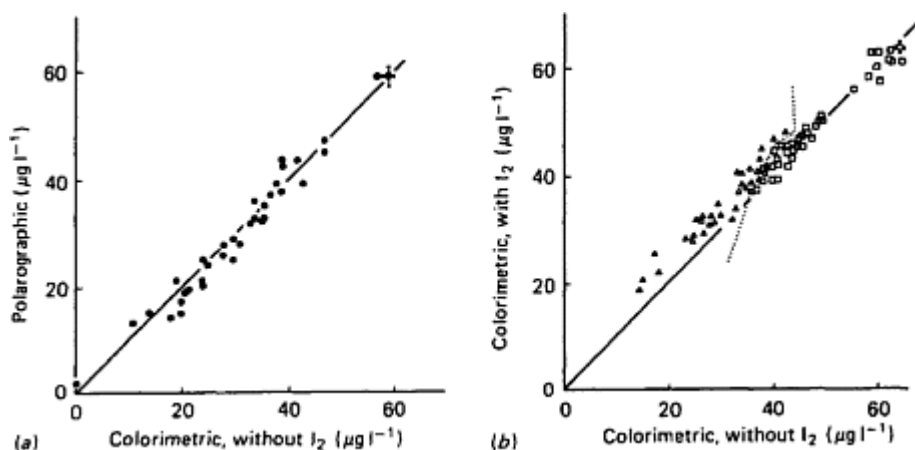


Fig. 3.6 The distribution of sample concentrations encountered in the comparisons of the colorimetric method without iodine with (a) the polarographic method and (b) the colorimetric method with iodine water. For convenience the line of unit gradient is shown in both cases. In each case the precision (95% confidence level) for each measurement is as shown for the most concentrated sample. In (b) the broken line divides onshore (Δ) and offshore ($\square$) samples

Source: Reproduced with permission from Elsevier Science [81]

Table 3.7 Results of testing the difference in the means obtained by the different iodate methods

<i>Method</i>		<i>No. of samples</i> ($\mu\text{g L}^{-1}$)	<i>Mean concn</i>	<i>Variance</i> ($\mu\text{g L}^{-1}$) ²	<i>t</i>
(a)	Two colorimetric procedures:				
	Without iodine	85	40.5	100.7	94.6
	With iodine	85	42.4	131.9	
(b)	Colorimetric/polarographic procedures:				
	Colorimetric	36	31.1	150.5	10.7
	Polarographic	36	30.3	161.5	

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15min, 1ml 0.1M sodium hydroxide and 0.5ml 0.1M potassium permanganate are added and the mixture heated on a steam bath for 1h. The cooled solution is filtered and the residue washed. The filtrate and washings are diluted to 16ml and 1ml of a 0.25M phosphate solution added (containing 0.3 μg iodine as iodate per ml) at 0°C Then 0.7ml 0.1M ferrous chloride in 0.2% v/v sulphuric acid, 5ml 10% aqueous sulphuric acid phosphoric acid (1:1) are added at 0°C followed by 2ml starch-cadmium iodide reagent. The solution is diluted to 25ml and after 10–15min the extinction of the starch-iodine complex is measured in a 5cm cell. To determine iodate the same procedure is followed as is described above except that the oxidation stage with sodium hydroxide-potassium permanganate is omitted and only 0.2ml ferrous chloride solution is added. A potassium iodate standard was used in both methods.

The total iodine procedure is claimed to be relatively free from interference by foreign ions. The iodate procedure is subject to interference by bromate and sulphite ions. This method is claimed to be capable of determining down to 0.1 μg iodine in the presence of 800mg chloride ion and 5mg bromide ion.

3.18 Iodide

Iodine species in seawater exist as iodide (I^-) and iodate (IO_3^-). Iodide, which is thermodynamically unstable in oxygenated water, is usually a minor species in seawater compared to iodate, and total inorganic iodine concentration is approximately in the range of 50–60 $\mu\text{g L}^{-1}$ [78,83,85–96]. However, iodide concentration ranges from 30 $\mu\text{g L}^{-1}$ near the shore and in ocean surface and bottom waters) to below 1 $\mu\text{g L}^{-1}$ (deep ocean water) [83,85–87,90,91,93,96,95]. Iodine is an essential micronutrient for many organisms. Iodide in seawater is produced by biologically mediated reduction of iodate [97] and is also produced under reducing conditions. Thus, the distribution of iodide and iodate gives clues for understanding the marine environment [88,89,94–96]. Iodide has been determined mainly by difference between total inorganic iodine (I^- and IO_3^-) and IO_3^- iodate has been determined by differential pulse polarography [83,89, 90,92,95,96]

and the spectrophotometric method after conversion of iodate to I_3^- in acidic solution [78,85,94]. Total inorganic iodine was determined after converting iodide to iodate by using chemical or photochemical means [78,83,85,86,88,89,92,94,95]. However, as the detection limit of iodide by the difference technique is not very good (for example, 1.3–2.5 $\mu\text{g L}^{-1}$ for differential pulse polarography [83,89]), it is desirable to detect iodide directly.

To date, a few methods have been proposed for direct determination of trace iodide in seawater. The first involved the use of neutron activation analysis [87], where iodide in seawater was concentrated by a strongly basic anion-exchange column, eluted by sodium nitrate, and precipitated as palladium iodide. The second involved the use of automated electrochemical procedures [83,91]; iodide was electrochemically oxidised to iodine and was concentrated on a carbon wool electrode. After removal of interference ions, the iodine was eluted with ascorbic acid and was determined by a polished Ag_3SI electrode. The third method involved the use of cathodic stripping square wave voltammetry [93]. Iodide reacts with mercury in a one-electron process, and the sensitivity is increased remarkably by the addition of Triton X. The three methods have detection limits of 0.7 (250 mL of seawater sample), 0.1 (50 mL), and 0.02 $\mu\text{g L}^{-1}$ (10 mL), respectively, and could be applied to almost all the samples. However, neutron activation analysis is not generally employed. The second method uses an automated system but is a special apparatus just for determination of iodide. The first and third methods are time-consuming.

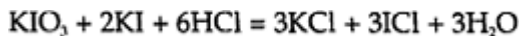
Recently, attention has been paid to ion chromatography as a simple method for determining trace iodide in seawater [96,98–102]. Two factors are essential in order to attain good sensitivity:

- (1) separation of iodide from an excess of anions in seawater and
- (2) highly sensitive detection of iodide.

Iodide was determined by an iodide-selective electrode ($\text{Ag}_2\text{S}/\text{AgI}$) after other anions were separated by sodium nitrate eluent [98]. However, the electrode that was stabilised by 0.5 μM iodide responded to chloride ion in seawater, and the detection limit of iodide was $\sim 2 \mu\text{g L}^{-1}$ Ito [103] (see section 3.18.4) showed that 0.1 M sodium chloride eluent was effective for the separation of iodide in seawater, due to faster elution of an excess of anions in seawater and slow elution of iodide with hydrophobicity on conventional low-capacity anion-exchange columns.

3.18.1 Titration method

Iodine in seawater can be determined by the procedure described below which is capable of determining down to 0.1 mg L^{-1} iodide [104]. In this method the sample is strongly acidified with hydrochloric acid titrated with 0.00125 M potassium iodate solution which converts iodide via iodine into iodine monochloride:



The end-point, which occurs with the complete conversion of iodide to iodine

monochloride, is indicated by the disappearance of the violet iodine colour from a chloroform layer present in the titration flask.

3.18.2 Spectrophotometric method

Sugawara [105] has described a method for the determination of iodide in seawater. Various workers [106,107] have modified this procedure.

Matthews and Riley [106] preconcentrated iodide by co-precipitation with chloride ions. This is achieved by adding 0.23g silver nitrate per 500ml seawater sample. Treatment of the precipitate with aqueous bromine and ultrasonic agitation promote recovery of iodide as iodate which is caused to react with excess of iodide under acid conditions, yielding I_3^- . This is determined either spectrophotometrically or by photometric titration with sodium thiosulphate. Photometric titration gave a recovery of $99.0 \pm 0.4\%$ and a coefficient of variation of $\pm 0.4\%$ compared with $98.5 \pm 0.6\%$ and $\pm 0.8\%$ respectively for the spectrophotometric procedure.

Shizuo [107] allowed the silver halide precipitate obtained in the co-precipitation process to stand in contact with the solution for more than 20h to ensure quantitative collection of iodide on the precipitate. They then evaporated the oxidised iodate solution to 5–10ml and again allowed the solution to stand for more than 12h before the colorimetric determination. No interference occurred by bromine compounds. The errors were then within $\pm 3\%$.

3.18.3 Cathodic stripping voltammetry

Luther *et al.* [93] have described a procedure for the direct determination of iodide in seawater. By use of cathodic stripping square wave voltammetry, it is possible to determine low and sub-nanomolar levels of iodide in seawater, freshwater and brackish water. Precision is typically $\pm 5\%$ (1σ). The minimum detection limit is 0.1–0.2nM (12 parts per trillion) at a 180s deposition time. Data obtained on Atlantic Ocean samples show similar trends to previously reported iodine speciation data. This method is more sensitive than previous methods by 1–2 orders of magnitude. Triton X–100 added to the sample enhances the mercury electrode's sensitivity to iodine.

3.18.4 Ion chromatography

Ito *et al.* [99] have described an ion chromatographic method for determining trace iodide in concentrated salt solutions. The method had a detection limit of $5\mu\text{g}$ of iodide L^{-1} , and a relative standard deviation ($n=5$) of 3% at 0.1mg of iodide L^{-1} .

In a more recent work Ito [103] has described a simple and highly sensitive ion chromatographic method with ultraviolet detection for determining iodide in seawater. A high-capacity anion-exchange resin with polystyrene-divinylbenzene matrix was used for both preconcentration and separation of iodide. Iodide in artificial seawater (salinity, 35 ‰) was trapped quantitatively ($98.8 \pm 0.6\%$) without peak broadening on a preconcentrator column and was separated with 0.35M sodium perchlorate+0.01M phosphate buffer (pH 6.1). On the other hand, the major anions in seawater, chloride and

sulphate ions, were partially trapped (5–20%) and did not interfere in the determination of iodide. The detection limit for iodide was $0.2\mu\text{g L}^{-1}$ for 6mL of artificial seawater. This method was applied to determination of iodide ($\text{ND}—18.3\mu\text{g L}^{-1}$) and total inorganic iodine ($\text{I}^- + \text{IO}_3^- - \text{I}, 50.0–52.7\mu\text{g L}^{-1}$) in seawater samples taken near Japan.

3.18.5 High performance liquid chromatography

Varma *et al.* [108] determined iodide in seawater in amounts down to 2ng L^{-1} by a method based on precolumn derivatization of the iodide into 4-iodo-2,6-dimethylphenol. An ultraviolet detector was employed.

3.18.6 Electrostatic ion chromatography

The application of this technique is discussed under multianion analysis in section 3.32.2.

3.18.7 Miscellaneous

Buchberger *et al.* [109] carried out a selective determination of iodide in brine. The performance of a potentiometric method using an ion selective electrode and of liquid chromatography coupled with ultraviolet detection at 230nm were compared as methods for the determination of iodide in the presence of other iodine species. Satisfactory results were obtained from the potentiometric method provided the solution was first diluted ten-fold with 5M sodium nitrate and external standards were used. Better reproducibility was, however, achieved with high performance liquid chromatography provided precautions were taken to prevent reduction of iodine to iodide in the mobile phase, for which extraction of iodine with carbon tetrachloride prior to analysis was recommended. This was the preferred method for automated analyses of iodine brines (iodide concentrations of 30–40mg per litre).

Krishnamoorthy and Iyer [110] have reported a method for determining nanogram levels of iodide in saline water samples containing a large excess of interfering chloride ion. The anions are first bound to a strong base anion exchanger, from which the chloride ion is readily eluted. The iodide is then eluted with 2M ammonium nitrate and the iodide is determined based on its catalytic effect on the reduction of cerium(IV) by arsenic(III). The method is claimed to have an accuracy comparable to that obtained by neutron activation analysis.

3.19 Molybdate

3.19.1 Atomic absorption spectrometry

A limited amount of work has been carried out on the determination of molybdenum in seawater by atomic absorption spectrometry [111–113] and graphite furnace atomic absorption spectrometry [114]. In a recommended procedure a 50mL sample of seawater at pH 2.5 is preconcentrated on a column of 0.5g *p*-aminobenzylcellulose, then the

column is left in contact with 1mol L^{-1} ammonium carbonate for 3h, after which three 5ml fractions are collected. Finally, molybdenum is determined by atomic absorption at 313.2nm with use of the hot-graphite-rod technique. At the 10mg L^{-1} level the standard deviation was $0.13\mu\text{g}$.

3.19.2 Determination and preconcentration

The determination and preconcentration of molybdate is discussed in section 15.3.1.

3.20 Nitrate

3.20.1 Spectrophotometric methods

Spencer and Brewer [115] have reviewed methods for the determination of nitrate in seawater. Classical methods for determining low concentrations of nitrate in seawater use reduction to nitrite with cadmium/copper [116] or zinc powder [117] followed by conversion to an azo dye using *N*-1-naphthylethylenediamine dihydrochloride and spectrophotometric evaluation. Malhotra and Zanoni [118] and Lambert and Du Bois [119] have discussed the interference by chloride in reduction-azo dye methods for the determination of nitrate.

Jones [120] has described a cadmium reduction method involving shaking the sample with spongy cadmium as an alternative to the use of cadmium columns. Shaking is carried out for a period of 90min followed by colorimetric determination of the nitrite formed using sulphanilamide-*N*-(phthaloyl) ethylene diamine dihydrochloride colour reaction. This technique has advantages over using a cadmium column in that sample/cadmium contact time can be more consistently controlled for a large series of samples and that problems of progressive deterioration in reduction capacity met in column methods are avoided. Recoveries of nitrate-spiked non saline water samples with up to 12 parts per thousand salinity were 94–106%.

One of the most appealing features of this method employing a shaker instead of a cadmium column is that the cadmium-sample contact time for a number of samples can be consistently controlled simultaneously. Samples can be shaken in covered flasks, but racks of screw-capped centrifuge tubes are handled more efficiently between work bench and shaker table. Shaking for 60–90min gave complete reduction at concentrations between 1 and $100\mu\text{mol L}^{-1}$ nitrate. There was slight but inconsistent evidence of reduction of nitrite when $1\mu\text{mol L}^{-1}$ samples were shaken for longer than 60min.

Table 3.8 Absorbance and coefficients of variation (CV) for potassium nitrate standards ($n=3$)

$\mu\text{mol L}^{-1}$ Nitrate	Optical path (cm)	Mean absorbance	%CV
0.0	10	0.050	14

0.5	10	0.197	2.1
1.0	10	0.343	1.0
2.0	10	0.619	0.61
0.0	1	0.006	36
2.0	1	0.070	0.82
5.0	1	0.167	1.5
10	1	0.330	0.30
20	1	0.649	0.15

Source: Reproduced with permission from Elsevier Science [120]

Mean absorbance and coefficient of variation for potassium nitrate standards analysed in triplicate by this method are given in Table 3.8. Absorptivity (ratio of absorbance to the product of optical path length and concentration) was 0.029 and 0.032 for the 10 and 1cm optical paths, respectively.

Suspended solids and coloured organic matter interfere with the analysis and should be eliminated by filtration and precipitation as described in the procedure. To assess the extent to which other components of non saline waters affect the accuracy of the proposed method, known amounts of nitrate were added to a number of sample types with salinities of 0–12% (Table 3.9). Recoveries for these nitrate-spiked samples were 94–106%.

Mubarek *et al.* [121] showed that the loss of nitrate in the presence of chloride in the phenoldisulphonic acid spectrophotometric method is eliminated by complexing the chloride with mercuric ion.

3.20.2 Ultraviolet spectroscopy

Ultraviolet spectrometry has also been used to determine nitrates. In a method for determining high levels of nitrate described by Mertens and Massart [122] the sample, diluted to contain 0.5–1mg L⁻¹ nitrate is acidified, filtered through a 0.5µm filter and the extinction measured against a blank at 210–220nm. The concentration of nitrate is obtained from a calibration graph. Interference from chloride, bromide, organic matter, carbonate, bicarbonate and nitrite is largely removed by using as blank a solution prepared by boiling 10ml of the sample with 0.5g Raney

Table 3.9 Recovery of known additions of NO₂⁻ nitrite

Sample	Salinity PP 10 ³	n	Concn mean (µmol L ⁻¹)	CV(%)	% recovery
A. Pamlico River	8	5	1.58	6.71	
+1µmol L ⁻¹ NO ₃ ⁻		5	2.55	2.20	97.0

	+2 $\mu\text{mol L}^{-1}$ NO ₃ ⁻	5	3.47	3.77	94.5
B. Jacks Creek		0 5	0.918	17.9	
	+1 $\mu\text{mol L}^{-1}$ NO ₃ ⁻	5	1.87	4.01	95.2
	+2 $\mu\text{mol L}^{-1}$ NO ₃ ⁻	5	2.96	3.50	102
C. Peat bog pore		0 2	0.776	1.18	
	+1 $\mu\text{mol L}^{-1}$ NO ₂ ⁻	2	1.74	3.54	96.4
	+2 $\mu\text{mol L}^{-1}$ NO ₂ ⁻	2	2.90	2.12	106
D. Neuse River		0m 4	8.07	2.14	
	+5 $\mu\text{mol LL}^{-1}$ NO ₃ ⁻	4	13.1	3.79	101
	+10 $\mu\text{mol L}^{-1}$ NO ₂ ⁻	4	18.1	1.22	100
E. Neuse River		12 4	0.160	12.5	
	+1 $\mu\text{mol L}^{-1}$ NO ₂ ⁻	4	1.11	8.64	95.3
	+2 $\mu\text{mol LL}^{-1}$ NO ₃ ⁻	4	2.12	2.45	98.0
F. Pamlico pore H ₂ O		0 3	1.07	1.62	
	+0.5 $\mu\text{mol L}^{-1}$ NO ₂	3	1.59	2.18	104
	+1 $\mu\text{mol LL}^{-1}$ NO ₃ ⁻	3	2.01	0.860	94.0

Source: Reproduced with permission from Elsevier Science [120]

nickel for 30min and then stirring for 90min at 90°C, to reduce nitrate to ammonia. The ϵ value is 8500 at 210nm and 4100 at 220nm. Beer's law is valid up to 10mg L⁻¹ at 210nm and up to 15mg L⁻¹ at 220nm. The standard deviations for a sample containing 17.4mg L⁻¹ of nitrate were 0.3 and 0.5mg L⁻¹ at 210 and 220nm respectively. No systematic errors were detected.

Previous ultraviolet methods for determining nitrate have attempted to allow for humic acid interference [123–126]. However, with the exception of Morries [126] these methods of allowance are inaccurate at humic acid concentrations above about 3.5mg L⁻¹. Unfortunately, none of these methods have attempted to make any allowance for ultraviolet absorbing pollutant organic compounds or interfering inorganic ions. Thus their applications to water analyses other than for relatively unpolluted fresh waters is open to question.

Brown and Bellinger [127] have proposed an ultraviolet technique that is applicable to both polluted and unpolluted fresh and some estuarine waters. Humic acid and other organics are removed on an ion exchange resin. Bromide interference in seawater samples can be minimised by suitable dilution of the sample but this raises the lower limit of detection such that only on relatively rich (0.5mg L⁻¹ N^O₃N) estuarine and inshore waters could the method be used. Chloride at concentrations in excess of 10,000mg L⁻¹ do not interfere.

The method is either not affected by or can allow for interference from phosphate, sulphate, carbonate, bicarbonate, nitrite, coloured metal complexes, ammonia dyes,

detergents, phenols and other ultraviolet absorbing substances. The method incorporates three features designed to reduce interferences:

- (1) Humic acid interference is reduced by carrying out measurements at 225nm, a higher wavelength than that used by previous workers (210–220nm).
- (2) Removal of inorganic interferences, particularly the removal of bromide interference in seawater by diluting the sample five-fold, the removal of nitrite by the addition of sulphamic acid and the removal of metals by passage through Amberlite IR 120 cation exchange resin.
- (3) Removal of ultraviolet absorbing organics by passage through a specific ion exchange resin such as Amberlite XAD-2.

Table 3.10 compares nitrate determinations in the presence of various interfering substances for this method and for two alternate methods—phenoldisulphonic acid and ion selective electrode methods. In general, the method proposed by Brown and Bellinger [127] is less subject to interference.

The speed of the nitrate selective ion electrode makes its use potentially ideal for nitrate determinations on a large number of samples. However, the results from adding various interfering substances (Table 3.10) seem to cast some doubt upon the values obtained in the presence of chloride and bicarbonate for, although the results are precise, they are not accurate—approximately 20–30% high.

3.20.3 Chemiluminescence method

Chemiluminescent techniques have been used to determine nanomolar quantities of nitrate and nitrite in seawater [128,129]. This method depends on the selective reduction of these species to nitric oxide which is then determined by its chemiluminescent reaction with ozone, using a commercial nitrogen oxides analyser. The necessary equipment is compact and sufficiently sturdy to allow shipboard use. A precision of $\pm 2 \text{ nmol L}^{-1}$ is claimed and an analytical range of 2 nmol L^{-1} with analytical rates of 10–12 samples hourly.

In this method [128] nitrate, nitrate plus nitrite or nitrite alone are selectively reduced to nitric oxide which is swept from the sample in a helium carrier gas flow. Nitric oxide is allowed to react with ozone in a nitrogen oxides analyser where it forms excited nitrogen dioxide. The

Table 3.10 The effects of various interferences on the determination of nitrates by three methods. For all determinations (with the exception of non saline river waters) the concentration of NO_3N was 1.125 mg L^{-1} . All concentrations are given in mg L^{-1}

Interference	Method					
	Phenoldisulphonic add		Uv method		Selective ion electrode	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected

Chloride:

100	0.62	1.07*	1.08	1.08	1.55§
1000			1.05		

Bicarbonate-carbonate:

100	1.13		1.06	7.87	1.24¥
200	1.23				
1000			1.13		

Bicarbonate-chloride:

100					1.581¶
Cl:200HCO ₃					
100					1.46¶
Cl:100HCO ₃					
50					1.46¶
Cl:100HCO ₃					

Nitrate:

0.304	1.11	1.48	1.10†		
1.500					1.31¶
3.040	1.13		1.06†		

Ammonium:

1.4	0.98				
14.0		0.66		1.08	1.13¶
1400.0			1.08		

*Interference**Method**Phenoldisulphonic add**Uv method**Selective ion electrode**Uncorrected Corrected Uncorrected Corrected Uncorrected Corrected*

Phenol:

1.0	1.10		1.29	1.10‡	1.13¶
10.0			1.86	1.08‡	

Daz**:

1.0			1.12		2.48¶
10.0			1.56	1.05‡	202.5¶

Unpolluted
river water
thymic acid-

1.69			1.77	1.77‡	3.15¶

inorganic salts
 NO_3N by
 polarography
 1.170

*Addition of exact amount of silver sulphate to precipitate chloride with no excess silver

†Addition of sulphamic acid (final concentration, in sample approximately 20mg L^{-1})

‡Treatment with Amberlite XAD-2 resin

§Addition of saturated silver sulphate (1–10ml sample). Not recalibrated

¥Addition of 2M acetic acid to sample (0.09ml per 30ml sample). Not recalibrated

¶Calibrate for presence of 3ml saturated silver sulphate and 0.09ml 2M acetic acid in 30ml sample

**Daz—a commercially available household detergent

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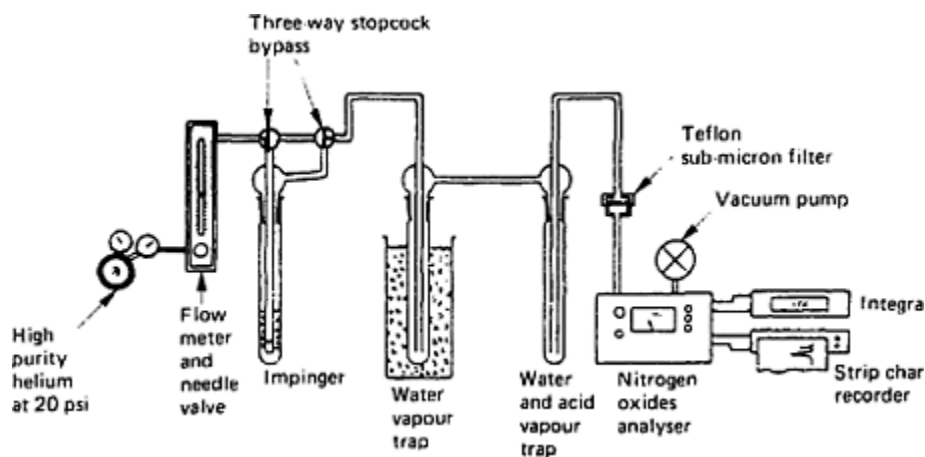


Fig. 3.7 Schematic diagram of apparatus

Source: Reproduced with permission from Elsevier Science [128]

return of the nitrogen dioxide to the ground state is accompanied by release of a photon which is detected by a photomultiplier. The integrated output of the photomultiplier over the time that the nitric oxide is purged from the sample is proportional to the nitrate or nitrite content of the sample.

The apparatus is shown schematically in Fig. 3.7. Helium is supplied to the system at a pressure of 20psi (138kpa) and the flow is regulated by means of a precision needle valve and flowmeter. The flow is adjusted to provide a small positive pressure at the input to the nitrogen oxides analyser. The helium flow is directed through an impinger consisting of a coarse porosity sintered glass frit (20–50 μm) in a 20 $\times$ 3.5cm diameter glass sample tube fitted with a 24/40 ground-glass joint. The sample tube can be bypassed from the helium flow by means of a pair of three-way stopcocks to allow changing of samples. Polyethylene 0.6cm od tubing and nylon Swagelock connectors are used at this point in

the system. Comparable Teflon tubing and connectors are used downstream from the impinger.

The helium carrier gas and nitric oxide from the sample pass sequentially through a salt/ice cold trap to condense water vapour, an anhydrous sodium carbonate drying tube to remove remaining traces of water vapour and acid gases and a Teflon submicron filter to exclude particles. The gas stream then enters a Bendix Model 8101-C Nitrogen Oxides Analyser operated in the 'NO only' mode, where nitric oxide is determined chemiluminescently.

The instantaneous concentration in the gas flow is recorded on a strip chart recorder operated at an input sensitivity of 10mV full scale, and a chart speed of 0.2in min⁻¹ (5mm min⁻¹). The integrated area is recorded by using an Analog Devices AD537J V to f converter connected to the 1V output of the nitrogen oxides analyser and the output of the V to f converter is totalled using a Heath Model IM 4100 frequency counter operated in the totalise mode. The V to f converter is mounted internally in the frequency counter and power is supplied from its logic circuits.

Linear calibration plots are obtained by this procedure covering the range up to 1nmol L⁻¹ for nitrate and for nitrite.

3.20.4 Continuous flow analysis

Hydes and Hill [239] used the copper-cadmium reduction method to determine nitrate in seawater. The construction of a copper-cadmium (50–50 w:w) reductor column for use during continuous flow analysis at sea is described. A 100% yield could be obtained using a 20cm×3mm column fitted with grains of copper-cadmium alloy between 500 and 350µm in size. The column maintained its reactivity during 3 months storage prior to an oceanographic cruise, and during the 4-week cruise period. Its performance was similar to that of the Stainton-type cadmium wire column but it had the advantages of easier preparation and easier control of reductor volume.

3.20.5 Flow injection analysis

Flow injection analysis is another technique that has been applied to the determination of nitrate and nitrite in seawater. Anderson [130] used flow injection analysis to automate the determination of nitrate and nitrite in seawater. The detection limit of his method was 0.1µmol L⁻¹. However, the sampling rate was only 30 per h which is low for flow injection analysis. Reactions seldom go to completion in a determination by flow injection analysis [131,132] because of the short residence time of the sample in the reaction manifold. Anderson selected a relatively long residence time so that the extent of formation of the azo dye was adequate to give a detection limit of 0.1µmol L⁻¹. This reduced the sampling rate because only one sample is present at a time in the post-injector column in flow injection analysis. Any increase in reaction time causes a corresponding increase in the time needed to analyse one sample.

Johnson and Petty [133] reduced nitrate to nitrite with copperised cadmium which was then determined as an azo dye, but the method is automated by means of flow injections analysis technique [134]. More than 75 determinations can be made per hour. The

detection limit is $112 \mu\text{mol L}^{-1}$ and precision is better than 1% at concentrations greater than $10 \mu\text{mol L}^{-1}$.

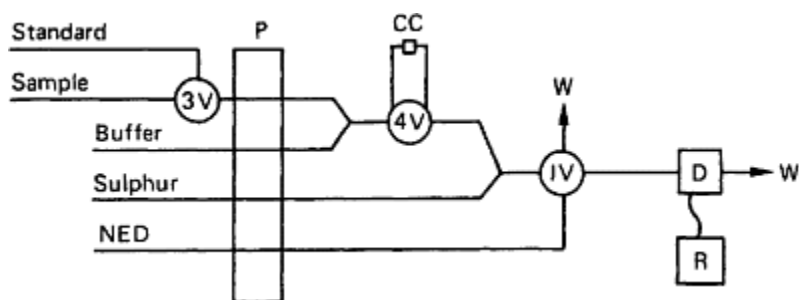


Fig. 3.8 Block diagram of the apparatus used to determine nitrate and nitrite. P=Pump; CC=cadmium reduction column; 3V=three-way valve used to switch between the sample and the standard; 4V=switching valve used to take the cadmium column out of line; IV= injection valve; D=detector; W=waste; R=recorder; Sulf. and NED are the sulphanilamide and N-(1 naphthyl)ethylenediamine dihydrochloride reagents

Source: Reproduced with permission from Springer-Verlag [133]

A block diagram of the equipment used is shown in Fig. 3.8. The reaction manifold was made from 0.8mm id. PTFE tubing. A four-channel Buchler peristaltic pump was used to propel the seawater and reagents. Tygon pump tubes (1.6mm id) were used to pump the sample (seawater or standard) and the ammonium chloride buffer. The sulphanilamide and diamine reagents were pumped with 0.8mm id Tygon tubing. The flow rates of these reagents were 4.5 times smaller than the sample and buffer flow rates. Altex low pressure fittings were used to make all of the connections between pump and manifold tubing and at the T fittings.

All of the tubing in which the sample was carried from the inlet, through the pump and reduction column to the confluence with the sulphanilamide line was made as short as possible.

The reduction column consisted of a piece of copperised cadmium, 1cm long in a piece of PTFE tubing 3cm long and 3.2mm id ($\frac{1}{4}$ in.). Glass wool plugs (3mm long) were placed in each end to retain the cadmium powder and were in turn held in place by short pieces of PTFE tubing (1.6mm id, 3.2mm od). Connections to the reaction manifold tubing (1.6mm od) were simply press fit into these adapters until the ends were flush.

The peaks obtained for a series of standard solutions are shown in Fig. 3.9. A small amount of carryover between samples, amounting to about 1%, is evident. A calibration curve obtained from these standards is distinctly non-linear; errors in accuracy, under 1%, appear at concentrations above $10 \mu\text{mol L}^{-1}$ if a linear calibration is assumed.

Fig. 3.10 shows distributions of nitrate determined by this method and chlorophyll and water temperature in a sea cruise over a thermal front. The concentrations of nitrate changed by nearly an order of magnitude within a few minutes; these changes are highly

correlated with the temperature and with chlorophyll fluorescence.

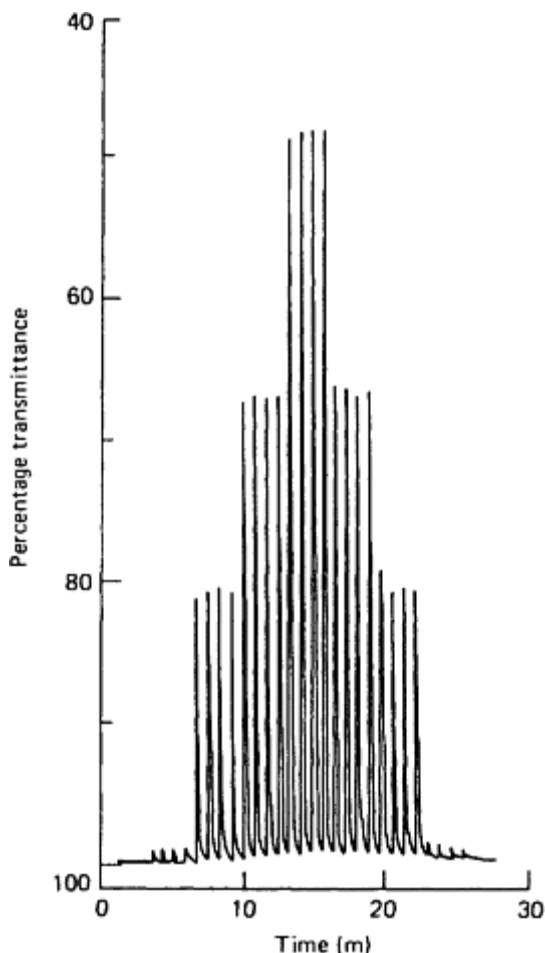


Fig. 3.9 Detector response for a series of nitrate standards with concentrations of 0, 10, 20 and $40\mu\text{mol L}^{-1}$

Source: Reproduced with permission from Springer Verlag [133]

3.20.6 Cathodic stripping voltammetry

Van den Berg [135] used this technique to determine nanomolar levels of nitrate in seawater. Samples of seawater from the Menai Straits were filtered and nitrite present reacted with sulphanilamide and naphthyl-amine at pH 2.5. The pH was then adjusted to 8.4 with borate buffer, the solution de-aerated and then subjected to adsorptive cathodic stripping voltammetry. The concentration of dye was linearly related to the height of the reduction peak in the range 0.3–200nM nitrate. The optimal concentrations of sulphanilamide and naphthylamine were 2mM and 0.1mM respectively at pH 2.5. The

standard deviation of a determination of 4nM nitrite was 2%. The limit of detection was 0.3nM for an adsorption time of 60s. The sensitivity of the method in seawater was the same as in fresh water.

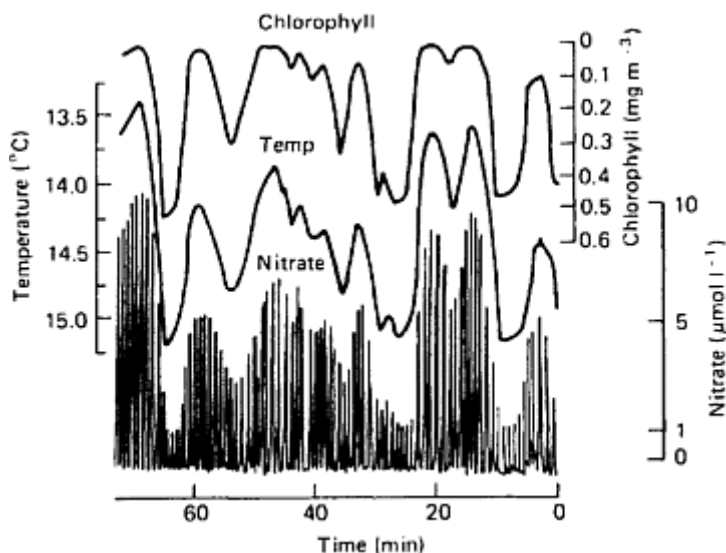


Fig. 3.10 Nitrate, temperature and chlorophyll measured at 15m in the Santa Barbara Channel (34°01'56"N, 119° 19'30"W). Temperature and chlorophyll were determined with a thermistor and a Turner Designs fluorometer at the effluent of the debubbler

Source: Reproduced with permission from Springer Verlag [133]

3.20.7 Ion chromatography

Tyree and Bynum [136] describe an ion-chromatographic method for the determination of nitrate and phosphate in seawater. The pretreatment comprised vigorous mixing of the sample with a silver-based cation-exchange resin, followed by filtration to remove the precipitated silver salt.

The application of electrostatic ion chromatography is discussed under multianion analysis in section 3.32.2.

3.21 Nitrite

3.21.1 Spectrophotometric methods

Spencer and Brewer [115] have reviewed methods for the determination of nitrite in seawater. Workers at the Water Research Centre, UK [137] have described an automated procedure for the determination of oxidised nitrogen and nitrite in estuarine waters. The procedure determines nitrite by reaction with N-1 naphthyl-ethylene diamine

hydrochloride under acidic conditions to form an azo dye which is measured spectrophotometrically. The reliability and precision of the procedure were tested and found to be satisfactory for routine analyses provided that standards are prepared using water of an appropriate salinity. Samples taken at the mouth of an estuary require standards prepared in synthetic seawater while samples taken at the tidal limit of the estuary require standards prepared using deionised water. At sampling points between these two extremes there will be an error of up to 10% unless the salinity of the standards is adjusted accordingly. In a modification of the method nitrate is reduced to nitrite in a micro cadmium/copper reduction column and total nitrite estimated. The nitrate content is then obtained by difference.

Matsunaga *et al.* [138] have also described a similar procedure for the determination of nitrite in seawater. To 500ml of sample is added 10ml 1% solution of sulphanilamide in 2M hydrochloric acid and 5ml 0.1% aqueous N-1-naphthylethylene-diamine hydrochloride. After 10min 5ml 0.5% aq. dodecylbenzenesulphonate is added and the mixture extracted for 2min with 50ml carbon tetrachloride; 75ml acetone and 10ml 0.1M hydrochloric acid are added to the separated organic layer and the azo-dye back-extracted into the acid. The extinction of the acid layer is measured at 543nm in a 2cm cell. The sensitivity for 0.001 extinction in 1cm cells is 0.7ng atom nitrite-N per litre.

Gianguzza and Orecchio [139] have carried out comparative trials of various methods for estimating nitrites in seawaters. These workers compared a method using sulphanilic acid/ α -naphthylamine complexes, with a method using sulphanilamide/N(1-naphthyl) ethylenediamine complexes for the determination of nitrites in saline waters. The second method has the greater sensitivity and lower detection limits. The former method is subject to interference from chlorides and this interference can be completely eliminated by the coupling diazotisation procedure of the latter method.

Anion exchange resins have been used to determine extremely low concentrations of nitrite down to nanomoles in seawater. Wada and Hattori [140] formed an azo dye from the nitrite using N-1 naphthylethylene diamine dihydrochloride and then adsorbed the dye in an anion exchange resin. The dye is then eluted from the column with 60% acetic acid and evaluated spectrophotometrically at 550nm.

3.21.2 Flow injection analysis

Fogg *et al.* [141] used flow injection voltammetry to reduce nitrite at a glassy carbon electrode in acidic bromide or chloride medium to determine nitrite in sea water.

3.22 Nitrate and nitrite

3.22.1 Spectrophotometric methods

Bajic and Jaselskis [142] described a spectrophotometric method for the determination of nitrate and nitrite in seawater. It included the reduction of nitrate and nitrite to hydroxylamine by the zinc amalgam redactor (Jones reductor) at pH 3.4 and reoxidation of the product with iron(III) in the presence of Ferrozine. Interference by high levels of

nitrite could be eliminated with azide treatment. Levels of nitrate of 0.1mg L^{-1} could be detected with a precision of 3% in the presence of large amounts of nitrite and chloride.

Nagashima *et al.* [143] used second derivative spectrometry to determine nitrate and nitrite in seawater.

Samples of artificial seawater, pure water and chlorinated water were pumped through a column containing cadmium/copper powder which converted nitrate to nitrite. The produced and existing nitrite were reduced to nitrogen monoxide and the mixture fed through a gas-liquid separator. Evolved nitrogen monoxide was purged by nitrogen into a heated optical cell where the second derivative absorbance was recorded at 214nm. Various experimental conditions were investigated. A reducing agent of 0.13M sodium iodide/13M phosphoric acid, a mixing coil 5m long operated at 50°C and a separator 50cm long with outer tube heated to 90°C were selected. Nitrite was determined directly and nitrate indirectly by measuring differences in nitrite with and without the converter.

The Department of the Environment UK [144] has described a number of alternative methods for the determination of total oxidised nitrogen (nitrate plus nitrite) in aqueous solution, while specific methods for nitrate and nitrite are also included. Among the methods for total oxidised nitrogen, one is based on the use of Devarda's alloy for reduction of nitrate to ammonia, and another uses copperised cadmium wire for reducing nitrate to nitrite, which is determined spectrophotometrically. Nitrate may also be determined spectrophotometrically after complex formation with sulphosalicylic acid, or following reduction to ammonia, the ammonia is eliminated by distillation and determined titrimetrically. Other methods include direct nitrate determination by ultraviolet spectrophotometry, measurements being made at 210nm, and the use of a nitrate-selective electrode. Details of the scope, limits of detection and preferred applications of the methods are given in each case.

Various other workers have discussed spectrophotometric methods for the determination of nitrate and nitrite [145–152].

3.22.2 Ultraviolet spectroscopy

Suzuki *et al.* [153] determined total nitrogen in seawater by oxidising the sample with potassium persulphate, boiling with sulphuric acid and potassium permanganate at pH 1.3 to remove bromide and bromate, removal of the excess potassium permanganate and manganese dioxide with sodium thiosulphate, and measuring the absorbance of the treated solution at 220nm.

Nakamura and Namiki [154] have determined total nitrogen in seawater by ultraviolet spectrophotometry and correcting for background absorption due to bromide ion.

3.22.3 Continuous flow analysis

Workers at the Department of the Environment UK [155] have described continuous flow methods for the determination of total oxidised nitrogen and nitrite in seawater. Limits of detection are $1.3\mu\text{g L}^{-1}$ (total oxidised nitrogen) and $0.26\mu\text{g L}^{-1}$ (nitrite). Within-batch standard deviations for total oxidised nitrogen range from $0.28\mu\text{g L}^{-1}$ to $17.5\mu\text{g L}^{-1}$ at the total oxidised nitrogen level to $0.96\mu\text{g L}^{-1}$ at the $560\mu\text{g L}^{-1}$ total oxidised nitrogen

level. Within-batch standard deviations for nitrite range from $0.056\mu\text{g L}^{-1}$ at the $3.5\mu\text{g L}^{-1}$ nitrite level to $0.042\mu\text{g L}^{-1}$ at the $70\mu\text{g L}^{-1}$ nitrite level.

Reduction of nitrate to nitrite is achieved by the use of a mixing coil containing copperised cadmium wire; spectrophotometric evaluation of the produced nitrite is achieved by the sulphanilamide N-1 naphthylethylene diamine hydrochloride system.

3.22.4 Flow injection analysis

Flow injection analysis has been adapted to automatic air-segmented continuous flow systems, eg the Technicon AutoAnalyzer system. Several reducing agents such as zinc [146], cadmium [147], amalgamated [148, 149] or copperised cadmium [150,151] have been investigated. Reductor columns are, however, difficult to operate in an air-segmented stream. This problem can be avoided by using the continuous flow injection technique developed by Ruzicka and Hansen [132,156].

The flow injection technique is based on three main principles: sample injection, reproducible timing and controlled dispersion [132]. The dispersion can be described as limited, medium or large; in a colorimetric system based on a reaction between the sample and a suitable reagent, a medium dispersion is preferred. Thus in the flow injection determination of nitrate, the reductor column should not excessively increase the dispersion. In a copperised cadmium reductor, more than 90% of the total nitrate is reduced within 1–2s with minimum risk of further reduction of nitrite [157]. Consequently, the reductor can be made very small which results in a minimal increase of dispersion.

In this development of a flow injection method for the determination of nitrate and nitrite, Anderson [130] chose the Shinn [158] method of reduction of nitrate to nitrite because of its high sensitivity and relative freedom from interferences. Anderson [130] used the flow injection principle in the photometric determination of nitrite and nitrate with

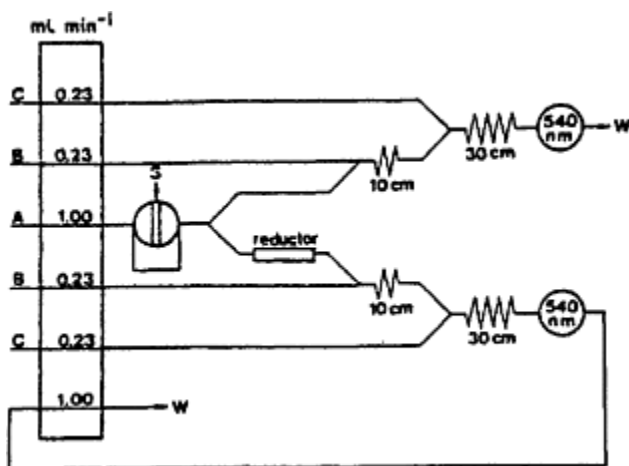


Fig. 3.11 Flow diagram for the colorimetric determination of nitrite and nitrate.

The internal diameter of the tygon tubing was 0.64mm for the 0.23ml min^{-1} flow rates and 1.30mm for the 1.00ml min^{-1} flow rates; all other tubing was of 0.7mm i.d. The reagents were: (A) carrier stream; (B) sulphanilamide solution and (C) diamine solution. S denotes the point of injection and W waste

Source: Reproduced with permission from Elsevier Science [130]

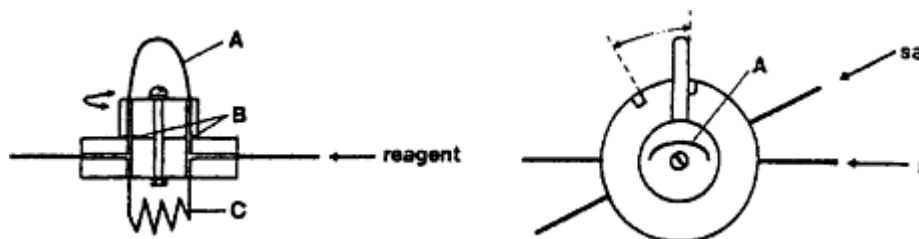


Fig. 3.12 Rotary-valve injection port. (A) Sample loop; (B) O-rings; (C) bypass of higher hydrodynamic flow resistance than the sample loop (100cm length and 0.5mm id)

Source: Reproduced with permission from Elsevier Science [130]

sulphanilamide and *N*-(1-naphthyl)ethylenediamine as reagents as discussed below. An on-line copper-coated cadmium reductor reduces nitrate to nitrite. The detection limit is $0.05\mu\text{M}$ for nitrite and $0.1\mu\text{M}$ for nitrate at a total sample volume of $200\mu\text{L}$. Up to 30 samples can be analysed per hour with a relative precision of ca 1%.

A schematic diagram of the flow injection system used by Anderson [130] is shown in Fig. 3.11. An Ismatec model MP13 peristaltic pump was used. Different flow rates were obtained by changing the pump tube diameters as indicated in the legend to Fig. 3.11. The injection port was a rotary valve [132,159]. The sample volume could be varied between 10 and $1000\mu\text{L}$ simply by changing the length of the sample loop (see Fig. 3.12).

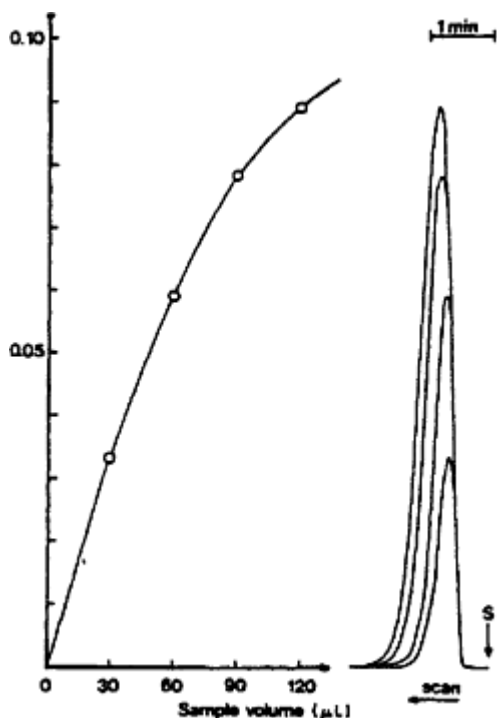


Fig. 3.13 Response curves obtained by injecting different sample volumes of a 1 μ M nitrite standard

Source: Reproduced with permission from Elsevier Science [130]

Peaks obtained by injecting different sample volumes of a 1 μ M nitrite standard are shown in Fig. 3.13. The optimum sample volume is of the order of 100 μ L. Peak broadening is due to mixing in the manifold.

The spectrophotometric signal is due not only to the absorbance but also to the refraction of the sample. Refraction is of no practical importance at absorbance values above 0.05. The detection limit is determined by the difference in refraction between the reagent stream and the sample. Thus, in order to achieve low detection limits—0.05 μ M for nitrite and 0.1 μ M for nitrate—it was necessary to adjust the refractive index of the reagents to a value as close as possible to those of the samples. For seawater analysis, this was achieved by adding sodium chloride to the reagents. This also improved the reproducibility of dispersion because density differences were found to cause turbulence.

In the analysis of sea water, the only significant interference arises from turbidity caused by particles in the sample. Prior filtration of the sample is therefore necessary. For anoxic waters, however, sulphide concentrations over 2 μ M were found to decrease the absorbance. This was overcome by adding an excess of either Cd^{2+} or Hg^{2+} to the sample [160,161],

3.22.5 Reverse phase ion interaction liquid chromatography

Ito *et al.* [162] used this technique employing octadecyl silane reverse phase columns coated with cetyltrimethyl ammonium chloride for the determination of nitrite and nitrate in seawater.

3.23 Perrhenate

3.23.1 Determination and preconcentration

This is discussed in section 15.3.2.

3.24 Phosphate

3.24.1 Spectrophotometric method

Spencer and Brewer [115] have reviewed methods for the determination of phosphate in seawater. Earlier methods for the determination of phosphate in seawater are subject to interferences, particularly by nitrate. In one early method [163] the filtered seawater sample is acidified with nitric acid and perchloric acid in the presence of hydroxylammonium chloride and ammonium chloride and the phosphomolybdate complex extracted with methylisobutyl ketone. This extract is then reduced with acidic stannous chloride and ascorbic acid and the extinction measured at 725nm. Hosokawa and Ohshima [164] heated the sample (50ml) for 20min on a boiling water bath with 2ml Mo(VI)-Mo(V) reagent (hydrochloric acid added (10ml) to 2M-Mo(VI) (10ml) then added zinc (0.3g), and after the zinc dissolved added hydrochloric acid to 100ml). The mixture was cooled and the extinction at 830nm measured. The resulting blue complex remains stable for at least 2 months and has an ϵ value of 26000. Nitrate interferes if present in concentrations more than $1\mu\text{g L}^{-1}$ and should first be reduced to nitrite with zinc in acidic medium, AsO_4^{3-} interfere at 10mg L^{-1} . The salt error was about 5% at a chloride concentration of 1.9%.

Isaeva [165] described a phosphopolybdate method for the determination of phosphate in turbid seawater. Molybdenum titration methods are subject to extensive interferences and are not considered to be reliable when compared with more recently developed methods based on solvent extraction [166–171] such as the solvent extraction-spectrophotometric determination of phosphate using molybdate and malachite green [172]. In this method the ion-pair formed between malachite green and molybdophosphate is extracted from the seawater sample with an organic solvent. This extraction achieves a useful 20-fold increase in the concentration of the phosphate in the extract. The detection limit is about $0.1\mu\text{g L}^{-1}$ standard deviation 0.05ng L^{-1} ($4.3\mu\text{g L}^{-1}$ in tap water) and relative standard deviation 1.1%. Most cations and anions found in non saline waters do not interfere, but arsenic(V) causes large positive errors.

In earlier work Motomizu *et al.* [171] used ethyl violet as counter-ion for

molybdophosphate. The spectrophotometric determination of phosphate by solvent extraction of molybdophosphate with ethyl violet is more sensitive than those previously reported [163,171–174], and less troublesome; a single extraction is adequate. However, in the determination of phosphorus at ng mL^{-1} levels in waters it has certain disadvantages. First, the absorbance of the reagent blank becomes too large for the concentration effect achieved by the solvent extraction to be of much use; for example, when 20ml of sample solution and 5ml organic solvent were used, the absorbance of the reagent blank was 0.14. Secondly, the shaking time needed was long and the colour of the extract faded gradually if the shaking lasted more than 30min.

However malachite green [172] gave a stable dark yellow species in 1.5M sulphuric acid (probably a protonated one), whereas ethyl violet became colourless within 30min even in only 0.5M sulphuric acid.

In this procedure 10ml of the sample solution containing up to $0.7\mu\text{g}$ phosphorus as orthophosphate, was transferred into a 25ml test tube. To this solution was added 1ml each of 4.5M sulphuric acid and the reagent solution. The solution was shaken with 5ml of a 1:3 v/v mixture of toluene and 4-methylpentan-2-one for 5min. After phase separation, the absorbance of the organic phase was measured at 630nm against a reagent blank, in 1cm cells.

The absorption spectra of the ion-pair and the reagent blank are shown in Fig. 3.14. Linear calibration graphs are obtained even when the aqueous phase volume is increased to 100ml (and 7ml of extracting solvent are used). The results obtained by varying the volume of sample solution are shown in Table 3.11, which shows that when 50ml of sample solution are used, $0.1\mu\text{g L}^{-1}$ of phosphorus can be detected.

Arsenic(V) causes large positive errors; arsenic(V) at a concentration of $10\mu\text{g L}^{-1}$ produces an absorbance of 0.07 but can be masked with tartaric acid (added in the reagent solution). When arsenic(V) was present at concentrations of $50\mu\text{g L}^{-1}$ it was masked with $0.1\text{ml } 10^{-4}\text{M}$ sodium thiosulphate added after the sulphuric acid.

For a 25ml sample, almost all of the foreign ions tested, when present at the concentrations listed in Table 3.12, produced an absorbance of less than 0.005.

Table 3.13 shows the results for determination of phosphorus in waters. Less than 15ml of seawater was taken as sample and was diluted to 25ml with distilled water because of its high chloride content ($>0.5\text{M}$).

Recovery tests were done by adding known amounts of phosphate. The results are also shown in Table 3.13. The recovery of phosphorus was good; 99–103%. The relative standard deviation for phosphorus was 0.6% for $21.0\mu\text{g L}^{-1}$ in seawater.

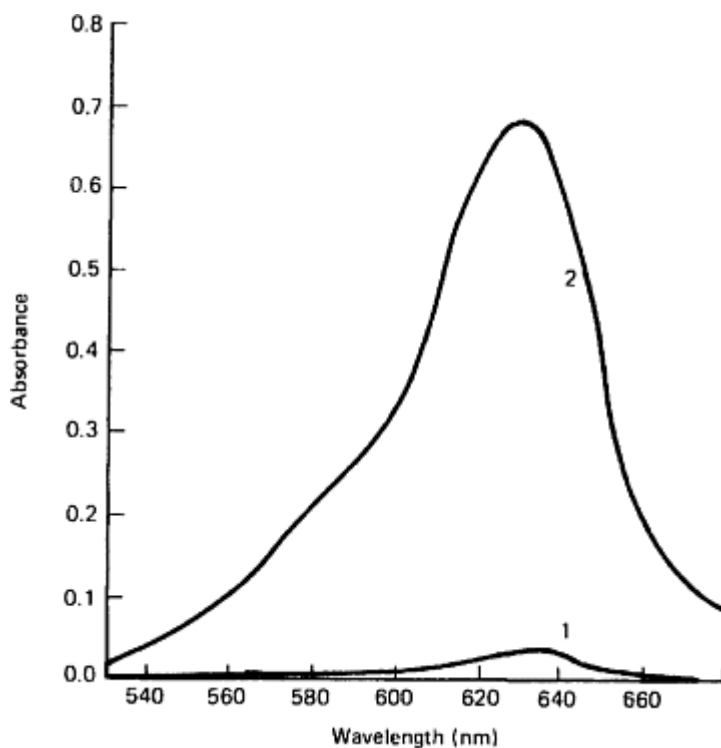


Fig. 3.14 Absorption spectra in the organic phase (curve 1) reagent blank (reference, extracting solvent); (curve 2) phosphorus, 0.428 μg (reference, extracting solvent); aqueous phase, 12ml, organic phase 5ml

Source: Reproduced with permission from Elsevier Science [172]

Table 3.11 Effect of volume of sample solution

Sample solution taken (ml)	Sulphuric acid added (ml)	Reagent solution added (ml)	Absorbance of reagent blank	Absorbance units for $\mu\text{g L}^{-1}$ phosphorus	Molar absorptivity* ($105\text{L mol}^{-1}\text{cm}^{-1}$)
5	0.5	0.5	0.034	0.007	2.30
10	1.0	1.0	0.044	0.015	2.26
25	2.5	2.5	0.062	0.038	2.31
50	5.0	5.0	0.078	0.080	2.48
100†	10.0	10.0	0.122	0.124	2.69

Extracting solvent 5ml of a 1:3 mixture of toluene and 4-methylpentan-2-one Phosphorus 0–0.8µg

*Organic phase volume was assumed to be 5ml

†7ml of extracting solvent were used

Source: Reproduced with permission from Elsevier Science [172]

Table 3.12 Effect of other ions

<i>Ion</i>	<i>Added as</i>	<i>Concentration mol L⁻¹</i>	<i>Absorbance*</i>
None			0.549
Na ⁺ , Cl ⁻	NaCl	0.3	0.545
K ⁺	KCl	1×10 ⁻²	0.548
SO ₄ ²⁻	Na ₂ SO ₄	1×10 ⁻²	0.552
Ca ²⁺	CaCl ₂	1×10 ⁻²	0.551
Mg ²⁺	MgCl ₂	1×10 ⁻²	0.548
HCO ₃ ⁻	NaHCO ₃	1×10 ⁻²	0.556
Al ³⁺	K Al(SO ₄) ₂	1×10 ⁻³	0.550
Fe ³⁺	FeNH ₄ (SO ₄) ₂	1×10 ⁻³	0.551
NH ₄ ⁺	NH ₄ Cl	1×10 ⁻³	0.557
NO ₃ ⁻	NaNO ₃	1×10 ⁻³	0.548
Cr ³⁺	CrCl ₃	1×10 ⁻³	0.549
Mn ²⁺	MnCl ₂	1×10 ⁻³	0.549
Co ²⁺	CoCl ₂	1×10 ⁻³	0.549
Cd ²⁺	CdCl ₂	1×10 ⁻³	0.552
Ni ²⁺	NiCl ₂	1×10 ⁻³	0.549
Cu ²⁺	CuCl ₂	1×10 ⁻³	0.553
Zn ²⁺	ZnCl ₂	1×10 ⁻³	0.546
Br ⁻	NaBr	1×10 ⁻³	0.546
B(III)	Na ₂ B ₄ O ₇	1×10 ⁻³	0.552
SiO ₃ ²⁻	Na ₂ SiO ₃	5×10 ⁻⁴ †	0.553
VO ₃ ⁻	NH ₄ VO ₃	1×10 ⁻⁵	0.556
WO ₄ ²⁻	(NH ₄) ₁₀ W ₁₂ O ₄₁	1×10 ⁻⁵	0.554
I ⁻	Nal	1×10 ⁻⁵	0.550
Laurylsulphate	Na salt	5×10 ⁻⁶ †	0.549

Laurylbenzenesulphonate	Na salt	$5 \times 10^{-6} \dagger$	0.547
ClO_4^-	NaClO_4	$1 \times 10^{-6} \dagger$	0.557
Ti^{4+}	TiCl_4	$\times 10^{-6}$	0.551

*Sample solution 1 0ml; organic phase 5ml; phosphorous 0.366 μg ; measured against reagent blank

$\dagger$ Tolerance limit

Source: Reproduced with permission from Elsevier Science [172]

A commonly used procedure for the determination of phosphate in seawater and estuarine waters uses the formation of the molybdenum blue complex at 35–40°C in an autoanalyser and spectrophotometric evaluation of the colour produced. Unfortunately, when applied to seawater samples depending on the chloride content of the sample, peak distortion or even negative peaks occur which make it impossible to obtain reliable phosphate values (Fig. 3.15). This effect can be overcome by the replacement of the distilled wash-wash solution used in such methods by a solution of sodium chloride of an appropriate concentration

Table 3.13 Determination of phosphorus in river and seawater and recovery test

Sample	Recovery test					
	Phosphorus found $\mu\text{g L}^{-1}$	Sample taken (ml)	P in sample (ng)	P added (ng)	P found (ng)	Recovery (%)
Seashore of Seto Inland Sea						
Kojima	46.0	5	230	248	477	100
Shibukawa	17.4	8	139	148	391	101
Tamano	15.3	8	122	248	381	103
Ushimado	12.8	8	102	248	351	100
Nishiwaki	20.9	8	167	248	419	101

The samples were adjusted to about pH 3 with dilute sulphuric acid after sampling, and filtered through a membrane filter (0.45 μm). An appropriate amount of sample was transferred to a 25ml test tube, 1ml of 4.5M sulphuric acid was added, and the mixture was heated at 95°C for 30min. The seawater samples were diluted to 25ml with distilled water. A 10ml sample was used, except for Yoshii River sample D and the Kojima seawater for which 5ml samples were used. In the recovery tests, the river water was diluted to 10ml with distilled water after the addition of 248ng of phosphorus (as phosphate), and the seawater was diluted to 25ml with distilled water after the addition of phosphorus

*The values are the means of three determinations

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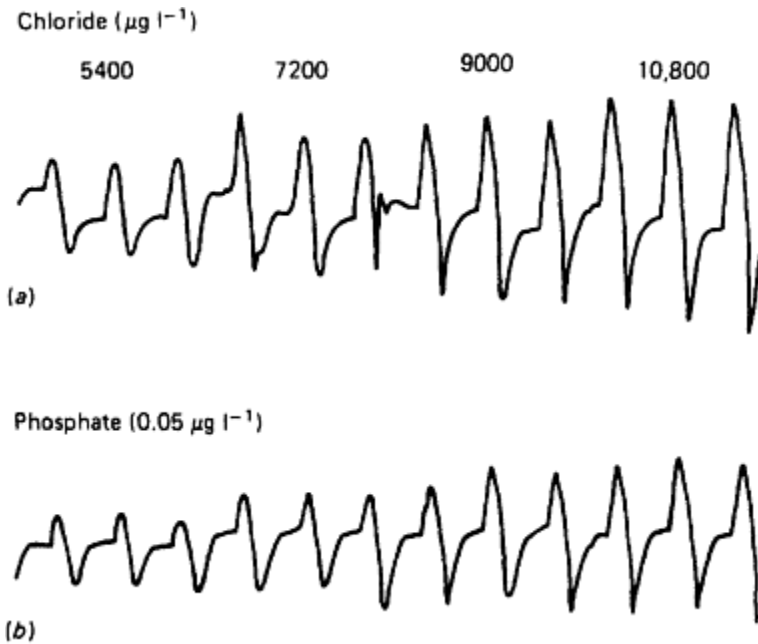


Fig. 3.15 Interference by chloride in the autoanalyser determination of phosphate

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Table 3.14 Dependence of chloride content of wash liquid on chloride content of sample

Chloride content of wash (mg L^{-1})	Chloride content of sample (mg L^{-1})
0	0–1800
4850	1800–7200
10000	7200–12600
15200	12600–18000

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related to the chloride concentration of the sample. The chloride content of the wash solution need not be exactly equal to that of the sample. For chloride contents in the sample up to $18\,000\text{ mg L}^{-1}$, (ie seawater) the chloride concentration in the wash should be within $\pm 15\%$ of that in the sample (Table 3.14). The use of saline standards is optional but the use of saline control solutions is mandatory. Using good equipment, down to 0.02 mg L^{-1} phosphate can be determined by such procedures. For chloride contents above $18\,000\text{ mg L}^{-1}$ the chloride content of the wash should be within $\pm 5\%$ of that in the

sample.

Flynn and Meehan [175] have described a solvent extraction phosphomolybdate method using iso amyl alcohol for monitoring the concentration of ^{32}P in sea and coastal waters near nuclear generating stations.

Fujiwara *et al.* [176] have proposed a method for the colorimetric determination of traces of phosphorus with molybdenum blue, making use of the laser-induced thermal lensing effect. The procedure is described, and the results obtained on samples of sea water and lake water are presented.

In this method an Ar^+ laser pumped rhodamine 101 laser was used as the heat and probe source. The signal from a silicon photocell with a 1mm^2 photosensitive surface, which was used as a laser radiation detector, was processed with an inexpensive personal computer. The detection limit is 5pg of P mL^{-1} which is determined mainly due to the deviation in the colour development with the molybdenum blue method.

Yoshimura *et al.* [177] carried out microdeterminations of phosphate by gel-phase colorimetry with molybdenum blue. In this method phosphate reacted with molybdate in acidic conditions to produce 12-molybdophosphate. The blue species of molybdophosphate were reduced by ascorbic acid in the presence of antimony ions and adsorbed on Sephadex G-25 gel beads. Attenuation at 836 and 416nm (adsorption maximum and minimum wavelengths) was measured and the difference used to determine trace levels of phosphate. The effects of nitrate, sulphate, silicic acid, arsenate, aluminium, titanium, iron, manganese, copper and humic acid on the determination were examined.

Eberlein and Kattner [178] have described an automated method for the determination of orthophosphate and total dissolved phosphorus in the marine environment. Separate aliquots of filtered seawater samples were used for the determination of orthophosphate and total dissolved phosphorus in the concentration range $0.01\text{--}5\mu\text{g L}^{-1}$ phosphorus. The digestion mixture for total dissolved phosphorus consisted of sodium hydroxide (1.5g), potassium peroxodisulphate (5g) and boric acid (3g) dissolved in doubly distilled water (100ml). Seawater samples (50ml) were mixed with the digestion reagent, heated under pressure at $115\text{--}120^\circ\text{C}$ for 2h, cooled and stored before determination in the autoanalyser system. For total phosphorus, extra ascorbic acid was added to the aerosol water of the autoanalyser manifold before the reagents of the molybdenum blue reaction were added. For the measurement of orthophosphate, a phosphate working reagent composed of sulphuric acid, ammonium molybdate, ascorbic acid and antimony potassium tartrate solution was prepared. Up to 30 samples per h could be analysed.

The application of this technique is discussed under multianion analysis in section 3.32.1.

3.24.2 Reverse flow injection analysis

This technique differs from flow injection analysis in the sense that whereas in the latter technique the sample plug is injected into a flowing stream of reagent, in the former technique plugs of reagent are injected into a continuous stream of the sample. Under these conditions the amount of sample in the zone of the reagent will increase as the dispersion increases. The sample will become well mixed with the reagent as its

concentration increases so that well-formed peaks will result. Thus an analysis can be successfully performed by this technique with a sample concentration in the zone of the reagent that is typically in the range from 67% to 90% of the sample concentration in the carrier stream.

Johnson and Petty [179] adapted reverse flow injection analysis to the well-known Murphy and Riley [180] colorimetric phosphomolybdate reduction method for the determination of phosphate.

Fig. 3.16 shows flow sheets for the determination of phosphate by flow injection analysis and reversed flow injection analysis. A block diagram of the apparatus used for the determination of phosphate in seawater is shown in Fig. 3.16(b).

The effects of residence time on the peak height of a $2.5\mu\text{mol L}^{-1}$ phosphate standard are shown in Fig. 3.17. The residence time was defined as the time from injection of the reagent to appearance of the maximum signal at the detector. Residence times were varied by

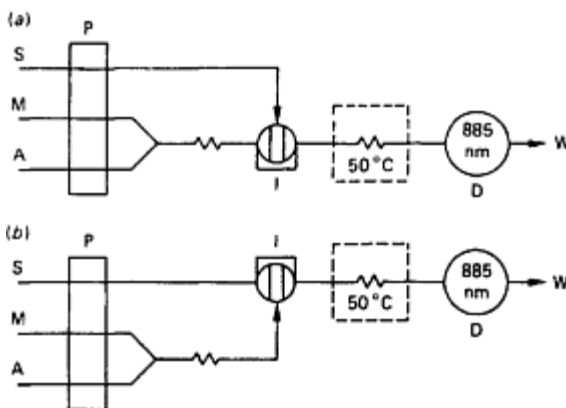


Fig. 3.16 Analytical manifolds for the determination of phosphate by flow injection analysis (a) and reverse flow injection analysis (b). The symbols S, M and A are the seawater, mixed reagent and the ascorbic acid solutions. The pump, injection valve and detector are represented by P, I and D respectively. W=waste

Source: Reproduced with permission from the American Chemical Society [179]

changing the flow rate ($1.0\text{--}3.5\text{ml min}^{-1}$ in 0.5ml min^{-1} increments) and the length of the reaction tube (0.5, 1.0 and 1.5m). The peak height increased rapidly with residence time in both 0.5 and 0.8mm id tubes and then levelled off after 15s. The change is about the same when the residence time is increased by using longer tubes. This suggests the increased peak height is due mainly to an increased extent of reaction.

3.24.3 Ion chromatography

Tyree and Bynum [136] have described an ion-chromatographic method for the

determination of phosphate and nitrate in seawater.

3.24.4 Preconcentration

The preconcentration of phosphate is discussed in section 15.3.3.

3.25 Propionate

3.25.1 Ion chromatography

This technique is discussed under multianion analysis in section 12.3.1.

3.26 Pyruvate

3.26.1 Ion chromatography

This technique is discussed under multianion analysis in section 12.3.1.

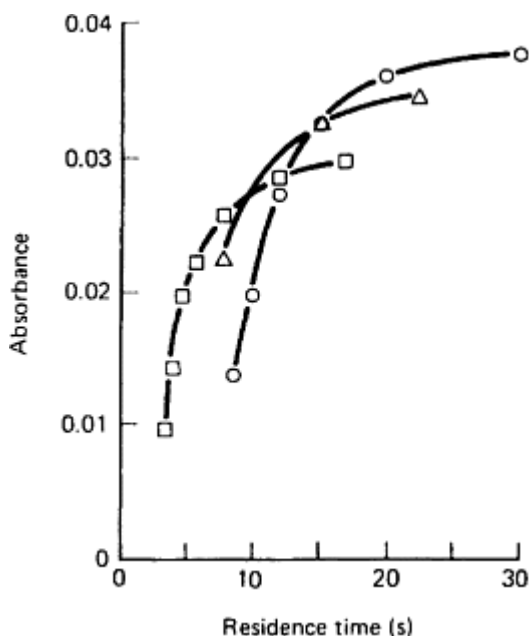


Fig. 3.17 Effect of residence time on peak height. The squares (0.5mm id tubing) and circles (0.8mm id) were obtained by changing the flow rate through a 1 m reaction tube. The square at the extreme right corresponds to 0.7 ml min^{-1} . The triangles were obtained by using a 0.8mm id tube and a flow rate of 2.0 ml min^{-1} . Residence time was

varied by changing the tube length

Source: Reproduced with permission from the American Chemical Society [179]

3.27 Selenate/selenite

3.27.1 Fluorometric method

Itoh *et al.* [181] determined selenium(IV) in sea and estuarine waters by an anion-exchange resin modified with bismuthiol(II) and diaminonaphthalene fluorophotometry. An Amberlite IRA-400 anion-exchange resin was modified by mixing with an aqueous solution of bismuthiol(II) to give 0.2mmol bismuthiol per resin. Sample solution was eluted through a column packed with the modified resin.

Selenium(IV) adsorbed as selenotrisulphate was then eluted from the column with either 0.1M penicillamine or 0.1M cysteine. The eluate was then subjected to an acid digestion procedure to reduce selenium to the tetravalent state with diaminonaphthalene for fluorometric determination. Approximate agreement with the tellurium coprecipitation method was obtained. The application of both methods to the analysis of estuarine waters permitted the separate determination of both selenium(IV) and selenium(VI) since the tellurium coprecipitation method did not differentiate between the two species.

3.28 Silicate

3.28.1 Spectrophotometric methods

Silicon is an essential and, in some cases, growth-limiting micronutrient for marine organisms that form siliceous tests [182]. Concentrations of available silicon are often low ($<1\mu\text{M}$) in surface waters of high productivity. Although most of the silicon is recycled near the surface, a fraction reaches the sediment surface where it may dissolve. As a result, deep waters may have dissolved silicon concentrations as high as $200\mu\text{M}$. Upwelling returns the dissolved silicon to the surface and the cycle is repeated. Dissolved silicon is an important species to monitor because of its influence on plankton growth [182] and because of its use as a tracer of water mass movement [183].

Various approaches to the analysis of dissolved silicon have been tried. Most of them are based on the formation of β -molybdosilic acid [184–188]. Dissolved silicon exists in seawater almost entirely as undissociated orthosilic acid. This form and its dimer, termed 'reactive silicate', combine with molybdate to form α - and β -molybdosilic acid [189]. The molybdosilic acid can be reduced to molybdenum blue, which is determined photometrically [190]. The photometric determination of silicate as molybdenum blue is sufficiently sensitive for most seawater samples. It is amenable to automated analysis by segmented continuous flow analysers [191,192]. Most recent analyses of silicate in seawater have, therefore, used this chemistry. Furthermore, reactive silicate is probably the only silicon species in seawater that can be used by siliceous organisms [189],

Spencer and Brewer [115] have reviewed methods for the determination of silicate in seawater. Various workers [193–196] have studied the application of molybdosilicate spectrophotometric methods to the determination of silicate in seawater. In general, these methods give anomalous results due, it is believed, to erratic blanks and uncertainty regarding the structure of the silicomolybdate formed.

A more promising approach to the analysis of silicate is that of Thomsen and Johnson [197], who used flow injection analysis. These workers achieved an analysis rate of 80 samples per h with a detection limit of 0.5M Si and a precision better than 1% at concentrations above $10\mu\text{mol L}^{-1}$ Si.

Brzezinski and Nelson [198] have described a solvent extraction procedure for the spectrophotometric determination of nanomolar concentrations of silicic acid in seawater.

Beta silicomolybdic acid was formed by the reaction of silicic and molybdic acids at low pH. The combined acid was extracted into n-butanol and reduced with a mixture of p-methylaminophenol sulphate and sulphite. After phase separation, the samples were cleared by chilling in ice followed by centrifuging, and the colour was determined spectrophotometrically at 810nm. The molar absorbance of the mixed acid was 229,000 in seawater and the precision was $\pm 2.5\text{nmol L}^{-1}$ silicon for concentrations less than or equal to standard aqueous analyses. Sensitivity in seawater was 70% of that in distilled water because of a significant salt effect. Natural concentrations of arsenate, arsenite and germanic acid caused negligible interference. Phosphate interference was equivalent to $10^{-1} \text{ } ^2\text{nmol L}^{-1}$ silicon over a broad range of phosphate concentrations.

3.28.2 Flow injection analysis

Flow injection analysis is a rapid method of automated chemical analysis that allows a quasi-continuous recording of nutrient concentrations in a flowing stream of seawater [134,199]. The apparatus used for flow injection analysis is generally less expensive and more rugged than that used in segmented continuous flow analysis. A modified flow injection analysis procedure, called reverse flow injected analysis [179,200], was adopted by Thompson *et al.* [197] and is adapted here for the analysis of dissolved silicate in seawater. The reagent is injected into the sample stream in reverse flow injection analysis, rather than vice versa as in flow injection analysis. This results in an increase in sensitivity [179].

This analytical procedure is based on the work of Truesdale and Smith [201,202], who studied the optimum analysis conditions for segmented continuous flow analysis. The sample is combined with a molybdate solution at a pH between 1.4 and 1.8 to form the β -molybdosilic acid. After an appropriate time for reaction, a solution of oxalic acid is added, which transforms the excess molybdate to a non-reducible form. The oxalic acid also suppresses the interference from phosphate by decomposing phosphomolybdic acid. Finally, a reductant is added to form molybdenum blue. Both ascorbic acid and stannous chloride were tested as reductants.

The kinetics of each step in the reaction have an important influence since the reaction mixture would typically have a residence time of less than 1min in the flow injection analysis manifold. Previous studies [203, 204] indicate that the reaction requires several minutes to go to completion. Fig. 3.18 shows the formation rate of β -molybdosilic acid

(line 1). The rates of formation of molybdenum blue from β -molybdosilic acid using ascorbic acid (line 2) and stannous chloride (line 3) as the reductants are also shown. Line 1 was obtained from the absorbance measured at 390nm, while the absorbance at 810nm was recorded to obtain lines 2 and 3. All lines have been normalised to the absorbance A_{∞} measured after completion of the reaction.

The formation of molybdosilic acid is the rate limiting step in flow injection analysis when stannous chloride is used as a reductant. The

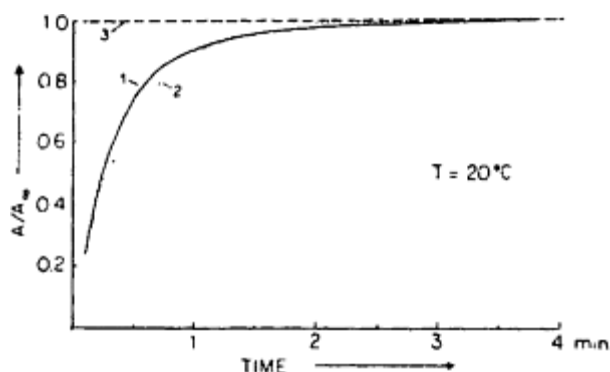


Fig. 3.18 Rate of formation of β -molybdosilic acid (line 1) and of molybdenum blue using ascorbic acid (line 2) and stannous chloride (line 2) as the reductants

Source: Reproduced with permission from the American Chemical Society [197]

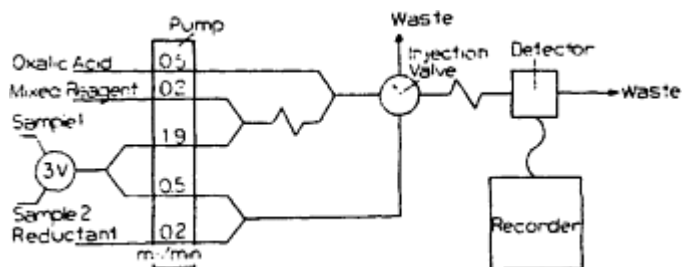


Fig. 3.19 Block diagram for the determination of silicate by flow injection analysis

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reduction of the molybdosilic acid by ascorbic acid is slower than with stannous chloride. The reduction step will also limit the extent of the reaction when ascorbic acid is used.

A block diagram of the manifold used by Thompson *et al.* [197] is shown in Fig. 3.19. A four-channel peristaltic pump (Buchler, Polystaltic) was used to propel five solutions by placing two pump tubes in one channel. Vinyl pump tubing with i.d. of 1.52mm for

the sample, 0.50mm for the acidic molybdate solution, and 0.76mm for the oxalic acid was used. The reductant (0.50mm) was mixed with a portion of the sample pumped by a 0.76mm tube.

The sample stream could be directed either through a short reaction coil of 1mm id PTFE tubing or through a long coil of 1.6mm id Tygon tubing after the confluence of the sample and the molybdate streams. The long coil, which could be heated, was used to increase the sensitivity when necessary. The line between the confluence with oxalic acid and the injector was 25cm of 1mm id. The line between the injector and the detector was 25cm of 0.8mm id. PTFE when stannous chloride was used as the reductant. Longer post-injector reaction coils had to be used with ascorbic acid as the reductant because of the slower reaction kinetics. The post-injector coil could also be heated to accelerate the reduction rate with ascorbic acid.

The reductant was injected by a rotary injection valve (Rheodyne Model 5041) with a pneumatic actuator. The injection loop was shortened to give a volume of 20 μ L. It was necessary to match the salinity of the reductant solution to that of the acidified sample. Otherwise false blank peaks occurred due to the difference in refractive index of the carrier stream and the injected solution [205]. Matching of the refractive indexes was best accomplished by mixing the reductant solution with a portion of the sample (Fig. 3.19).

A light emitting diode photometer [205] as used as the detector. The flow cell had a path length of 2cm and an id of 1.5mm. A high output infrared light emitting diode and a silicon phototransistor (Radio Shack 276–143 and 276–130) were used as light source and detector, respectively. The maximum output of the light emitting diode was measured to be at 886nm with a bandwidth of 37nm. The molybdenum blue complex formed by reduction with ascorbic acid has an absorption maximum at 820nm. The amplified voltage of the phototransistor, which is proportional to the transmittance, was recorded on a strip chart recorder. The light emitting diode could be switched off to set 0% transmittance.

The low concentration of reactive silicate in seawater requires a high sensitivity from the analytical method. Thompson *et al.* [197] as a consequence of a study of the effect of reaction time, temperature and type of reducing agent were able to optimise conditions for obtaining good sensitivity.

In the determination of silicate, a detection limit of 0.5 μ mol L⁻¹ was achieved with a relative precision of better than 1% at concentrations above 10 μ mole L⁻¹ Si.

The analysis rate is 80 per h when a continuous stream of seawater is analysed. Thirty discrete samples can be analysed in duplicate per h. The refractive index interference was eliminated. This allowed a slow detection limit to be obtained for a wide range of salinities. A lower detection limit of 0.1 μ M Si can be obtained with longer reaction coils and a lower sampling rate. There is a small salt effect and little interference from phosphate. The method was tested on an oceanographic cruise from Monterey Bay (California) to San Francisco Bay).

The method using stannous chloride was tested aboard the *R/V Cayuse* on a cruise from Monterey Bay to San Francisco Bay. The analysis rate was 60 per h. The quasi-continuous record of the reactive silicate

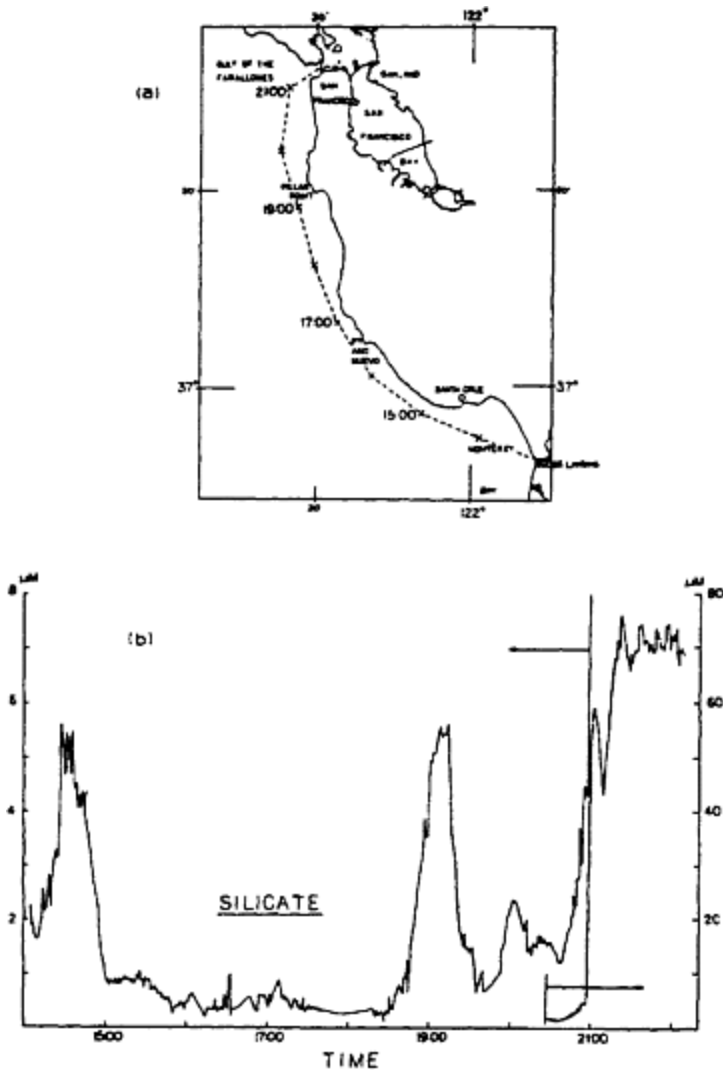


Fig. 3.20 Concentration of silicate measured at 2m (b) on the cruise track shown in (a). Note the scale change at 21:00

Source: Reproduced with permission from the American Chemical Society [197]

concentration in seawater pumped from a depth of 2m is shown in Fig. 3.20. Typical concentrations of reactive silicate were less than $1\mu\text{M}$. However, three instances of high silicate were encountered. The first two, at 14:30 and 19:00, are probably due to the upwelling of nutrient-rich water induced by the headlands at Santa Cruz and Pillar Pt. The third, at 21:00 (note scale change), occurred when the ship entered the plume of

water from San Francisco Bay. It was accompanied by a decrease in salinity from 33‰ to 20‰.

3.28.3 Ion exclusion chromatography

Hioki *et al.* [206] have described an on-line determination of dissolved silica in seawater by ion-exclusion chromatography in combination with inductively coupled plasma atomic emission spectrometry.

This method was developed as a second, independent method to complement the usual colorimetric procedure in the determination of a certified concentration of dissolved silica in a planned seawater reference material. Ion exclusion affords a separation of the dissolved silica not only from the major seawater cations but also from potentially interfering anions. The detection limit, conservatively estimated at 2.3 ng g^{-1} as Si ($0.08 \mu\text{M}$), is superior to that achievable by direct analysis by inductively coupled plasma atomic emission spectrometry.

Other studies on the application of this technique have been carried out [207–210].

3.28.4 Miscellaneous

Determinations of the so-called ‘micronutrients’ (eg nitrate, phosphate, and dissolved silica) in seawater are among the most commonly performed analyses in oceanographic research and survey work. Surprisingly, there exists no certified reference material that can be used to check the accuracy of such analyses, although intercomparison exercises were conducted on a regular basis during the 1980s [211]. The lack of a seawater certified reference material for micronutrients can be attributed both to the difficulty of preparing a suitable material with an adequate shelf life [212,213] and to the dearth of independent methods available for the determinations.

The National Research Council of Canada has undertaken a project, in collaboration with the Bedford Institute of Oceanography of the Canadian Department of Fisheries and Oceans, to address the need for a seawater certified reference material for micronutrients, with the initial objective being the preparation of a material with certified values for nitrate, phosphate and dissolved silica.

3.29 Sulphate

3.29.1 Titration method

Sulphate has been determined in seawater by photometric titration with hydrochloric acid in dimethyl sulphoxide [214]. The sample (5ml) is added slowly to dimethyl sulphoxide (230ml) and titrated with 0.02M hydrochloric acid (standardised against sulphate) with bromocresol green as indicator. Since borate, carbonate and bicarbonate interfere, a separate determination of alkalinity is necessary.

Table 3.15 Plasma system components, and operating conditions

Spectrometer	ARL 3400 C Quantovac; 1 m Paschen-Range mounting; grating ruled 1080 lines mm^{-1} , 0.309nm mm^{-1} reciprocal linear dispersion (3rd order). Primary slit width $20\mu\text{m}$, secondary slit $50\mu\text{m}$, Hamamatsu R-306 photomultiplier tube
Wavelength	180.73nm. 3rd order
Readout	Digital readout of mean signal from three 1 0s integrations
Frequency	27.12MHz
Forward power	1080W
Reflected power	5W
Observation height	17mm above load coil
Argon flow rates	Coolant 11 L min^{-1} , plasma 1.2L min^{-1} , carrier 1L min^{-1} , light path purge 1.5L min^{-1}
Nebuliser	Concentric glass, J.E.Meinhard model TR-30-A3

Source: Reproduced with permission from Elsevier Science [218]

Lebel [215] has described an automated chelometric method for the determination of sulphate in seawater. This method utilises the potentiometric end-point method for back-titration of excess barium against EDTA following precipitation of sulphate as barium sulphate. An amalgamated silver electrode was used in conjunction with a calomel reference electrode in an automatic titration assembly consisting of a 2.5ml electrical autoburette and a pH meter coupled to a recorder. Recovery of added sulphate was between 99 and 101% standard deviations of successive analyses less than 0.5% of the mean.

3.29.2 Spectrophotometric method

Sulphate has been determined spectrophotometrically by means of the methylthymolblue method [216,217]. In this method the seawater is passed through a cation exchange column to exchange metal ions for the hydrogen form sulphate ion then reacts with barium methylthymol blue complex to form barium sulphate. The released grey coloured methylthymol blue in alkaline medium is evaluated spectrophotometrically at 460nm.

3.29.3 Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma emission spectrometry has also been used to determine sulphate directly in non saline waters [218].

By monitoring the 180.73nm sulphur line, it was possible to detect 0.08mg L^{-1}

sulphate with a precision of 0.8% RID at the 200mg L⁻¹ sulphate level. Instrument operating conditions are seen in Table 3.15.

Table 3.16 Comparison of results for sulphate by inductively coupled plasma emission spectrometry with certified values for standard waters

<i>Sample</i>	<i>Sulphate content (mg L⁻¹)</i>	
	<i>ICPES</i>	<i>Certified value</i>
EPA Quality Control Standard 2	7.3	7.2
IOS Standard Seawater	2800	2781

Source: Reproduced with permission from Elsevier Science [218]

Of the elements characteristically present as major components of non saline waters, only calcium produced a slight interference. A weak calcium line at approximately 190.734nm partially overlaps the sulphur line such that 1000mg L⁻¹ Ca produces an apparent sulphate signal of 25mg L⁻¹ sulphate. Correction for this interference is easily achieved by establishing the relationship between calcium concentration and apparent sulphate signal and inserting this information in the controlling software. The effect of calcium was then automatically subtracted during the measurement of sample.

Non saline water samples are normally acidified to stabilise them during storage. There is an effect due to hydrochloric acid concentration on the sulphur emission signal. This effect is conveniently overcome by making the acid content of samples and standards identical at, for example 1 vol.%.

The accuracy of the inductively-coupled plasma procedure was assessed by analysing waters of known sulphate composition, and by comparing measured sulphate values for a wide range of samples with those obtained for the same waters by an automated spectrophotometric procedure. Table 3.16 shows good agreement between the sulphate measurements obtained and the nominal values for International Standard Sea Water and an EPA Quality Control Standard.

3.29.4 Polarography

Polarography has also been used to determine sulphate [219]. In this method sulphate is precipitated as lead sulphate in a 20% alcoholic medium, followed by polarographic determination of the excess lead. It is claimed that there is little interference in this method; 25–30 samples can be analysed in a 5h period with a precision of 0.2% or less.

In this procedure up to 70ml seawater, 10ml 0.01M lead nitrate, 20ml 95% ethanol, 0.2ml of 0.1% methyl red maximum current suppressor and two drops 3M nitric acid are added to a 100ml volumetric flask which is then diluted to 100ml with distilled water.

The dropping mercury electrode had a drop time of 3–4s under an open head of 50cm Hg. A saturated calomel electrode was the reference electrode. Before recording, the solutions were well shaken. After recording, the electrodes were well rinsed with distilled

water and wiped dry. A starting potential of 0.2V was used and the solutions were degassed with dry nitrogen for 2min prior to recording. A full-scale sensitivity of 10 μ A was used.

As an indication of the accuracy of the technique the correlation coefficients for the calibration curves indicate a precision of 0.2% or less. The standard deviation of the measured samples is 0.70%.

The precision of the technique indicates its suitability for sulphate analysis. The technique appears not to be subject to any interferences normally present in seawater samples.

3.29.5 Ion chromatography

Singh *et al.* [220] have determined sulphate in deep sub-surface waters by suppressed ion chromatography.

3.30 Sulphide

3.30.1 Capillary isotachoelectrophoresis

Fukishi and Hiroy [221] determined sulphide in seawater by this technique. The method is based on the generation of hydrogen sulphide by the addition of sulphuric acid to the water sample. The gas permeated through a microporous PTFE tube, and was collected in a sodium hydroxide solution. The carbon dioxide in the permeate was removed by the addition of a barium cation-exchange resin to the sodium hydroxide solution. Injection into the isotachopheresis apparatus followed. A linear graph for sulphide concentrations of up to 2mg L⁻¹ was obtained.

3.30.2 Gas chromatography

Cutter and Oatts [222] determined dissolved sulphide and studied sedimentary sulphur speciation using gas chromatography in conjunction with a photoionisation detector. The determination of dissolved sulphide and sedimentary sulphur is important to studies of trace element cycling in the aquatic environment. A method employing selective generation of hydrogen sulphide, liquid-nitrogen-cooled trapping, and subsequent gas chromatographic separation/photoionisation detection has been developed for such studies. Dissolved sulphide is determined via acidification and gas stripping of a water sample, with a detection limit of 12.7nM and a precision of 1% (relative standard deviation). With preconcentration steps the detection limit is 0.13nM. Hydrogen sulphide is generated from sedimentary acid volatile sulphides via acidification, from greigite using sodium borohydride and potassium iodide, and from pyrite using acidic chromium (II). The detection limit for these sulphur species is 6.1 μ g of S/g, with the precision not exceeding 7% (relative standard deviation). This method is rapid and free of chemical interferences, and field determinations are possible.

Lech and Bagander [223] determined reduced sulphur compounds (hydrogen sulphide,

methyl mercaptan, carbon disulphide, dimethyl sulphide and dimethyldisulphide) in water by gas chromatography using flame detection. Detection limits ranged from 0.2ng L⁻¹ (ass) for carbon disulphide to 0.6ng L⁻¹ (ass) for methyl mercaptan. Hydrogen sulphide was determined at the 1ng L⁻¹ (ass) level.

3.31 Valerate

3.31.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.3.1.

3.32 Multianion analysis

3.32.1 Spectrophotometric methods, phosphate, arsenate, arsenite and sulphide

Nasu and Kan [224] determined phosphate, arsenate and arsenite in non saline water by flotation spectrophotometry and extraction indirect atomic absorption spectrometry using malachite green as an ion-pair reagent. A floated (between aqueous and organic phase) ion-pair of malachite green with molybdophosphate was dissolved by the addition of methanol to the organic layer. Phosphate and arsenate were determined by measuring absorbance of the organic phase. An oxidative (potassium dichromate) or a reductive (sodium thiosulphate) reaction of arsenic was used for the determination of phosphate, arsenate and arsenite. A positive interference effect was observed in the presence of large amounts of silicon. This was overcome by acidification with concentrated hydrochloric acid. The method was applied to samples of hot spring water, sea water and ground water with almost complete recovery of added amounts (0.2–1.0µg per 5ml).

Johnson and Pilson [225] have described a spectrophotometric molybdenum blue method for the determination of phosphate and arsenate and arsenite in estuary water and sea water. A reducing reagent is used to lower the oxidation state of any arsenic present to +3, which eliminates any absorbance caused by molybdoarsenate, since arsenite will not form the molybdenum complex. This results in an absorbance value for phosphate only.

Table 3.17 Dependence of chloride content of wash liquid on chloride

<i>Content of sample</i>	
<i>Chloride content of wash mg L⁻¹</i>	<i>Chloride content of sample mg L⁻¹</i>
0	0–1800
4850	1800–7200
10000	7200–12600

Source: Reproduced with permission from Elsevier Science [225]

A commonly used procedure for the determination of phosphate in sea water and estuarine waters involves the formation of the molybdenum blue complex at 35–40°C in an Autoanalyser and spectrophotometric evaluation of the colour produced. Unfortunately when applied to sea water samples, depending on the chloride content of the sample, peak distortion or even negative peaks occur which make it impossible to obtain reliable phosphate values. This effect can be overcome by the replacement of the distilled water used in such methods by a solution of sodium chloride of an appropriate concentration related to the chloride concentration of the sample. The chloride content of the wash solution need not be exactly equal to that of the sample. For chloride contents in the sample up to 18,000mg L⁻¹ (ie seawater) the chloride concentration in the wash should be within ±15% of that in the sample (Table 3.17). The use of saline standards is optional but the use of saline control solutions is mandatory. Using good equipment, down to 0.02mg L⁻¹ phosphate can be determined by such procedures. For chloride contents above 18,000mg L⁻¹ the chloride content of the wash should be within ±5% of that in the sample.

Airey *et al.* [226] have described a method for the removal of sulphide prior to the determination of phosphate in anoxic estuarine waters. Mercury(II) chloride was used to precipitate free sulphide from samples of anoxic water. The sulphide-free supernatant liquid was used to estimate sulphide by measuring the concentration of unreacted mercury(II), as well as to determine phosphate by a spectrophotometric method in which sulphide interferes. The detection limit for phosphate was 1µg L⁻¹.

3.32.2 Electrostatic ion chromatography, bromide, nitrate and iodide

In a series [227–233] employing stationary phases coated with zwitterionic surfactants (ie those containing both positively and negatively charged functional groups but carrying no formal net charge), it has been demonstrated that inorganic anions can be separated using pure water as eluent, with unique separation selectivity. This method has been termed electrostatic ion chromatography the separation has been attributed to a simultaneous electrostatic attraction and repulsion mechanism occurring at both the positive and the negative charges on the stationary phase. A drawback of electrostatic ion chromatography is that when the sample contains multiple anions and cations, each analyte anion may be eluted as more than one peak, with each peak being a specific combination of the anion with one of the cations of the sample. Recently, Hu *et al.* [234] showed that addition of a small quantity of a suitable electrolyte to the eluent causes analyte anions to be eluted only as a single peak, irrespective of the number and type of cations in the sample. In further studies, Hu *et al.* [235] investigated the separation mechanism in more detail and have applied the method to the determination of nitrate, bromide, and iodide in seawater.

The determination of nitrate, bromide, and iodide in seawater is of importance to oceanographic research [236–238]. Ion exchange chromatography is generally inapplicable to this analysis for several reasons. First, the large amount of matrix ions

(chloride, sulphate) saturate the active sites of the stationary phase and thereby impede the separation of the target analytes. Second, the high ionic strength of the sample causes self-elution of the sample band during injection, leading to peak broadening and loss of separation efficiency. Third, the levels of the target analytes are often very low so that detection becomes a major problem, especially when the eluted peaks are poorly defined in shape.

To overcome these difficulties, Ito and Sunahara [99] suggested the use of the matrix ions as the eluent ions, for example, the use of relatively high concentrations of sodium chloride solution.

In the most recent method described by Hu *et al.* [235] for the direct determination of ultraviolet-absorbing inorganic anions in saline matrixes an octadecylsilica column modified with a zwitterionic surfactant (3-(NN-dimethylmyristylammonio) propanesulfonate) is used as the stationary phase, and an electrolytic solution is used as the eluent. Under these conditions, the matrix species (such as chloride and sulphate) are only retained weakly and show little or no interference. It is proposed that a binary electrical double layer is established by retention of the eluent cations on the negatively charged (sulphonate) functional groups of the zwitterionic surfactant (forming a cation-binary electrical double layer) and by retention of eluent anions on the positively charged (quaternary ammonium) functional groups of the zwitterionic surfactant (forming an anion-binary electrical double layer). Sample anions are able to distribute into the cation-binary electrical double layer and to form pairs with the binary electrical double layer cations, while at the same time experiencing repulsion from the anion-binary electrical double layer. Anions are therefore eluted in order of increased propensity to form ion pairs. The method has been applied to the determination of bromide, nitrate, and iodide in artificial seawater, giving detection limits of $0.75\mu\text{g L}^{-1}$ for bromide, $0.52\mu\text{g L}^{-1}$ for nitrate, and $0.5\mu\text{g L}^{-1}$ for iodide using ultraviolet absorbance detection at 210nm and relative standard deviations of <1.2%. Real seawater samples have also been analysed successfully.

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Chapter 4

Anions in estuary and coastal waters

Very limited work has been published on the determination of anions in estuary and coastal waters. However, there is no doubt that the open seawater analysis methods discussed in Chapter 3 would in many instances be applicable to estuary and coastal waters.

4.1 Nitrate

4.1.1 Ultraviolet spectroscopy

Brown and Bellinger [1] have proposed an ultraviolet technique which is applicable to both polluted and unpolluted fresh waters and some estuarine waters. Humic acid and other organics are removed on an ion exchange resin. Bromide interference in seawater samples can be minimised by suitable dilution of the sample but this raises the lower limit of detection such that only on relatively rich (0.5mg L^{-5} nitrate) estuarine and inshore waters could the method be used. Chloride at concentrations in excess of $10,000\text{mg L}^{-1}$ does not interfere.

The method is either not affected by or can allow for interference from phosphate, sulphate, carbonate, bicarbonate, nitrite, coloured metal complexes, ammonia, dyes, detergents, phenols and other ultraviolet absorbing substances.

The determination of nitrite is also discussed under multianion analysis in section 4.6.1.

4.2 Nitrate and nitrite

4.2.1 Autoanalyser method

Petts [2] has described a procedure for the determination of total nitrate plus nitrite in estuary waters ranging in salinity from 2.17 to 33.1g kg^{-1} . In this method oxidised nitrogen in the sample is reduced to nitrite by a copper/cadmium reduction column, and the total nitrite in the sample is then reacted with sulphanilamide and N-1-naphthylethylene diamine dihydrochloride under acidic conditions to produce an azo dye which is evaluated spectrophotometrically at 550nm. The range of application of the method is $1\text{--}800\mu\text{g NL}^{-1}$. Standard deviations range from $0.42\mu\text{g NL}^{-1}$ at the $14\mu\text{g NL}^{-1}$ level to $2.8\mu\text{g NL}^{-1}$ at the $70\mu\text{g NL}^{-1}$ level.

4.3 Phosphate

4.3.1 Spectrophotometric method

A commonly used procedure for the determination of phosphate in seawater and estuarine waters involves the formation of the molybdenum blue complex at 35–40°C in an autoanalyser and Spectrophotometric evaluation of the colour produced [3]. Unfortunately when applied to seawater samples, depending on the chloride content of the sample, peak distortion or even negative peaks occur which make it impossible to obtain reliable phosphate values. This effect can be overcome by the replacement of the distilled water used in such methods by a solution of sodium chloride of an appropriate concentration related to the chloride concentration of the sample. The chloride content of the wash solution need not be exactly equal to that of the sample. For chloride contents in the sample up to 18,000mg L⁻¹ (ie seawater) the chloride concentration in the wash should be within ±15% of that in the sample. The use of saline standards is optional but the use of saline control solutions is mandatory. Using good equipment down to 0.02mg L⁻¹ phosphate can be determined by such procedures. For chloride contents above 18,000mg L⁻¹ the chloride content of the wash should be within ±5% of that in the sample.

The determination of phosphate is also discussed under multianion analysis in section 4.6.1.

4.4 Selenate and selenite

4.4.1 Spectrofluorometric method

Itoh *et al.* [4] determined selenium(IV) in estuarine waters by an anion exchange resin modified with bismuthiol(II) and diaminonaphthalene. An Amberlite IRA-400 anion exchange resin was modified by mixing with an aqueous solution of bismuthiol(II) to give 0.2mmol bismuthiol per resin. Sample solution was eluted through a column packed with the modified resin. Selenium(IV) adsorbed as selenotrisulphate was then eluted from the column with either 0.1mol L⁻¹ penicillamine or 0.1mol L⁻¹ cysteine. The eluate was then subjected to an acid digestion procedure to reduce selenium to the tetravalent state with diaminonaphthalene for fluorometric determination. Approximate agreement with the tellurium coprecipitation method was obtained. The application of both methods to

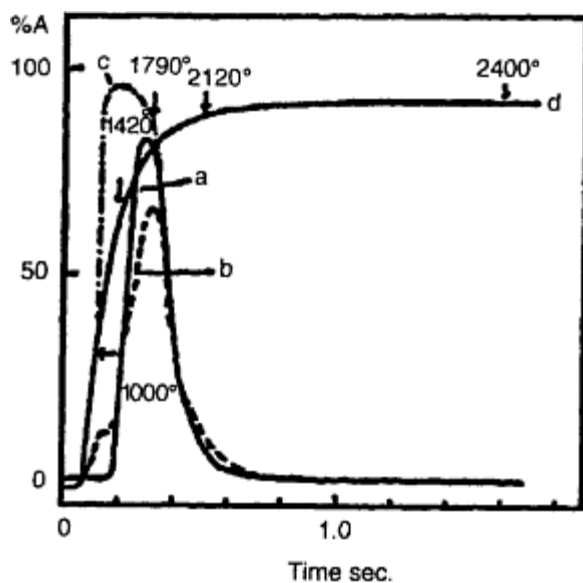


Fig. 4.1 Memoriscope traces for effect of sodium chloride on atomisation of selenium: (a) 0.73ng Se(IV); (b) 0.63ng Se(IV) and 6.25ng NaCl; (c) 0.63ng Se(IV) and 6.25µg NaCl; (d) temperature increase. Gas flow rate 500ml Ar min⁻¹

Source: Reproduced with permission from Springer Verlag [4]

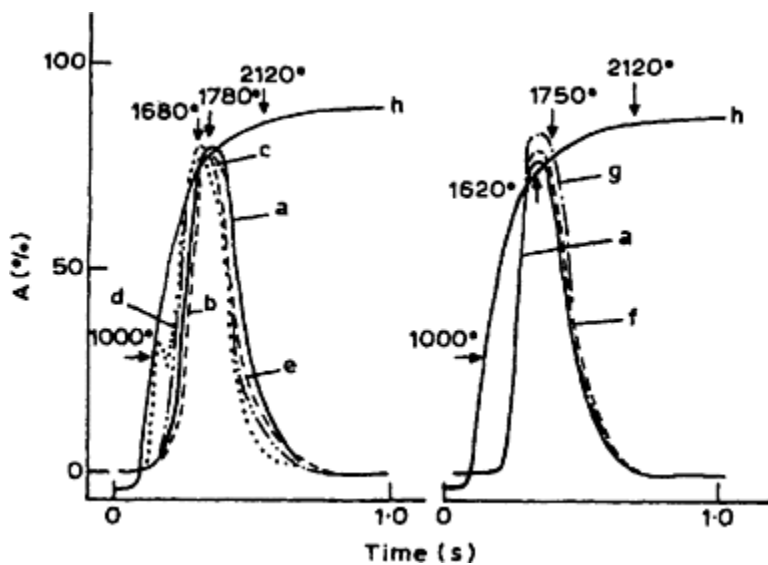


Fig. 4.2 Memoriscope traces for effect of diverse elements: (a) 0.63ng Se(IV);

(b) 0.63ng Se(IV) and 63ng Pb; (c) 0.63ng Se(IV), 63ng Pb and 63ng Cu; (d) 0.63ng Se(IV) and 63ng As; (3) 0.63ng Se(IV), 63ng As and 63ng Cu; (f) 0.63ng Se(IV) and 63ngTe; (g) 0.63ng Se(IV), 63ng Te and 63ng Cu; (h) temperature increase. Gas flow rate 500ml Ar min⁻¹
 Source: Reproduced with permission from Springer Verlag [4]

the analysis of estuarine waters permitted the separate determination of both selenium (IV) and selenium(VI) since the tellurium coprecipitation method did not differentiate between the two species.

Most cations and anions have interferences on atomisation of selenium. Fig. 4.1 shows the effect of sodium chloride on selenium. The effects of 100-fold amounts of lead, arsenic and tellurium on atomisation of selenium are shown in Fig. 4.2. Samples were checked for background effects and reagent blank. Bismuth and antimony also depressed the selenium absorption.

Arsenic lowered somewhat the peak temperature in atomisation profile for selenium. Copper tends to suppress the interferences of diverse elements on atomisation of selenium. However, the interferences from large concentrations of diverse elements and matrices were not improved even in the presence of copper at the atomisation step. Therefore, the separation of selenium from matrices was recommended.

Selenium is extracted as diethyldithiocarbamate complex from the solution containing citrate and EDTA [5]. Ohta and Suzuki [6] found that only a few elements, such as copper, bismuth, arsenic, antimony and tellurium, are also extracted together with selenium. They examined this for effects of 100-fold amounts of elements co-extracted with the selenium diethyldithiocarbamate complex. An appreciable improvement of interferences from diverse elements was observed in the presence of copper. Silver depressed the selenium absorption in the case of atomisation of diethyldithiocarbamate complex, but the interference of silver was suppressed in the presence of copper. The atomisation profile from diethyldithiocarbamate complex was identical with that from selenide.

No selenium(VI) is extractable from citrate buffered solution containing EDTA and copper. Therefore, tetra- and hexavalent selenium could be determined separately.

The recovery of selenium was satisfactory. The forms of selenium in waters are known to be selenite and selenate [7]. Selenium occurs in non saline water at concentrations ranging from less than 0.0002µg L⁻¹ to greater than 50µg L⁻¹. Therefore, a large sample size is necessary for analysis at lower concentration level.

4.5 Sulphate

4.5.1 Spectrophotometric method

The determination of sulphate is discussed under multianion analysis in section 4.6.1.

4.6 Multianion analysis

4.6.1 Spectrophotometric method, sulphate, phosphate and nitrate

Airey *et al.* [8] have described a method for removing sulphide prior to the determination of the above anions in anoxic estuarine waters. Mercury(II) chloride was used to precipitate free sulphide from samples of anoxic water. The sulphide-free supernatant was used to estimate sulphide by measuring the concentration of unreacted mercury(II), as well as to determine sulphate, inorganic phosphate and nitrate by spectrophotometric methods, in which sulphide interferes. Sulphide concentrations in the range 0.5–180,000 L⁻¹ sulphur could be measured, while the lower limits for sulphate, ammonia, nitrite and inorganic phosphate were respectively 0.024, –1.0 and 1 µg L⁻¹.

4.7 Sulphide

4.7.1 Spectrophotometric method

See section 4.6.1.1.

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Chapter 5

Anions in aqueous precipitation

This chapter discusses the determination of anions in aqueous precipitation including rain, snow, fog and aerosols.

Aqueous precipitation from the atmosphere occurs in many forms notably rain water, dew, mists, snow, ice and hail. Anions, cations and indeed, organic substances can occur in aqueous precipitation and measurements of these are of great interest in areas such as acid rain studies, radioactive fallout from bomb tests and nuclear accidents and of course, general pollution of the atmosphere, hence of the rivers and oceans. A growing volume of measurements have been carried out in this field and these are discussed below under two headings: rain water and snow/ice.

5.1 Rain

5.1.1 Bromate

5.1.1.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 5.1.14.3.

5.1.2 Bromide

5.1.2.1 Spectrofluorometric method

Fishman *et al.* [1] compared an automated fluorescein method and ion chromatography for determination of bromide in rain water, and deionised water, at intervals over a period of 30 d. The fluorescein method involved buffering the sample to pH 5.6, oxidation of bromide to hypobromous acid with chloramine-T, and addition of fluorescein which reacted with hypobromous acid to form tetrabromofluorescein (eosin), the pink colour of which indicated bromide ion concentration. The results obtained by the two methods were not significantly different at a confidence level of 95% for samples containing 0.015–0.5mg bromide L⁻¹, and the correlation coefficient for the same sets of paired data was 0.9987. There appeared to be no loss of bromide from solution during storage in either polyethylene or polypropylene bottles. It was concluded that, where large numbers of samples were to be analysed, the automated fluorescein technique would be the method of choice, since it was more rapid than ion chromatography.

5.1.2.2 Continuous flow analysis

The application of this technique is discussed under multianion analysis in section 5.1.14.1.

5.1.2.3 Flow injection analysis

The application of this technique is discussed under multianion analysis in section 14.4.2.1.

5.1.2.4 X-ray fluorescence spectroscopy

The application of this technique is discussed under multianion analysis in section 14.7.1.1.

5.1.2.5 Neutron activation analysis

Slanina *et al.* [2] claim that a detection limit of $1\mu\text{g L}^{-1}$ can be achieved in the determination of bromide in rainwaters by neutron activation analysis. Typical accuracy was 5% relative using a 1ml sample.

5.1.2.6 Ion chromatography

Ion chromatography using an amperometric detector has been used to determine down to $10\mu\text{g L}^{-1}$ bromide in rainwater and ground waters [3]. The equipment features an automated ion chromatograph, including a programme controller, an automatic sampler, an integrator and an amperometric detector. A fixed potential is applied to the cell. Any electroactive species having an oxidation-reduction potential near the applied potential will generate a current that is directly proportional to the concentration of the electroactive species.

The detection limits for bromide is 0.01mg L^{-1} and the relative standard deviation is less than 5% for bromide concentrations between 0.05 and 0.5mg L^{-1} . Chloride interferes if the chloride to bromide ratio is greater than 1000:1 for a range of 0.01– 0.1mg L^{-1} bromide; similarly, chloride interferes in the 0.1– 1.0mg L^{-1} range if the ratio is greater than 5000:1. In the latter case, a maximum of 2000mg L^{-1} chloride can be tolerated. Recoveries of bromide ranged from 97 to 110%.

This analysis is performed using a Dionex Model 12 ion chromatograph with $200\mu\text{L}$ sample loop, an eluent flow rate of 2.3ml min^{-1} (30% of full capacity) and a sample pump flow rate of 3.8ml min^{-1} (50% of full capacity). Pulse damper is installed just before the injection valve to reduce flow pulsation. A Dionex amperometric detector consisting of cell and potentiostat. The cell contains a silver working electrode, a platinum counter electrode and an Ag/AgCl reference electrode. This cell is installed between separator and suppressor columns. The working silver electrode should be cleaned monthly by polishing the surface with a small amount of an abrasive toothpaste

on a paper tissue to remove the grey tarnish and then rinsing with deionised water. An applied potential of 0.10V and a detector output range of 100nA V⁻¹ were used.

A Technicon autosampler IV automatically delivered the sample to the ion chromatograph and a Spectra Physics SP-4100 integrator measured the peak heights.

All reagent solutions prepared in deionised water. Use reagent grade sodium bromide for the preparation of standards. The eluent mixture, consists of 0.003mol L⁻¹ sodium bicarbonate and 0.002mol L⁻¹ sodium carbonate. The precolumn mix is Dionex 4×50mm fast run anion and the separator column is 4×250mm.

The eluent is allowed to flow for approximately 30min to reach equilibrium. It takes about 10min to complete the chromatogram using a 200μL sample loop. The retention time of bromide was 5.4min. Use two calibration graphs, one for bromide concentration of 0.10–1.0mg L⁻¹ (with a 10V input) using a quadratic fit, and another for bromide concentrations of 0.01–0.10mg L⁻¹ (with a 1V input) using single point calibration with intercept of zero. A reference water sample is used in every twentieth position of the tray.

To determine recoveries, known concentrations of bromide were added to several non saline water samples; recoveries ranged from 97 to 110%. Typical results are given in Table 5.1.

The application of ion chromatography is also discussed under multianion analysis in sections 5.1.14.3, 12.4.1 and 12.4.2.

5.1.2.7 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.3.1.

5.1.2.8 Ion exchange chromatography

The application of this technique is discussed under multianion analysis in section 13.3.2.1.

Table 5.1 Recovery of bromide in filtered water samples.

Sample No.	Concentration (mg L ⁻¹)				
	Chloride	Bromide	Bromide added	Bromide found	Recovery (%)
1	31	0.59	0.5	1.13	108
2	263	0.46	0.5	1.03	108
3	63	0.33	0.3	0.65	107
4	56	0.30	0.3	0.61	103
5	2.28	0.22	0.3	0.51	97
6	5.95	0.040	0.05	0.089	98
7	4.59	0.037	0.05	0.086	98

8	4.78	0.031	0.03	0.062	103
9	4.89	0.029	0.01	0.039	100
10	5.05	0.031	0.03	0.064	110

Source: Reproduced with permission from Elsevier Science [3]

5.1.2.9 Gas chromatography

The application of this technique is discussed under multianion analysis in section 14.1.2.2.

5.1.2.10 Miscellaneous

Henmann *et al.* [4] determined chloride and bromide in snow and rain and also measured the concentrations of these at different distances away from a highway. Unlike the concentrations of bromide, the chloride concentration in snow continually decreased, the further the snow is from the highway, a considerable proportion of the bromide originated from traffic exhausts.

See also section 14.1.2.2.

5.1.3 Chloride

5.1.3.1 Continuous flow analysis

O'Hara *et al.* [5] have described a system for the continuous flow determination of chloride in rain and snow using a tubular chloride ion selective electrode. Down to $0.1\mu\text{g L}^{-1}$ chloride could be determined.

The application of this technique is discussed under multianion analysis in sections 5.1.14.1 and 14.5.1.1.

5.1.3.2 Flow injection analysis

The application of this technique is discussed under multianion analysis in section 5.1.14.4.

5.1.3.3 Isotachoelectrophoresis

The application of this technique is discussed under multianion analysis in section 14.6.2.1.

5.1.3.4 X-ray fluorescence spectroscopy

The application of this technique is discussed under multianion analysis in section 14.7.1.1.

5.1.3.5 Mass spectrometric isotope dilution analysis

Mass spectrometric isotope dilution analysis has been applied to the determination of chloride ion in rainfall and snow [4]. Detection limits of $1\mu\text{g L}^{-1}$ or lower can be achieved by this technique. For the isotope ratio measurement of chlorine and bromine a single focusing mass spectrometer (Varian MAT, type $\text{CH}_5\text{-TH}$) with a double filament ion source and a Faraday cup as a detector was used. The filaments consist of rhenium. The best precision of the isotope ratio measurement is achieved when a solution of $(\text{Ag}(\text{NH}_3)_2)^+ \text{X}^-$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-$) is deposited on the evaporation filament and dried under a heat lamp. In the ion source the temperature of the ionisation filament is increased stepwise up to a temperature of 1850°C .

Using samples amounts of $1\mu\text{mol}$ halide with natural isotope composition, ion intensities are achieved on the Faraday cup in the range of 10^{-11} – 10^{-10} A for 35Cl^- and in the range of 10^{-11} – 5×10^{-11} for 79Br^- .

5.1.3.6 Ion chromatography

Various workers [6–15] have discussed the application of this technique to the determination of chloride in rain. The application of this technique is discussed under multianion analysis in sections 5.1.14.3, 12.4.1 and 12.4.2.

5.1.3.7 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.3.1 and 13.1.3.3.

5.1.3.8 Ion exchange chromatography

The application of this technique is discussed under multianion analysis in section 13.3.2.1.

5.1.3.9 Gas chromatography

The application of this technique is discussed under multianion analysis in section 14.1.2.2.

5.1.4 Fluoride

5.1.4.1 Isotachoelectrophoresis

The application of this technique is discussed under multianion analysis in section 14.6.2.1.

5.1.4.2 Ion selective electrode

Warner and Bressan [16] carried out direct measurements of less than $1\mu\text{g L}^{-1}$ fluoride in rain, fog and aerosols with an Orion lanthanum fluoride ion selective electrode.

Fucsko *et al.* [17] applied ion selective electrodes combined with a flow injection system to the determination of fluoride in rainwater.

Slanina [2] has discussed the application of ion selective electrodes to the determination of fluoride in rainwater. Detection limits of 0.005mg L^{-1} were achieved with a relative accuracy of 3–5% using a sample volume of 0.5ml.

5.1.4.3 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 5.1.14.3 and 12.4.1.

5.1.5 Formate

5.1.5.1 High performance liquid chromatography

Kieber *et al.* [18] have developed an enzymatic method to quantify formic acid to non saline water samples at submicromolar concentrations. The method is based on the oxidation of formate by formate dehydrogenase with corresponding reduction of β -nicotinamide adenine dinucleotide ($\beta\text{-NAD}^+$) to reduced $\beta\text{-NAD}^+$ ($\beta\text{-NADH}$); $\beta\text{-NADH}$ is quantified by reversed-phase high performance liquid chromatography with fluorometric detection. An important feature of this method is that the enzymatic reaction occurs directly in aqueous media, even seawater, and does not require sample pretreatment other than simple filtration. The reaction proceeds at room temperature at a slightly alkaline pH (7.5–8.5) and is specific for formate with a detection limit of $0.5\mu\text{M}$ ($S/N=4$) for a $200\mu\text{L}$ injection. The precision of the method was 4.6% relative standard deviation ($n=6$) for a $0.6\mu\text{M}$ standard addition of formate to Sargasso seawater. Average recoveries of 2–5 additions of formate to seawater were 103%. Intercalibration with a Dionex ion chromatographic system showed an excellent agreement of 98%. Concentrations of formate present in natural samples ranged from 0.4 to $10\mu\text{M}$ for Miami rain.

5.1.6 Iodide

5.1.6.1 Spectrophotometric method

Sub-microgram elements of iodide in rainwater have been determined spectrophotometrically [19] by its catalytic effect on the substitution reaction of the mercury 11–4–(2-pyridylazo) resorcinol complex with 1, 2-diaminocyclohexane NN,N',N' -tetraacetic acid. The sample solution is first freed from cations by passage through a column of Amberlite IR 120-B. The eluate is buffered to pH 9, then treated

with mercuric ions and 4-(2-pyridylazo) resorcinol and then absorbance at 500nm recorded automatically as a function of time. The extinction after 30s is measured and compared with iodide standards which have been treated in the same way.

5.1.6.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.4.2.

5.1.6.3 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.3.1 and 13.1.3.3.

5.1.6.4 X-ray fluorescence spectroscopy

The application of this technique is discussed under multianion analysis in section 14.7.1.1.

5.1.7 Nitrate

5.1.7.1 Spectrophotometric methods

A requirement of methods for the determination of nitrate in rainwater is that it has sufficient sensitivity to determine the very low levels of this anion encountered in this type of sample. With this in mind, Osibanjo and Ajaya [20] have modified the usual distillation procedure for the determination of low levels of nitrate using 3, 4 xylenol as a chromogenic reagent. In this method the nitration product is extracted with toluene. The method is relatively free from interferences, is rapid and is highly sensitive, being capable of determining down to $5\mu\text{g L}^{-1}$ nitrate in unpolluted surface and ground waters and rain with a recovery rate of 96–108%.

Nitration of 3, 4-xyleneol by nitrate is carried out instantaneously at 0°C in 80% sulphuric acid and the nitration layer extracted into toluene. The toluene layer is treated with sodium hydroxide to form a coloured product in the aqueous layer, the absorbance of which is measured at 432nm. Between 0.5 and 2.2mg L^{-1} of nitrate was found in rainwater samples by this procedure.

Spectrophotometric methods, based on the use of diphenylamine or diphenylbenzidine [21], and xylenol [20] have been used for the determination of nitrate in rainwater. The methods using amines are insufficiently sensitive for rainwater analysis ($\text{LD } 0.5\text{mg L}^{-1}$) whereas the 3, 4-xyleneol method is capable of analysing at the $5\mu\text{g L}^{-1}$ nitrate level. In this method, nitration of 3, 4-xyleneol by nitrate in the sample is carried out instantaneously at about 0°C in 80% sulphuric acid and the nitration product is extracted into toluene, the excess of the reagent remaining in the aqueous layer. The toluene layer is then treated with sodium hydroxide solution to form a coloured product (the sodium salt of the nitrophenol) in the aqueous layer, the absorbance of which is measured at 432nm.

In the 3, 4 xynol method [20] a calibration graph is prepared by transferring with a semi-micro burette 1.0ml each of $100\mu\text{g ml L}^{-1}$ nitrate solutions, containing between 10 and $100\mu\text{g mg L}^{-1}$ of nitrate, into two-necked 100ml round bottom flasks. Evaporate each solution nearly to dryness, heating each flask gently on a hot plate. Cover the flask and cool in ice. Add 5ml of 80% sulphuric acid followed by 1ml of 2% 3, 4-xynol solution. A reagent blank is taken through the same procedure. The flask is covered and shaken for 60s. The contents of the flask are transferred into a separating funnel with 80ml of ice-cooled distilled water dispensed from a wash bottle.

10ml of toluene is added to each solution, and the funnel shaken for 60s and the phases allowed to separate. The lower aqueous layer is discarded and the toluene extract washed with 10ml of distilled water by shaking the flask for a further 1min. 5ml of 1% sodium hydroxide solution is

Table 5.2 Effects of various ions on the relative absorbances of nitrate ion values given are percentage changes in absorbance

Ion	NO_3^- to ion ratio			
	1:1	1:10	1:100	1:1000
F^-	0.77	4.26	4.26	6.60
Cl^-	1.16	6.59	2.32	80.62
Br^-	4.65	9.30	29.45	75.96
I^-	4.65	2.71	3.88	39.92
CO_3^{2-}	4.65	4.65	9.30	2.30
PO_4^{3-}	0.77	1.16	3.87	3.10
NO_2^-	0.38	10.79	11.24	11.62
SO_3^{2-}	0.77	5.42	6.98	9.30
NH_4^+	0.77	2.71	9.30	9.30

Source: Reproduced with permission from the Royal Society of Chemistry [20]

added from a pipette to convert the phenol into a phenoxide. The funnel is shaken for 1 min and the phases allowed to separate. The stem of the funnel is rinsed with few drops of the yellowish lower layer. The absorbance of the remaining portion is measured at 432nm using matched 1cm silica cells with distilled water as reference.

With rainwater samples, transfer 10–50ml of rainwater (filtered if necessary) into a two-necked 100ml round bottomed flask and evaporate nearly to dryness on a hot plate. Cover the flask and cool in ice. Then proceed as described above for the preparation of the calibration graph.

The effects of various interferences results are shown in Table 5.2. There are no serious interferences from most of the anions studied, including nitrite and chloride, to which most methods for nitrate determination are normally intolerant. However, bromide

interferes at the 1:100 level and above, and nitrite interferes slightly at the 1:10 level and above. These two interferents can be removed, however, by the addition of silver sulphate or mercury sulphate and sulphamic acid, respectively, to the sample solution prior to extraction with toluene.

5.1.7.2 Continuous flow analysis

This technique has been applied to the determination of nitrate in rainwater [22] (and chloride, nitrite, phosphate and sulphate).

A computer-controlled multichannel continuous flow analysis system has been applied to the measurement of nitrate (and chloride) in small samples of rainwater [23].

The application of this technique is discussed under multianion analysis in section 5.1.14.1.

5.1.7.3 Flow injection analysis

Madsen [24] used flow injection analysis with hydrazine reduction and spectrophotometric detection at 540nm to determine less than 1mg L^{-1} nitrate in rain water. Forty samples per h can be analysed with a precision of 30% in the range 1–10mg L^{-1} .

The application of this technique is discussed under multianion analysis in sections 5.1.14.4 and 14.4.2.1.

5.1.7.4 Electrochemical methods

Electrochemical methods that have been used to determine nitrate include polarography [25,26]. Bodini and Sawyer [27] described a voltammetric determination of nitrate at the $\mu\text{g L}^{-1}$ level. This electrocatalytic method utilises the concomitant reduction of cupric chloride and cadmium chloride on pyrolytic graphite to catalyse the reduction of nitrate ion.

5.1.7.5 Capillary isotachoelectrophoresis

Kamiansky *et al.* [28] determined nitrate and sulphate in rain water by capillary isotachophoresis. Separation conditions were chosen to eliminate potential interference from formate, acetate and propionate. Sulphate and nitrate were separated at pH 6.0 using histidine or 1, 3-bis (tris(hydroxymethyl)methyl)aminopropane as buffering agents. The complex forming cations, magnesium and calcium, were also suitable for optimising separating conditions. Sulphate was retarded, relative to nitrate, by using trimethylene-tetramine as a co-counter ion in the leading electrolyte.

5.1.7.6 Mass spectrometry

Ligon and Dorn [29] determined nitrate and sulphate in rain by mass spectrometry.

5.1.7.7 Ion chromatography

Various workers [6,7,10,13–15,30,31] have applied this technique to the determination of sulphate in rain (Table 5.3).

The application of this technique is discussed under multianion analysis in sections 5.1.14.3 and 12.4.1.

Table 5.3 Determination of nitrite in rain water by ion chromatography

<i>Type of water sample</i>	<i>Co-determined anions</i>	<i>Ref.</i>
Rain	Cl, PO ₄ , SO ₄	[10,30]
Rain	Cl, SO ₄	[13,14]
Rain	Cl, NO ₂ , PO ₄ , SO ₄	[31]
Rain	Cl, NO ₂ , SO ₄	[7]
Rain	Cl, F, Br, NO ₂ , SO ₄ , SO ₃ , PO ₄	[6]
Rain	Cl, Br, F, NO ₂ , PO ₄ , BrO ₃ , SO ₄	[15]

Source: Own files

5.1.7.8 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.3.1 and 13.1.3.2.

5.1.7.9 Gas chromatography

Faigle and Klockow [32] applied gas chromatography to the determination of traces of nitrate and (sulphate and phosphate) in rainwater. The dissolved salts are freeze-dried and converted to the corresponding silver salts. These are then converted to *n*-butyl esters with the aid of *n*-butyl iodide, the *n*-butyl esters being determined by direct injection into a gas chromatographic column. Sulphate and phosphate may be determined simultaneously on a column containing 3%OV-17 on Chromosorb G, while nitrate is determined separately with 3% tri-*p* cresylphosphate as the stationary phase on a similar support.

The application of this technique is also discussed under multianion analysis in section 14.1.2.1.

5.1.8 Nitrite

5.1.8.1 Continuous flow analysis

The application of this technique is discussed under multianion analysis in sections 5.1.14.1 and 14.5.1.1.

5.1.8.2 Flow injection analysis

The application of this technique is discussed under multianion analysis in section 5.1.14.4.

5.1.8.3 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 5.1.14.3 and 12.4.1.

5.1.8.4 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in sections 13.1.3.1 and 13.1.3.2.

5.1.9 Nitrate and nitrite

5.1.9.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 5.1.14.3.

5.1.9.2 High performance liquid chromatography

Alawi [33] has discussed the determination of nitrite and nitrate in rain.

5.1.10 Phosphate

5.1.10.1 Continuous flow analysis

Continuous flow analysis has been used to determine phosphate (and chloride, nitrite, nitrate and sulphate) in rainwater [22].

The application of this technique is also discussed under multianion analysis in sections 5.1.14.1 and 14.5.1.1.

5.1.10.2 Flow injection analysis

A computer controlled multichannel continuous flow analysis system has been applied to the measurement of phosphate (and nitrite, nitrate, chloride and sulphate) in rainwater [22,23].

The application of this technique is also discussed under multianion analysis in sections 5.1.14.4 and 14.4.2.1.

5.1.10.3 Gas chromatography

Faigle and Klockow [32] applied gas chromatography to the determination of traces of phosphate (and nitrate and sulphate) in rainwater. The salts were freeze dried and converted to the corresponding silver salts. These were then converted to *n*-butyl esters with the aid of *n*-butyl iodide, the *n*-butyl esters being determined by

Table 5.4 Determination of phosphate in rainwater by ion chromatography

<i>Type of water sample</i>	<i>Co-determined anions</i>	<i>Ref</i>
Rain	Cl, F, Br, NO ₂ , BrO ₂	[12]
Rain	NO ₃ , SO ₄	[15]
Rain	Cl, NO ₃ , SO ₄	[10]
Rain	Cl, NO ₂ , NO ₃ , SO ₄	[34]
Rain	Cl, I, Br, NO ₂ , NO ₃ , SO ₄ , SO ₃	[6]

Source: Own files

direct injection into a gas chromatographic column comprising 3%OV-17 on Chromosorb G.

The application of this technique is also discussed under multianion analysis in section 14.1.2.1.

5.1.10.4 Ion chromatography

Applications of ion chromatography to the determination of phosphate and other anions in rainwater are summarised in Table 5.4. The application of this technique is also discussed under multianion analysis in sections 5.1.14.3 and 12.4.1.

5.1.11 Sulphate

Sulphate is present in rain water at concentrations between 1 and 10mg L⁻¹ and its determination may provide valuable information on global pollution levels, atmospheric circulation and geophysical phenomena. Also, the recent adoption of the catalytic converter by the automobile industry has increased the interest in sulphate determinations in rain water. The sulphate ion is considered to be the best indicator of change [35] in aqueous precipitation composition due to anthropogenic activities.

Levels of this ion were 2–16 times greater in eastern North American precipitation than in that from remote areas.

5.1.11.1 Spectrophotometric methods

Burns *et al.* [36] determined down to 2mg L^{-1} sulphate indirectly in rainwater by a Spectrophotometric method using an excess of 2- aminopyridine hydrochloride which forms an insoluble complex with sulphate. After titration the excess reagent is determined spectrophotometrically at

Table 5.5 Comparison of the results of the examined methods in rainwater samples

Found $\mu\text{mol L}^{-1}$ sulphate							
<i>Cont flow photometry; thorin sd</i>		<i>Cont flow photometry; DMSA(III) sd</i>		<i>Cont flow photometry; DMSA(III) sd</i>		<i>Cont flow titrimetry; DMSA(III) sd</i>	
63	2	65.0	0.6	61.9	0.7	64.0	0.5
85	3	81.0	1.0	79.2	0.8	83.2	0.7
60	2	61.0	0.7	61.5	0.9	61.2	0.6

DMSA III—Dimethylsulphonazo(III)

Source: Reproduced with permission from Springer Verlag [37]

305.5nm. Unfortunately, only up to 10mg L^{-1} iron can be tolerated by this method, otherwise interferences are negligible.

5.1.11.2 Continuous flow analysis

Reijnders *et al.* [37] compared results obtained by the continuous flow method with those obtained using a continuous flow apparatus and a flow through titrimeter. In each case dimethyl-sulphonazo(III) was used as a chromogenic reagent. Results obtained by these three procedures were compared with those based on the thorin-barium reaction in a continuous flow analyser. The chemical system employed in the first three methods mentioned above basically involves a complex of barium ions with the indicator dimethylsulphonazo(III). Sulphate ions from the sample react with barium and set free the uncomplexed dimethylsulphonazo(III). The absorption spectra of complexed and free dimethylsulphonazo(III) are different.

Results obtained by the four methods are summarised in Table 5.5, which shows that there is no significant differences between the results from the various methods.

Significantly higher sulphate values were returned by the thorin based spectrophotometric method than by the three methods involving dimethylsulphonazo(III) when the samples contained water matrix components (sodium chloride, potassium

chloride, sodium bicarbonate, ammonium chloride, calcium nitrate and ferric nitrate) (Table 5.6).

Reijnders *et al.* [37] concluded that segmented continuous flow analysis and flow through titrimetry are suitable methods for the determination of sulphate in real samples. Results of (segmented) flow injection analysis

Table 5.6 Comparison of interferences with respect to the examined methods

Sulphate given $\mu\text{mol L}^{-1}$	Interference	Found $\mu\text{mol L}^{-1}$ sulphate			
		Cont flow photometry; thorin	Cont flow photometry; DMSA (III)	Flow-injection photometry; DMSA (III)	Cont. flow titrimetry; DMSA (III)
0.00	1	3	<1.4	<2.6	<5
0.00	2	140	3	7	<5
0.00	3	270	8	14	8
50.0	1	51	51	50	50
50.0	2	190	45	50	51
50.0	3	300	34	48	53
100.0	1	100	101	100	100
100.0	2	240	95	96	104
100.0	3	350	77	90	106

Key to interference:

1 No interference

2 Sulphate and interferences as specified in a 3 in a 1:1 dilution

3 Sulphate and 0.02mol L^{-1} NaCl, 0.0015mol L^{-1} KCl, 0.01mol L^{-1} NaHCO_3 , 0.005mol L^{-1} NH_4Cl , 0.0002mol L^{-1} $\text{Fe}(\text{NO}_3)_3$, 0.01mol L^{-1} $\text{Ca}(\text{NO}_3)_2$

Source: Reproduced with permission from Springer Verlag [37]

and flow through titrimetry are less affected by interfering ions. The dimethyl-sulphonazo (III) chemical system is superior to the system with thorin.

The application of this technique is discussed under multianion analysis in section 14.5.1.1.

Hara *et al.* [38] have described a continuous flow determination of sulphate in rain water using a lead selective electrode.

5.1.11.3 Flow injection analysis

Reijnders *et al.* [37] compared results obtained by the continuous flow method with those obtained using a continuous flow apparatus and a flow through titrimeter. In each case dimethylsulphonazo(III) was used as a chromogenic reagent. Results obtained by these

three procedures were compared with those based on the thorin-barium reaction in a continuous flow analyser. The chemical system employed in the first three methods mentioned above involves basically a complex of barium ions with the indicator dimethylsulphonazo(III). Sulphate ions from the sample react with barium and set free the uncomplexed dimethylsulphonazo(III). The absorption spectra of complexed and free dimethylsulphonazo(III) are different.

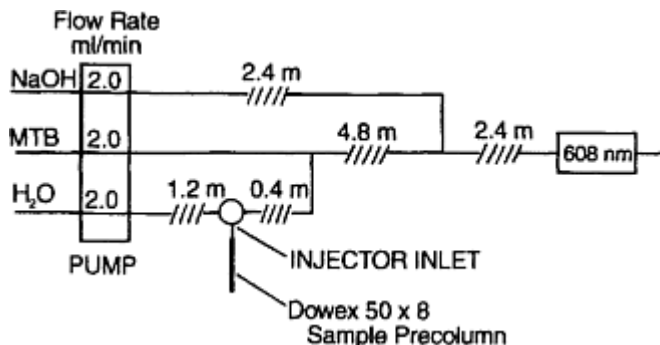


Fig. 5.1 Components of flow injection system

Source: Reproduced with permission from the American Chemical Society [39]

There is no significant difference in the results between the methods.

Reijnders *et al.* [37] concluded that segmented continuous flow analysis and flow through titrimetry are suitable methods for the determination of sulphate in real samples. Results of (segmented) flow injection analysis and flow through titrimetry are less affected by interfering ions. The dimethylsulphonazo(III) chemical system is superior to the system with thorin.

Madsen and Murphy [39] adapted the automated methylthymol blue method for the determination of sulphate in rainwater to flow injection analysis processing. The calibration curve is linear up to 6 mg L^{-1} , sensitivity is approximately 0.1 mg L^{-1} and sampling rate is 20 h^{-1} . Average precision and accuracy are 4.1% and 97% respectively.

The flow injection system used is shown in Fig. 5.1. The sodium hydroxide reagent comprised 0.036 mol L^{-1} sodium hydroxide in 40 vol% ethanol water. The methylthymol blue reagent which gave the highest sensitivity was prepared as follows: 0.116g methylthymol blue was dissolved in a solution which contained 6.0ml of 1.0 mol L^{-1} hydrochloric acid, 80ml of deionised water and 14.0ml or 1.526 g L^{-1} barium chloride dihydrate solution. Final dilution with 95% ethanol was to 1.01. Fresh reagent must be prepared daily.

The indirect determination of sulphate based on competitive reaction of sulphate and methylthymol blue with barium in solution can be accomplished by measurement of absorbance due to either uncomplexed methylthymol blue or the methylthymol blue barium complex. Absorbance at 460nm due to uncomplexed methylthymol blue will increase while absorbance due to the methylthymol blue barium complex will decrease as sulphate concentration increases.

Table 5.7 Determination of sulphate in rainwater samples

Sample no	Flow injection analysis	mg L ⁻¹ sulphate			Δ	% Δ
		s	%s	Ion chromatography		
1	0.78	0.08	10.3	0.91	-0.13	-14.3
2	3.75	0.08	2.1	3.90	-0.15	-3.8
3	3.50	0.02	0.6	3.52	-0.02	-0.6
4	2.60	0.04	1.5	2.51	+0.09	+3.6
5	1.75	0.05	2.9	1.67	+0.08	+4.8
6	0.82	0.01	1.2	0.83	-0.01	-1.2
6A ^a	0.80	0.03	3.8			
7	1.23	0.14	11.4	1.31	-0.08	-6.1
7A ^a	1.24	0.04	3.2			
8	0.67	0.03	4.5	0.69	-0.02	-2.9
9	2.23	0.07	3.1	2.37	-0.15	-6.3

^aSamples 6A and 7A were spiked with an additional 1.0mg L⁻¹ calcium. Standard deviations are based on N=3 except for sample 7A where N=6

Source: Reproduced with permission from the American Chemical Society [39]

The composition of reagent solution used will influence the applicability of the method. It was observed that the absorbance decrease at 608 μ m due to methylthymol blue barium complex was approximately three times greater than the corresponding absorbance increase at 460nm due to uncomplexed methylthymol blue. Absorbance base line stability measured in the absence of sulphate was essentially the same at both wavelengths. Measurement of the absorbance decrease (ΔA) at 608nm was therefore adopted in the method.

In Table 5.7 are some sulphate determinations obtained by Madsen and Murphy [39] on rainwater samples using their flow injection analysis system and by ion chromatography are compared. Differences in results by the two procedures are insignificant at the 95% confidence level.

Many cations interfere with the determination of sulphates using methylthymol blue. Sample pretreatment with a cation exchange resin in the H⁺ form will eliminate this interference. Rainwater samples typically contain 0.2mg L⁻¹ calcium and 0.2mg L⁻¹ magnesium. The addition of 1.0mg L⁻¹ calcium to two different rainwater samples did not alter results for sulphate by the flow injection method as can be seen from results presented in Table 5.7.

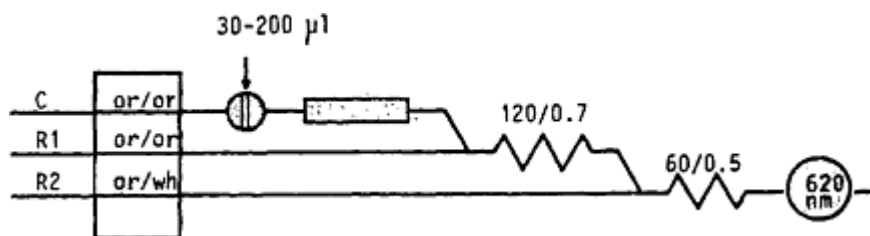


Fig. 5.2 Flow injection apparatus for determination of sulphate

C=distilled water

R₁=0.116mg methylthymol blue sodium salt, 6ml M hydrochloric acid, 80ml distilled water, 14ml barium chloride (1.526g L⁻¹, BaCl₂·2H₂O), made up to 1L with 95% ethanol

R₂=0.036M sodium hydroxide in 44% ethylalcohol

Source: Reproduced with permission from Tecator Ltd. [40]

Workers at Tecator Ltd [39,40,41] have described flow injection analysis methods for the determination of sulphate in rain in the concentration range 5–30mg L⁻¹. This method is based on the formation of a methylthymol blue complex with an adsorption maximum of 620nm with barium ions in an alkaline solution. When sulphate ions are added, the barium ions separate from the complex and form barium sulphate which results in a decrease in absorbance which is a direct measure of the sulphate content of the sample. The apparatus is illustrated in Fig. 5.2.

The application of this technique is also discussed under multianion analysis in section 5.1.14.4.

5.1.11.4 Flame emission spectrometry

Wagner and Steele [42] describe a technique for analysing 0–4mg L⁻¹ of sulphate in rain water, which is based on the change in the solubility of powdered barium sulphate in rain water, caused by the common ion (sulphate) at a constant temperature and ionic strength. The barium ion concentration, which measures barium sulphate solubility, is determined by flame emission spectroscopy.

5.1.11.5 Ion selective electrodes

Scheide and Durst [43] have described an indirect method for determining 2–100mg L⁻¹ sulphate in rainwater and non saline waters by an ion selective electrode. Isopropanol (80%) is added to the sample which is then titrated with lead nitrate solution, the end-point being determined with a lead ion selective electrode. The reproducibility of results is better than 2%.

Table 5.8 Analysis of sulphate in rainwater

Sample mg L ⁻¹ added		Ion selective electrode Found (mg L ⁻¹) %	
B	3.57	3.57 ± 0.02	100.0 ± 0.6
C	5.02	4.93 ± 0.08	98.2 ± 1.6
D	10.00	10.12 ± 0.13	101.2 ± 1.3
400 ^a	4.00	4.06 ± 0.04	101.5 ± 1.0
500 ^a	8.33	8.24 ± 0.08	99.0 ± 1.0
Turbidimetric Found % mg L ⁻¹			
B	3.57	3.5 ± 0.35	98.0 ± 10.0
Gravimetric Found % mg L ⁻¹			
D	10.00	10.03 ^b	100.3 ^b

^aSamples #400 and #500 were dilutions made from sample 'D'

^bOnly one analysis was performed

Source: Reproduced with permission from Marcel Dekker Inc [43]

It is seen in Table 5.8 that sulphates determined by this method are in good agreement with gravimetric and turbidimetric results. Rainwater often contains copper and cadmium and these ions interfere with and deactivate the lead electrode membrane surface. However, they were present in such low concentrations and reacted slowly enough that the rainwater samples could be analysed directly with no sample pretreatment. Because of this interference, however, the electrode has to be repolished after each run. This repolishing process takes about 30s.

Rainwater often contains copper and cadmium and these ions interfere with and deactivate the lead electrode membrane surface. However, they were present in such low concentrations and reacted slowly enough that the rain water samples could be analysed directly with no sample pretreatment. Because of this interference, however, the electrode has to be repolished after each run. This repolishing process takes about 30s.

5.1.11.6 Mass spectrometry

Ligon and Dorn [29] determined sulphate and nitrate in rain water by mass spectrometry.

5.1.11.7 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 5.1.14.3 and 12.4.1.

5.1.11.8 Gas chromatography

Faique and Klochow [32] applied gas chromatography to the determination of traces of sulphate (and nitrate and phosphate) in rainwater. The dissolved salts are freeze dried and converted to the corresponding silver salts. These are then converted to the *n*-butyl esters with the aid of *n*-butyl iodide, the butyl esters being determined by gas chromatography. Sulphate (and phosphate) are determined simultaneously on a column containing 3%OV-17 on Chromasorb, while nitrate is determined separately with 3% of tri-*p*-cresol phosphate on Chromasorb.

The application of this technique is also discussed under multianion analysis in section 14.1.2.1.

5.1.12 Sulphite

5.1.12.1 Ion chromatography

An ion chromatographic method for determining sulphite (and other ions) in rainwater uses formaldehyde (0.02%) for sulphite preservation and a solution containing potassium hydroxide and sodium carbonate as eluent [44]. The method has a linear range of 0–15mg L⁻¹, a detection limit of 0.125mg L⁻¹ and gives recoveries of 90–110%; relative standard deviation was 1.5% for six measurements of sulphite at 12mg L⁻¹ levels.

The application of this technique is also discussed under multianion analysis in section 12.4.1.

5.1.13 Thiocyanate

5.1.13.1 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.3.1.

5.1.14 Multianion analysis

5.1.14.1 Continuous flow analysis: nitrate, nitrite, sulphate, chloride, bromide and phosphate

A computer controlled multichannel continuous flow analysis system has been applied to the measurement of sulphate (and nitrate, nitrate chloride, bromide and phosphate) in small samples of rainwater [23,45,46]. Continuous flow methods (flow injection analysis and continuous flow analysis have been used [22] to determine sulphate, chloride, nitrate, nitrite and phosphate in rainwater. While the two methods are similar, they differ in certain important respect, such as the rate of flow, presence of air bubbles, diameter of the tubes and the reactions which are permissible within the retention period limits set by

the physical constraints.

5.1.14.2 Mass spectrometry: sulphate and nitrate

Ligen and Dorn [29] determined these two anions in rain by mass spectrometry.

5.1.14.3 Ion chromatography

Bromate, bromide, fluoride, chloride, nitrate, nitrite, sulphate and phosphate

Pyen and Erdmann [15] have described an ion chromatographic method for the determination of bromate (and bromide, fluoride, chloride, nitrite, phosphate, nitrate and sulphate) in rainwater.

Sulphite, fluoride, chloride, bromide, nitrate, nitrite, phosphate and sulphate

This technique has been applied to the determination of sulphite (and fluoride, chloride, bromide, nitrite, nitrate and phosphate) in rainwater [6].

5.1.14.4 Flow injection analysis: nitrate, chloride, nitrite, sulphate and phosphate

Flow injection analysis has been applied to the determination of nitrite in rainwater [22] (and chloride, nitrite, sulphate and phosphate).

5.2 Snow and ice

5.2.1 Total alkalinity

5.2.1.1 Titration method

Legrand *et al.* [47] carried out alkalinity and acidity titrations on polar snow. The method is accurate to $\pm 0.2 \mu$ equiv. L^{-1} acidity or alkalinity. Contamination free sampling and sample handling techniques are described.

5.2.2 Bromide

5.2.2.1 Isotope dilution analysis

The mass spectrometric isotope dilution method described by Henmann *et al.* [4,48] for the determination of down to $\mu g L^{-1}$ chloride in ice and snow had been applied to the determination of bromide. Down to $0.4 \mu g L^{-1}$ bromide could be determined.

5.2.3 Hydroxymethane sulphonate

5.2.3.1 Ion chromatography

Davies and Ivey [49] describe the ion chromatographic determination of the hydroxymethane-sulphonate form of sulphur(IV) after stabilisation by a stoichiometric excess of formaldehyde. The latter method gave a detection limit of $0.1\mu\text{g L}^{-1}$ and was used for determining sulphur(IV) in rainwater and Antarctic ice.

5.2.4 Nitrate

5.2.4.1 Spectrophotometric method

Parker *et al.* [50] have evaluated a Spectrophotometric method for the determination of nitrate in snow and ice.

5.2.4.2 Polarography

Hemmi *et al.* [51] used differential pulse polarography to determine down to $8 \times 10^{-7} \text{mol L}^{-1}$ nitrate in fresh snow. This method utilises the catalytic reaction between nitrate and uranyl ion in the presence of potassium sulphate. The differential pulse peak is proportional to nitrate concentration from 1 to $50\mu\text{mol L}^{-1}$. Between 350 and $700\mu\text{g g}^{-1}$ nitrate was found in snow samples by this method. Nitrite and phosphate interfere seriously in this method and should be absent if accurate results are to be obtained.

5.2.5 Sulphate

5.2.5.1 Spectrophotometric method

Suzuki *et al.* [52] have described a simple procedure for the Spectrophotometric determination of sulphate in snow. It involves reaction of sulphate with amino perimidine to form perimidinyl ammonium sulphate, and collection of this precipitate on a teflon filter followed by dissolution in nitric acid. The resulting solution is made alkaline and the absorbance of the violet colour is measured at 550nm. Both phosphate and nitrate interfere in the procedure.

A 5ml portion of sample solution containing up to $50\mu\text{g}$ of sulphate is placed in a funnel, followed by 3ml of 0.3% fresh aqueous 2-perimidinyl ammonium bromide solution. After 2min, the solution is removed by gentle suction. The funnel and the precipitate are washed with fine water droplets from a spray to remove excess of reagent. About 2ml of concentrated nitric acid is added dropwise to the precipitate until the washings become colourless. All the washings are collected in a 50ml beaker and the solution made basic with the addition of 3ml of 10mol L^{-1} caesium hydroxide, transferred to a 25ml volumetric flask and diluted to the mark with deionised water. The

absorbance is measured at 550nm against water. About 9mg L⁻¹ sulphate were found in snow samples by this method.

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Chapter 6

Anions in surface, ground, mineral, borehole and pure waters

Limited numbers of determinations are available for each of these types of water. However, in many cases, methods described for one type of water would be applicable to other types. In all methods have been described for 18 different anions, including total alkalinity, arsenite, borate, bromide, chloride, cyanide, fluoride, formate, iodide, nitrate, nitrite, phosphate, selenate, selenite, sulphate, sulphide, sulphite, thiosulphate and uranyl ion.

6.1 Surface waters

6.1.1 *Total alkalinity*

6.1.1.1 Titration method

Van Staden and Van Vleit [1] have described a simple automated titration procedure for determining total alkalinity in surface waters. Up to 120 samples per h can be analysed with a coefficient of variation of less than 1.4%.

6.1.2 *Borate*

6.1.2.1 Titration methods

Various workers [2,3] have described volumetric methods for the determination of borate based on titration in the presence of a monohydric alcohol.

6.1.2.2 Spectrophotometric method

Cherkida and Flyantikova [4] have described a method for determining borate in surface waters in which a 1 to 4 mixture of 2, 6 dimethyloctane 4, 6 diol and amyl alcohol is used to extract boron from non saline waters. The boron is then re-extracted into aqueous alkaline solution and can be determined colorimetrically, using fluorescein or H-resorcin (2, 4-dioxybenzene-azo-8-hydroxy naphthalene-3–6 disulphoxy acid). The detection limit is 0.05mg L^{-1} .

The maximum light absorption of the aqueous solution of a triple complex of boron with H-resorcin and with fluorescein is at 515nm and is characterised by a bathochromic

shift in relation to the maxima of light absorption of a solution of H-resorcin and fluorescein. The ratio of boron, H-resorcin and fluorescein in this complex, determined by the equilibrium shift method, is 1:1:1. The molar coefficient of darkening of this complex at 515nm is $1.5 \cdot 10^4$. Compliance with Beer's law is observed at a boron concentration from 0.5 to 15µg in 25ml of solution. The degree of extraction of boron at a concentration from 0.5 to 15µg in 10ml of solution is 94.5%.

For determination of boron the water samples are filtered to remove mechanical impurities and 10ml of the water is placed in a quartz separator funnel, 0.2ml of concentrated sulphuric acid and 1g of sodium chloride are added with agitation to full dissolution of the salt, then 12.5ml of a mixture of 2, 6-dimethyloctanediol-4, 6 and *n*-amyl or isoamyl alcohol (1:4) are added, and the mixture is shaken for 5min. The organic phase is transferred to another quartz separator funnel, and the water phase is shaken again with 12.5ml of a mixture of extraction agents for 5min. The organic phases are combined and washed with 25ml of acetate-ammonia buffer solution pH 5. The wash liquid is discarded, and 15ml of 0.2N sodium hydroxide is added to the organic phase with energetic agitation for 5min. The organic phase is discarded, and the re-extract is neutralised with hydrochloric acid solution (1:1) in the presence of several drops of 0.1% aqueous solution of *p*-nitrophenol until the indicator becomes colourless. Then this solution is transferred to a quartz test tube, 4ml of $1 \cdot 10^{-3}$ M of aqueous solution of H-resorcin and 1ml of $1 \cdot 10^{-3}$ M of aqueous solution of fluorescein are added and the volume of the solution is brought up to 25mm with acetate ammonia buffer of pH 5. After 2h the optical density of the solution is measured relative to the density of a blank experiment solution in a cuvette with a layer thickness of 10ml at 515nm. The boron concentration is determined from the calibration curve. The reproducibility of the method is quite satisfactory, as shown by the results of boron determination in non saline waters (Table 6.1).

In order to show the correctness of the data obtained water was analysed from the Kyual'nitskii Liman by the quinalizarin method [4]. The determination was 2.6 mg L^{-1} boric acid at $n=6$, $s=0.01$.

Curcumin [5], quinalizarin [6], carmine [7] and H-resorcin (2, 4 dioxy-benzene-azo-8-hydroxy naphthalene 3-6 disulphonxy acid) [8] have all been employed as chromogenic reagents in the determination of boron.

Table 6.1 Determination of borate in Soviet surface waters

Sample collection site	H ₃ BO ₃ , mg L ⁻¹	sd
Odessa estuary of Black Sea, at surface, 1km from shore, July 4 1980	1.64	0.16
Kyual'nitskii Liman, at surface, July 1 1980	2.91	0.10
Khadzhibeevskii Liman, at surface, July 6 1980	2.22	0.14
Dunai River, at surface, June 3 1980	1.00	0.10

Source: Reproduced with permission from Soviet Journal of Chemistry and Technology [4]

6.1.3 Chloride

6.1.3.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 6.1.13.1 and 12.5.1.

6.1.4 Fluoride

6.1.4.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 6.1.13.1 and 12.5.1.

6.1.5 Nitrate

6.1.5.1 Spectrophotometric method

Van Staden *et al.* [9] used a flow-injection Spectrophotometric method to determine nitrate in surface water, groundwater and domestic water samples. The nitrate is first reduced to nitrite with a copperised cadmium tube in the reaction manifold; the nitrite is diazotised with subfanilamide and the product is coupled with *N*-(1-naphthyl)-ethylenediammonium chloride to form a highly coloured azo dye which is measured at 520nm. The sampling rate is 50 samples/h, and the coefficient of variation is better than 1.5%.

6.1.5.2 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 6.1.13.1 and 12.5.1.

6.1.6 Nitrite

6.1.6.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 6.1.13.1 and 12.5.1.

6.1.7 Phosphate

6.1.7.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 6.1.13.1 and 12.5.1.

6.1.8 Sulphate

6.1.8.1 Flow injection analysis

The method involving the formation of a methylthymol blue complex with barium, described in sections 5.1.11.3 and 6.1.13 has been applied to the determination of 1–10 [33] or 100–1000mg L⁻¹ [34] of sulphate in surface waters.

6.1.8.2 Atomic absorption spectrometry

Little *et al.* [10] have described a method for the determination of 1mg L⁻¹ (asS) sulphate in surface waters in which the sulphate is precipitated vs lead sulphate in 40% aqueous ethanol medium in excess lead chloride. Unconsumed lead is determined by atomic absorption spectrometry with an air-coal gas flame. Lead recoveries are 95% at the 1mg L⁻¹ sulphate (asS) level and 99–100% at higher sulphate levels. The only interference found was from phosphate amounts exceeding 10mg L⁻¹ (asP) which could be overcome by the addition of aluminium nitrate.

6.1.8.3 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 6.1.13.1 and 12.5.1.

6.1.9 Sulphide

6.1.9.1 Miscellaneous

The application of this technique is discussed under multianion analysis in section 14.12.3.1.

6.1.10 Sulphite

6.1.10.1 Miscellaneous

The application of this technique is discussed under multianion analysis in section 14.12.3.1.

6.1.11 Thiosulphate

6.1.11.1 Miscellaneous

The application of this technique is discussed under multianion analysis in section 14.12.3.1.

6.1.12 Uranyl

6.1.12.1 Miscellaneous

Dolezal *et al.* [11] have reported on levels of uranyl ions found in surface waters.

6.1.13 Multianion analysis

6.1.13.1 Ion chromatography: chloride, fluoride, nitrate, nitrite, phosphate and sulphate

The Environmental Protection Agency US [12] have published a standard method for the determination of anions in surface waters.

The recommended operating conditions are listed in Table 6.2. Single operator accuracy and precision are listed in Table 6.3.

6.2 Ground waters

6.2.1 Alkalinity

6.2.1.1 Titration method

Van Staden and Van Vleit [1] have described a simple automated titration procedure for determining total alkalinity in ground waters. Up to 120 samples per h can be analysed with a coefficient of variation of better than 1.4%.

6.2.2 Arsenite

6.2.2.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 6.2.9.1.

Table 6.2 Chromatographic conditions and method detection limits in reagent water

Analyte	Retention ¹ time (min)	Relative retention time	Method ² Detection limit mg L ⁻¹
Fluoride	1.2	1.0	0.005
Chloride	3.4	2.8	0.015
Nitrite-N	4.5	3.8	0.004
O-phosphate-P	9.0	7.5	0.061
Nitrate-N	11.3	9.4	0.013
Sulphate	21.4	17.8	0.206

Standard conditions:
Columns as specified in 6.2. Detector as specified in 6.2. Eluent as specified in 7.3. Sample loop 100µL Pump volume 2.30mL min⁻¹
¹Concentrations of mixed standard (mg L⁻¹)
Fluoride 3.0
Chloride 4.0
Nitrate-N 30.0
O-phosphate-P 9.0
Nitrite-N 10.0
Sulphate 50.0
²MDL calculated from data obtained using an attenuator setting of 1 µMHO full scale. Other settings would produce an MDL proportional to their value
Source: Reproduced with permission from the Environmental Protection Agency [12]

Table 6.3 Single-operator accuracy and precision, determinations in surface water

Analyte	Spike (mg L ⁻¹)	No. of replicates	Mean recovery (%)	Standard deviation (mg L ⁻¹)
Chloride	1.0	7	105.0	0.139
Fluoride	0.50	7	74.0	0.0038
Nitrate-N	0.50	7	100.0	0.0058
Nitrite-N	0.51	7	88.2	0.0053
O-phosphate- P	0.51	7	94.1	0.020
Sulphate	10.0	7	111.6	0.709

Source: Reproduced with permission from the Environmental Protection Agency [12]

6.2.3 Bromide

6.2.3.1 Segmented flow analysis

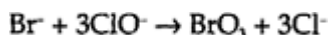
Basel *et al.* [13] have discussed methods for compensating for chloride, ammonia and bicarbonate in the automated phenol red segmented flow analysis method for the determination of bromide in groundwaters.

6.2.3.2 Polarography

In a specific method for determining down to 2mg L^{-1} bromide in groundwaters [14] bromide is first converted to silver bromide which is then oxidised to silver bromate which is then determined polarographically.

Polarographic methods for bromide are based on the oxidation of bromide to bromate followed by electro-reduction. In this technique, iodide is partially oxidised to iodate.

The oxidation reaction is



and the global electrode reaction



The half-wave potential for the reduction of iodate is less negative than is that of bromate.

Reagents. Merck unless otherwise stated.

Potassium chloride. Potassium bromate. Sodium acetate N.

Silver nitrate, 0.1N.

Sodium hydrochlorite (BDH), low in bromine.

Activated carbon (pa Baker).

The method is directly applicable to samples containing 1–150 μg bromide. Adequate volumes are sampled and processed to fall within this range of applicability.

For surface waters or ground waters containing organic compounds shake the sample for 30min after adding 1g L^{-1} activated carbon powder, and subsequently filter on a standard bacteriological membrane filter with a porosity of $0.45\mu\text{m}$. Organobromated compounds are eliminated.

To concentrate the sample, precipitate bromides simultaneously with chlorides and iodides by adding 25ml of 0.1N silver nitrate solution to 1L sample water and leaving in the dark for 12h. Bromate, if present, remains unprecipitated as silver bromate which is soluble.

The precipitate is filtered under vacuum on a membrane with pore size of $0.45\mu\text{m}$ and the membrane with the deposit is placed in a 100ml vessel for about 30min in a drying

oven at 40–45°C The precipitate is drawn off from the membrane and collected in the reaction vessel.

To convert bromide to bromate the isolated precipitate is poured into 5ml distilled water and treated with 4ml 0.35mol L⁻¹ hypochlorous acid/ sodium hypochloride at pH 7. (This reagent is obtained by partial neutralisation with a normal solution of sulphuric acid AnalaR of a sodium hypochlorite solution of appropriate grade, eg BDH AnalaR, low in bromide).

After mixing, the 9ml of solution is evaporated to dryness on an IR stand equipped with a 350W lamp. At this stage, bromide is quantitatively oxidised to bromate. The residue remaining after evaporation is taken up in 20ml distilled water and transferred into a 25ml volumetric flask. The pH is adjusted to 7.5 with N sulphuric acid, then the volume is adjusted to 25ml.

The polarograph is set in the pulse mode under the following conditions: nitrogen stripping 10min, mercury dropping frequency 0.5s, scanning rate 5mV s⁻¹. The half-wave potential for bromate in these experimental conditions is 0.64V vs SCE.

The reaction medium is a self-supporting electrolyte. No further additions are necessary and may even hinder by their side effects such as formation of deposits and coprecipitation of bromate (with calcium chloride), superposition of the waves (with alkali-chlorides) and finally hindering convection currents (with lanthanum trichloride). A stable diffusion current is obtained at pH 1–2.

Using this method Shirashi *et al.* [14] found levels of bromide in the range 20–280mg L⁻¹ in Belgian ground water samples.

6.2.3.3 Ion chromatography

Ion chromatography using an amperometric detector has been used to determine down to 10µg L⁻¹ bromide in rain water and groundwaters [15]. The equipment features an automated ion chromatograph, including a programme controller, an automatic sampler, an integrator and an amperometric detector. A fixed potential is applied to the cell. Any electroactive species having an oxidation-reduction potential near the applied potential will generate a current that is directly proportional to the concentration of the electroactive species.

The detection limit for bromide is 0.01mg L⁻¹ and the relative standard deviation is less than 5% for bromide concentrations between 0.05 and 0.5mg L⁻¹. Chloride interferes if the chloride to bromide ratio is greater than 1000:1 for a range of 0.01–0.1mg L⁻¹ bromide; similarly, chloride interferes in the 0.1–1.0mg L⁻¹ range if the ratio is greater than 5000:1. In the latter case, a maximum of 2000mg L⁻¹ of chloride can be tolerated. Recoveries of bromide ranged from 97 to 110%.

6.2.4 Iodide

6.2.4.1 Spectrophotometric method

Iodide has been determined in groundwaters [16] by utilising the reaction between cerium (IV) and arsenic(III) which is catalysed by iodide ion. This reaction is stopped by the

addition of *N, N'*-bis-(2-hydroxypropyl)-*o*-phenylene diamine, which combines with cerium(IV) to give a red colour, the intensity of which is proportional to the iodide concentration. The standard deviation of the method ranges from 0.3ng (10ng iodide) to 3.8ng (100ng iodide).

6.2.5 Nitrate

6.2.5.1 Ion selective electrode

Robowsky [17] evaluated a nitrate-selective electrode for use with groundwater samples. For concentrations in excess of 10mg of nitrate L⁻¹ the recoveries are ~99.6% and the coefficient of variation is ~2.5%; at lower nitrate concentrations there is a positive error in the determinations due to interference by chloride.

6.2.6 Phosphate

6.2.6.1 Spectrophotometric method

Stauffer [18] has carried out studies to optimise the determination of phosphate in groundwater using reduced molybdenum blue. High levels of silica may be responsible for phosphorus determinations being raised by three orders of magnitude.

Yoshimura *et al.* [19] used gel phase colorimetry to determine phosphate in groundwaters with molybdenum blue. In this method phosphate reacted with molybdate in acidic conditions to produce 12-molybdophosphate. The blue species of molybdophosphate were reduced by ascorbic acid in the presence of antimonyl ions and adsorbed on Sephadex G-25 gel beads. Attenuation at 836 and 416nm (absorption maximum and minimum wavelengths) was measured and the difference used to determine trace levels of phosphate. Conditions were optimised (acidity, stirring time, standing time, temperature). The effects of nitrate, sulphate, silicic acid, arsenate, aluminium, titanium, iron, manganese, copper and humic acid on the technique were examined.

6.2.7 Selenate and selenite

6.2.7.1 Ion chromatography

Reddy *et al.* [20] studied the speciation of selenium in groundwaters by adsorption of selenite and selenate onto copper oxide particles followed by hydride generation atomic absorption spectrometry and ion chromatography.

The application of this technique is also discussed under multianion analysis in section 6.2.9.1.

6.2.8 Sulphide

6.2.8.1 Inductively coupled plasma atomic emission spectrometry

Lewin *et al.* [21] have described a rapid and simple inductively coupled plasma atomic emission spectrometric technique for determinant dissolved sulphide at the ppb level in groundwater. Sulphide is stabilised on sampling by addition of potassium hydroxide and is later converted to hydrogen sulphide under acidic conditions and stripped from the solution in a gas-liquid separator by a stream of argon. The emission intensity is monitored at 180.7nm. Dissolved sulphate does not interfere and spectral interference from calcium is avoided.

6.2.8.2 Miscellaneous

Baedecker and Cozzarelli [22] have reviewed the determination and fate of unstable sulphide in ground waters.

6.2.9 Multianion analysis

6.2.9.1 Ion chromatography: selenate, selenite and arsenate

Hoover and Jager [23] have discussed the determination of selenite together with other anions (selenate and arsenite) in potable and groundwaters by ion chromatography.

6.3 Mineral waters

6.3.1 Arsenate

6.3.1.1 Polarography

An indirect polarographic method has been used to determine traces of arsenate in mineral waters [24]. In this method arsenate is converted to uranyl arsenate which is filtered off and excess uranyl ion is determined by polarography at -3.60V . Phosphates interfere in this procedure.

6.3.2 Cyanide

6.3.2.1 Ion selective electrodes

The application of this technique is discussed under multianion analysis in section 14.11.1.1.

6.3.3 Iodide

6.3.3.1 Gas chromatography

Wu *et al.* [25] have described a method for the derivatisation of iodide into pentafluorobenzyl iodide using pentafluorobenzyl bromide. The derivative was analysed at μg levels by gas chromatography with electron capture detection. The effects of solvent, water content, base or acid concentration, amount of pentafluorobenzylbromide, reaction time and reaction temperature were examined. Interferences by common anions were minimal. The method was applicable to iodide determination in spring water.

6.3.4 Nitrate and nitrite

6.3.4.1 Spectrometric and ultraviolet spectroscopic methods

A spectrophotometric method using 3,3'-dimethylnaphthidine as the chromogenic agent has been used to determine down to $5.0\mu\text{g L}^{-1}$ nitrate in mineral waters [26].

Spectrophotometric methods based on the use of resorcinol [27] and 2, 4-xylenol [28] have been described for the determination of nitrate in mineral and groundwaters.

Miles and Espejoi [28] compared results for nitrate in ground waters of low salinity obtained by the 2, 4-xylenol spectrophotometric method and by ultraviolet spectroscopy. The ultraviolet procedure is not subject to interference from the major cations present in typical groundwaters, and interference by high levels of nitrite can be overcome by addition of sulphamic acid. There was good agreement between nitrate levels determined by both methods on a number of ground water samples.

Nitrite, which absorbs in a similar part of the ultraviolet region, is a potential source of interference in this method. A solution containing 1mg L^{-1} of nitrite-nitrogen was scanned between 190 and 260nm and the spectrum is shown in Fig. 6.1, together with that of a 1mg L^{-1} solution of nitrate-nitrogen for comparison. The nitrite absorption maximum is at about 211nm and it absorbs less strongly than nitrate at a similar concentration. Solutions containing 0.5mg L^{-1} of nitrate-nitrogen and up to $100\mu\text{g L}^{-1}$ of nitrite-nitrogen were prepared and the interference from nitrite is significant only at concentrations above $20\mu\text{g L}^{-1}$. Interference by higher concentrations of nitrite can be removed by the addition of 0.1% m/v of sulphamic acid.

Iron does not interfere at concentrations below $100\mu\text{g L}^{-1}$ and chloride is without effect at concentrations below 100mg L^{-1} .

Table 6.4 compares results obtained for nitrate by ultraviolet spectroscopy and spectrophotometry. Good agreement was obtained for all groundwater samples analysed.

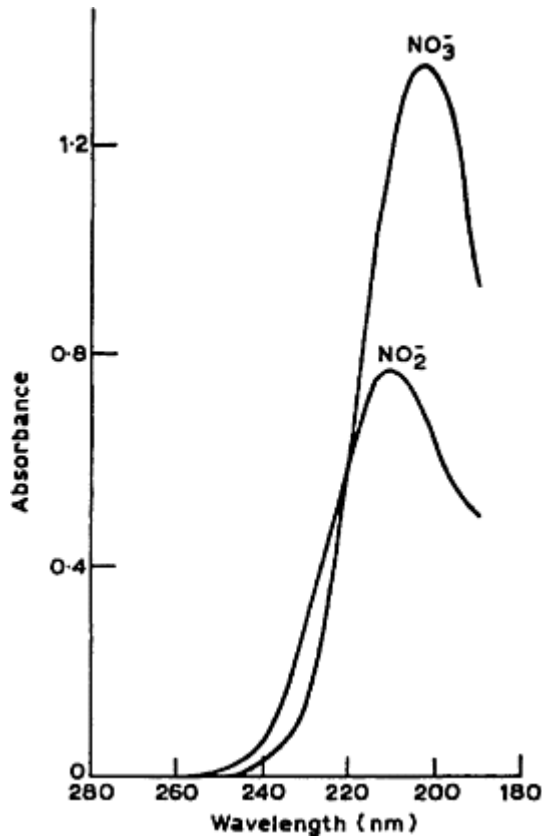


Fig. 6.1 Ultraviolet absorption spectre of nitrate and nitrite standard solutions containing 1 mg L⁻¹ of nitrogen
Source: Reproduced with permission from the Royal Society of Chemistry [28]

Table 6.4 Nitrate concentrations determined by ultraviolet and 2,4-xylenol methods (absorbance measurement measured in ion cells)

Type of water	Nitrate nitrogen mg L ⁻¹	
	Ultraviolet method	2, 4-xylenol method
Butler Sandstone	0.04	0.04 (4 in all)
Butler Sandstone	8.3	8.2 (4 in all)
Butler Sandstone	0.005 (4 in all)	0.04 (4 in all)
Butler Sandstone	0.54	0.55

Butler Sandstone	4.5	4.6
Lincolnshire Sandstone	7.9	7.9
Lincolnshire Sandstone	5.8	5.5
River Thames, Chiswick	11.0	10.9

Source: Reproduced with permission from the Royal Society of Chemistry [28]

6.3.5 Sulphate

6.3.5.1 Titration method

Pagenkopf *et al.* [29] have described a procedure for the determination of sulphate in mineral waters which uses back titration of excess barium with a standard solution of sulphate using nitrosulphonazo(III) indicator. The method was developed for the analysis of water samples for the mining areas of the northern Great Plains of USA which are often high in sulphate. Calcium and magnesium must be removed but phosphate, chloride, nitrate and fluoride do not interfere in amounts up to 200mg L⁻¹. Ten samples h⁻¹ can be analysed.

Reagents. As follows.

Barium chloride, 10⁻³mol L⁻¹. Nitrosulphanazo(III) (2,7-bis (4'-nitro-2' sulphophenylazo), 8-dihydroxy naphthalene-3, 6-disulphonic acid, sodium salt), 10⁻⁴mol L⁻¹. Acetone.

A 10.00ml aliquot of the sample is mixed with 10g of Dowex 50-X8 ion exchange resin. A 5.00ml aliquot of the supernatant liquid (filter or decant, avoiding fines) was transferred to a beaker, and 5.00ml of 10⁻³mole L⁻¹ barium chloride solution added and the pH adjusted to pH 1.90. At this point, 1.0ml of the indicator solution and 10ml of acetone are added and the resulting mixture titrated to a feint pink in the blue coloured solution with the standard sulphate solution. A blank is obtained by mixing 5.00ml of distilled water with 5.00ml of barium chloride solution, adjusting the pH, adding the indicator and acetone, and titrating with standard sulphate.

The use of a discontinuous titration is convenient for end-point detection when more than one sample is being titrated. The use of a fluorescent lamp and comparison with a solution that has been titrated to the equivalence point are helpful in assigning the end-point. The sample should have a sulphate concentration range of 20–90mg L⁻¹ for best results, so dilution of a mineral water sample may be necessary.

Analysis of sodium sulphate solutions which had a sulphate concentration range of 10–140mg L⁻¹ by this method exhibited a positive bias of 2.42% with a standard deviation of 4.38%. The positive bias results from a slightly premature assignment of the end-point in the titrations, and probably reflects the magnitude of the colour differences that the eye can detect.

Standard addition studies were made to evaluate the method and gave values listed in Table 6.5. The least squares correlation between sulphate observed and added is 0.997, with an interception value of 164mg L⁻¹ which is 1% above the expected amount. The

removal of calcium and magnesium by ion exchange is critical since these ions cause a premature indicator change. At least ten samples can be analysed per h with results comparable to, or better than, those obtained with the conventional turbidimetric procedure. The procedure is not affected by phosphate,

Table 6.5 Sulphate analysis for standard addition study

<i>Sulphate added (mg L⁻¹)</i>	<i>Sulphate found (mg L⁻¹)</i>	<i>Dilution 1:x</i>	<i>Recovery (%)</i>	<i>Sulphate added</i>	<i>Sulphate found (mg L⁻¹)</i>	<i>Dilution 1:x (mg L⁻¹)</i>	<i>Recovery (%)</i>
0 ^a	162	5	100.6	217 ^c	378	5	100.0
217	392	5	103.4	327 ^c	487	8.33	99.8
327 ^b	487	8.33	99.8	434 ^c	596	10	100.2
434	579	10	97.3	545 ^c	704	10	99.7
545	719	10	101.8	653 ^c	813	12	99.8
635	819	10	102.9				

^aTurbidimetric analysis gives 171 mg L⁻¹; ^bturbidimetric analysis gives 460 mg L⁻¹; ^cthese samples were treated with Dowex 50-X8 before addition of Na₂SO₄

Source: Reproduced with permission from Elsevier Science [29]

chloride, nitrate and fluoride in amounts up to 200 mg L⁻¹, although these anions can result in slightly different indicator colours.

6.3.6 Sulphide

6.3.6.1 Ion selective electrode

The application of this technique is discussed under multianion analysis in section 14.11.1.1.

6.4 Borehole waters

6.4.1 Iodide

6.4.1.1 Spectrophotometric method

In a further method [30] for determining iodide in borehole water, iodide is precipitated with nitron in sulphuric acid medium. The extinction of a dichloroethane extract of the reaction mixture is then measured. There is no interference from chloride or sulphate or from bromide if sufficient aqueous chlorine is added, and nitrate interferes only in so far

as it consumes nitrogen.

6.4.2 Phosphate

6.4.2.1 Spectrophotometric method

Potman and Lijkema [31] have discussed the following determination of down to $0.4\mu\text{g L}^{-1}$ phosphate in small samples of borehole and interstitial water.

Table 6.6 Interference of iron and silica in phosphate determination

μgP in sample	0.34	0.34	0.34	0.34	0.34
μgFe in sample	0	170	255	340	510
Abs. (corrected)	0.157	0.158	0.159	0.182	0.189
μgP recovered	0.34	0.34	0.35	0.40	0.41
μgP in sample	0.34	0.34	0.34	0.34	0.34
$\mu\text{g Si}$ in sample	0	17	25.5	34	51
Abs. (corrected)	0.163	0.168	0.161	0.168	0.205
μgP recovered	0.34	0.35	0.34	0.35	0.43

Source: Reproduced with permission from Elsevier Science [31]

Procedure. 5ml 2N hydrochloric acid, 6ml molybdate solution ($1.159\text{g (NH}_4)_6\text{Mo}_7\text{ 4H}_2\text{O}$ in 250ml water) and at most 25ml of the sample are mixed in a separating funnel. If necessary fill up with water to 25ml, After 10min 25ml of 5:1(v/v) ether :isobutanol solvent are added and the funnel shaken for 1min. The aqueous phase is removed. The organic solution is washed twice with 20ml 0.4N hydrochloric acid for 1min and the aqueous phase removed carefully. The ether solution is shaken for 1min with 10ml 0.1N sodium hydroxide, the alkaline solution separated completely and the extraction repeated with 5ml 0.1N sodium hydroxide, shaken for about 30s.

The combined alkaline solutions are mixed with 11ml of the copper sulphate solution ($0.04\text{g CuSO}_4 \cdot 4\text{H}_2\text{O}$ plus 1ml H_2SO_4 per litre), 8.5ml concentrated hydrochloric acid, 7ml acetone, 10ml of 5% ammonium thiocyanate solution and filled up with 3N hydrochloric acid to 50mL. The absorbance is measured after 45min at 470nm in a 1cm cell, comparing with standards after correction for the blank.

Iron and silicate interfere in the procedure but only at higher concentrations (Table 6.6) ie a 1000-fold excess of iron and a 100-fold excess of silica do not interfere.

6.5 Pore waters

6.5.1 Formate

6.5.1.1 High performance liquid chromatography

Using the method described in section 3.15.1 Kieber *et al.* [32] were able to determine formate at the 0.9 to 8.4 μM level in sediment porewaters.

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Chapter 7

Anions in potable waters

7.1 Alkalinity

7.1.1 Single point titration method

Basson and Van Staden [1] have described a single point titration system for the determination of total alkalinity in potable and domestic waters, based on flow injection analysis. Water samples are injected automatically into the flow system using a flow injection sampling unit. A sampling cycle of 30s allows 120 samples per h to be analysed. The sample is reacted with an acid linear response buffer solution and the pH of the resulting solution is measured with a glass electrode in a flow through assembly.

Details of the procedure are given below.

Reagents: Unless otherwise specified all reagents are of analytical grade quality.

The buffer solution is prepared by mixing 50ml of 6.01 g diethylmalonate in 7ml concentrated hydrochloric acid diluted to 500ml, 59ml of 7.88g citric acid diluted to 500ml, 150ml of 5.22g p-nitrophenol diluted to 500ml, 3.87g diethylbarbituric acid diluted to 500ml, 50ml of 2.32g boric acid diluted to 500ml and 50ml of 3.53g phenol diluted to 500ml. The final solution is made 0.1mol L⁻¹ with respect to sodium chloride.

Apparatus consisting of 30rpm flow injection sample, pH meter and micro blood electrode consisting of a micro sensor assembly (Beckman Part No 580621) and a pH-electrode (Beckman Part No. 39045), Hitachi model QPD 53 potentiometric recorder.

Procedure: A schematic flow diagram for the system is shown in Fig. 7.1 Tygon tubing of 0.50mm diameter was used and all connectors were made from Perspex. The carrier stream consists of 0.1mol L⁻¹ sodium chloride.

Water samples are automatically injected into the flow system by using a flow injection sampling unit. Use a sampling cycle of 30s between successive samples giving a capacity of 120 samples per h. Actuate the valve system on a time basis which is correlated with the sampler unit.

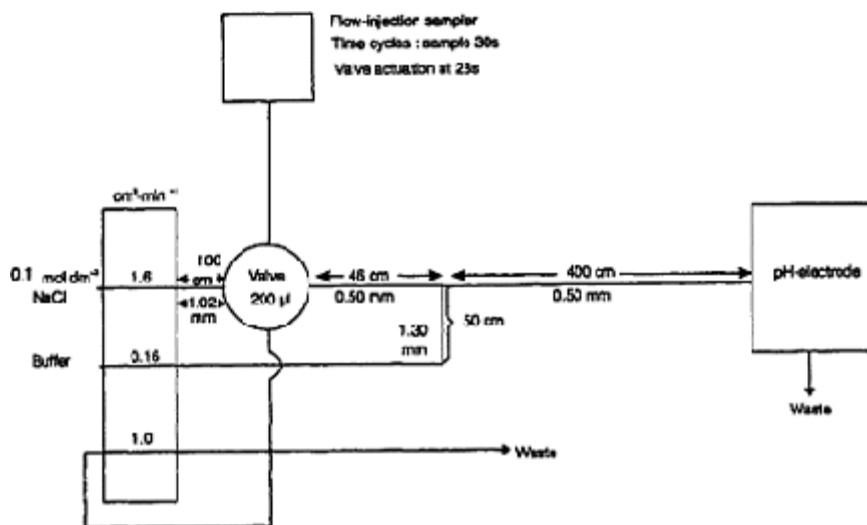


Fig. 7.1 Flow system for the determination of total alkalinity. Sampling rate 120 samples h⁻¹. Tube length and diameters are given in cm and mm
Source: Reproduced with permission from United Trades Press [1]

The sampling valve actuates every 28s after movement of the sampler to the next sample.

Fig. 7.2 shows the appearance of recorder tracing as well as calibration curves when analysing a series of standards in the range 20–300mg L⁻¹ bicarbonate solution. The results indicate linearity in the range 30–75mg L⁻¹.

In Table 7.1 a comparison is made of results obtained by the above flow injection method, by an electrometric titration method, and by an automated bromocresol green indicator method.

Flow injection results compare favourably with a standard electrometric method and in some instances better results were obtained when compared to the automated bromocresol green method. This is probably due to colour interferences from these water specific samples. Student's t-test was applied in comparing both sets of results with the manual electrometric method. Table 7.1 reflects these calculations. Both procedures give results that differ to a statistically insignificant extent when compared to the electrometric procedure. However, the difference between the procedures is smaller than the difference between the continuous flow procedure and the electrometric procedure.

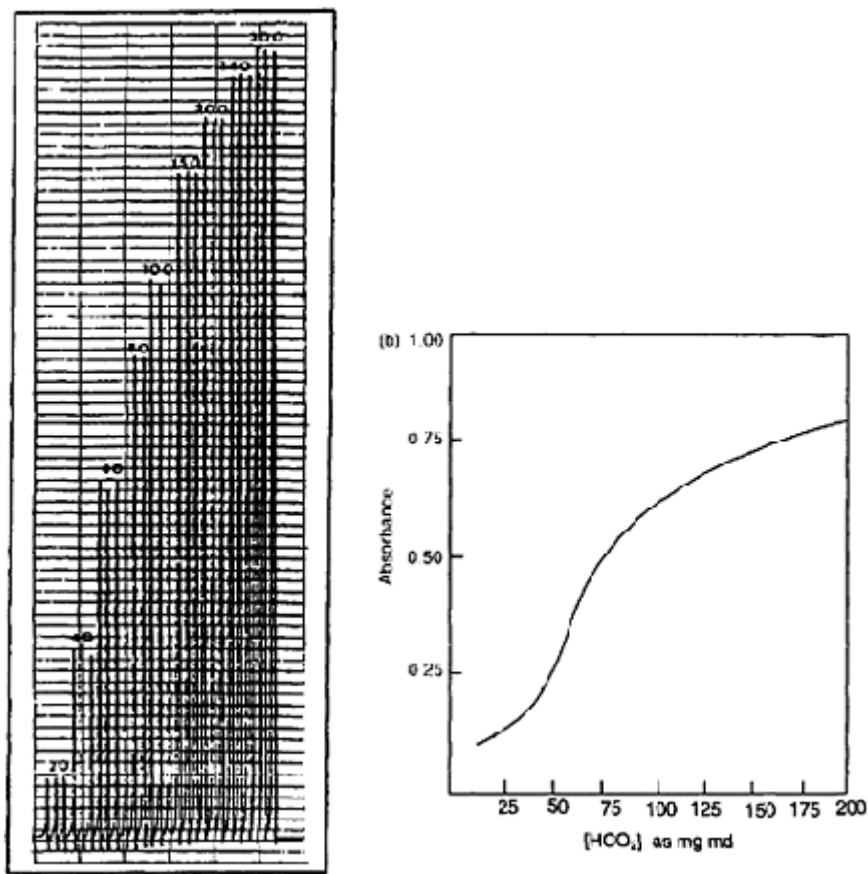


Fig. 7.2 Calibration peaks obtained with 10cm² buffer solution diluted to 100cm³ with distilled water. The values on top of the peaks represent mg L⁻¹ bicarbonate ions, (b) Corresponding calibration graph
Source: Reproduced with permission from United Trades Press [1]

7.1.2 Spectrophotometric method

Van Staden and Van Vleit [2] have described a dimple, automated procedure for determining total alkalinity in potable water. Up to 120 samples per h can be analysed with a coefficient of variation of better than 1.4%.

Table 7.1 Comparison of results obtained by the FIA method, the electrometric method and the automated segmented bromocresol green methoda

Sample	Automated	Electrometric method	FIA method	Coefficient of

	<i>segmented method</i>	[HCO ₃ ⁻] in mg L ⁻¹	[HCO ₃ ⁻] in mg L ⁻¹	<i>variation %</i>
1	226	268	248	0.99
2	485	546	532	0.46
3	266	298	305	0.98
4	266	306	313	0.56
5	213	232	236	0.71
6	250	276	288	0.66
7	120	142	135	0.98
8	160	259	287	0.48
9	267	291	324	0.31
10	480	317	332	0.56
11	107	120	110	0.26
12	117	123	110	0.27
13	119	123	112	0.24
14	120	125	113	0.31
15	113	109	110	0.42
16	113	117	108	0.55
17	96	98	95	0.30

^a15 tests were carried out on each sample

Source: Reproduced with permission from United Trades Press [1]

7.1.3 Flow injection analysis, alkalinity, pH and total ionic concentration

Canate *et al.* [3] have described a flow injection analysis system for the simultaneous determination of the alkalinity, pH and total ionic concentration of potable water. The pH measurements are performed by means of a glass calomel microelectrode inserted in to the water stream. The alkalinity and total ionic concentration are determined by flow injection analysis titrations, acid base reactions and spectrophotometric detection. In addition, the determination of the total ionic concentration requires the incorporation of an ion exchange mini-column. The results obtained are in agreement with those obtained by conventional methods for the determination of these parameters and are obtained with a higher degrees of automation, which results in a smaller reagent consumption, greater convenience and higher reproducibility and sampling frequency. A microcomputer is installed for on-line data collection and the treatment and display of results.

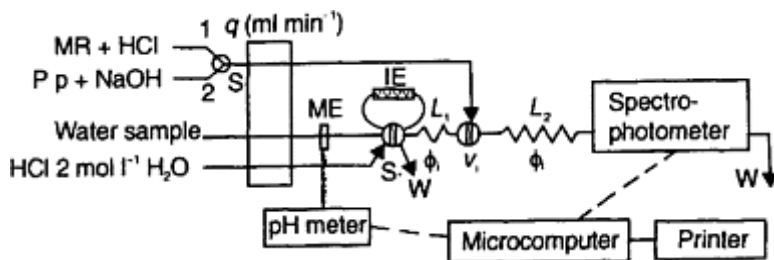


Fig. 7.3 Manifold for the simultaneous determination of pH, alkalinity and total ionic concentration, MR=methyl red, pp=phenolphthalein (for details see text)

Source: Reproduced with permission from the Royal Society of Chemistry [3]

Fig. 7.3 shows the reversed FIA configuration used. It involves the use of two detectors; a potentiometric detector ME (a glass microelectrode) located before the confluence of the sample with any reagent for the continuous monitoring of pH, and a spectrophotometric detector for the monitoring of the acid base reactions. Two serial injection valves are placed along the water stream. The first of these, S', is aimed at incorporating the ion exchange microcolumn (IE) into the stream in order to determine the total ionic concentration. This valve is synchronised with the selecting valve S and in the filling position of valve S', selects channel 1 (methyl red in an acidic medium) which fills the loop of V, (ordinary injection valve 1126 μ L). The alkalinity of the water sample is determined in this position. In the emptying position, S' incorporates the mini-column IE, S selects channel 2 (phenolphthalein in a basic medium) and the determination of the total ionic concentration is carried out. The flow rate adopted was 0.75 ml min⁻¹ and the reactor lengths $L_1=2.40$ cm and $L_2=110$ cm.

The microcomputer collects the data from both detectors and, by means of the computer program described below, processes the data and gives the pH, alkalinity and total ionic concentration for each sample.

The microcomputer collects the pH and absorbance values (measurement frequency, 0.2s) which are introduced into a BASIC program. The data acquisition process starts at a time from the reagent injection equal to the travel time, so that as little memory as possible is used. Data treatment is carried out according to the scheme in Fig. 7.4. The width of each peak (in seconds) at heights pre-fixed by the user for the sample, standards and blanks, is collected. The program features a subroutine for the optimisation of each system. The program also allows data to be discarded from anomalous peaks or standards that would give a low correlation coefficient for the linear range of the calibration graph.

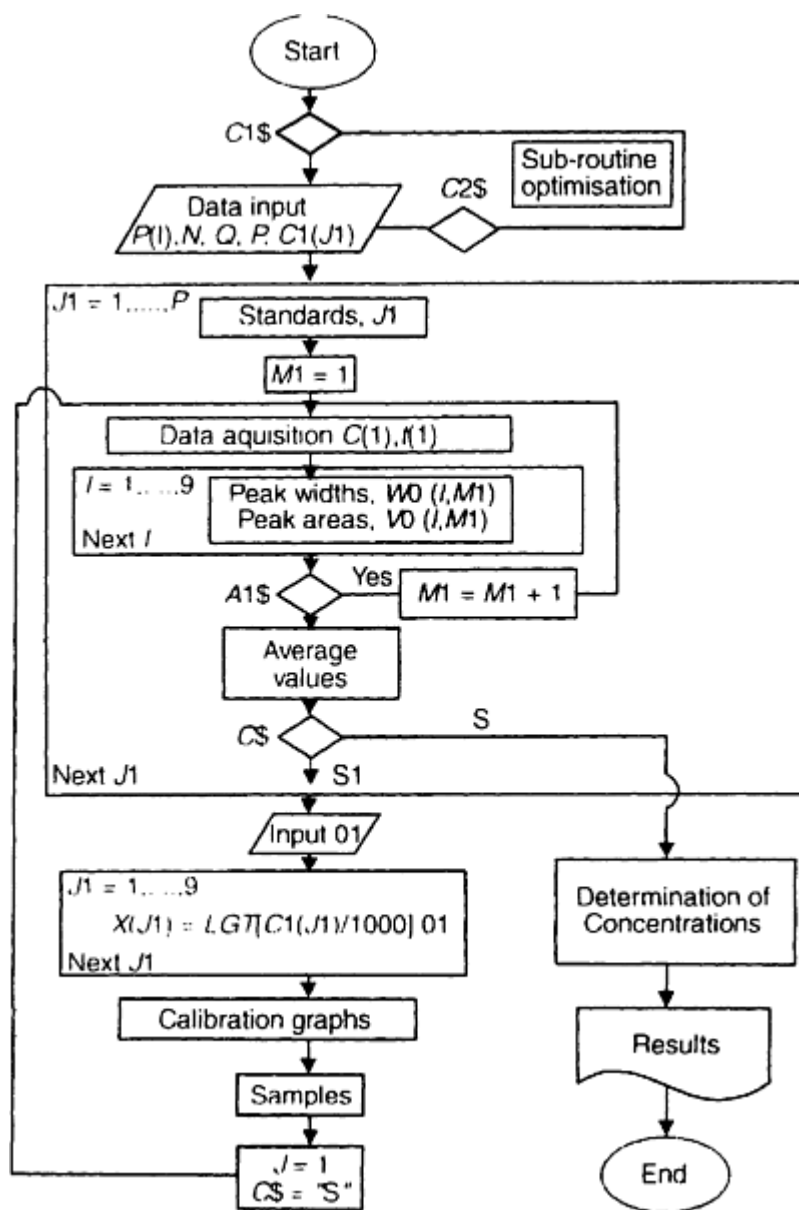


Fig. 7.4 Flow diagram of the computer program, C1\$=inquiries to the program; P(I) measurement height; N=number of absorbance-time data points; Q=interval between two consecutive data points; P=number of standards; C1 (JI)=concentration of standards; C(I)=concentration of analyte; t(I)=time; WO=peak width; VO=peak area; 01=molecular mass; S=sample; SI=standard and JI, MI and I=counters

Source: Reproduced with permission from the Royal Society of Chemistry [3]

This corresponds to the change in the width (Δt) at a height h as a function of $\log C$ (C =analyte concentration).

Alkalinity is measured by titration with hydrochloric acid to the methyl red end-point.

Similar to a conventional titration, the reaction is monitored after the equivalence point so that the blank signal (distilled water) shows a higher peak width. The greater the alkalinity, the smaller is the peak width. The analytical signal was $\Delta t_{\text{blank}} - \Delta t_{\text{sample}}$, so that the slopes of the calibration graphs were positive. To determine total ionic concentration the salts present in the water sample are transformed into their corresponding acids on passing through the cationic resin in the H^+ form. The acids are then titrated with sodium hydroxide and phenolphthalein. In this method the minicolumn is placed in the loop of valve S' (Fig. 7.3) which is inserted into the circulating stream in the emptying position. In the filling position, the minicolumn is regenerated with a sodium hydroxide stream and washed with distilled water, thus allowing continuous use for 4–5h.

The reaction is monitored at 552nm (after the equivalence point in the conventional titration) so that, as in the above system, the peak width is wider for the blank than for the samples.

As the insertion of a glass calomel microelectrode into the flow injection analysis configuration introduced no species that disturb the system, pH monitoring can be readily carried out by inserting the sensor prior to the reagent injection (Fig. 7.3) and calibrating it with standard buffer solutions at the working flow rate.

Table 7.2 summarises the features of the simultaneous determination of alkalinity, pH and total ionic concentration.

Canate *et al.* [3] tested the validity of their procedure by analysing a series of synthetic samples, the composition and results of which are shown in Table 7.3. In general, the errors in the determination of alkalinity are higher than those of the total ionic concentration.

The method was also applied to the determination of these parameters in potable water. The results (Table 7.4) have been compared with those of conventional manual methods (eg for alkalinity titration with hydrochloric acid and methyl orange as indicator and for total ionic concentration, passage of the water sample through a cationic ion exchange column in acidic form and titration of the eluate with sodium hydroxide and phenolphthalein as indicator). The results obtained were in good agreement with these conventional methods.

Hemmings and Shaw [4] have described a flow injection analysis method, based on methyl orange for the determination of $10\text{--}200\text{mg L}^{-1}$ alkalinity in potable waters with a detection limit of 4.2mg L^{-1} . Basic ions such as carbonate and hydroxide cause a reduction of the red acid components of the buffered indicator solution. Total alkalinity is

Table 7.2 Features of the simultaneous determination of pH, alkalinity and total ionic concentration

Parameter	Detection method	Range of determination ^a	Equation of calibration graph ^b	Repress/on coefficient	RSd % concentration
PH	Potentiometric (continuous control)	3–11			
Alkalinity	Spectrophotometric	$\Delta t=5.0\text{--}600\mu\text{g mL}^{-1}\text{ CaCO}_3$	$\Delta t=31.28 \log C+151.5$	0.9952	$\pm 1.5(11.9\mu\text{g mL}^{-1})$
		$\Delta S:10.0\text{--}600\mu\text{m ML}^{-1}\text{ CaCO}_3$	$\Delta S=3.48 \log C+17.3$	0.9965	$\pm 1.7 (11.9\mu\text{g mL}^{-1})$
Concentration	Spectrophotometric	$0.7\text{--}2.8\text{mequiv L}^{-1}\text{ Cl}^{-}$	$AS+3.09 \log C+9.4$	0.9998	$\pm 3.4 (7.04\text{mequiv L}^{-1})$
		$2.8\text{--}27\text{mequiv L}^{-1}\text{ Cl}^{-}$	$\Delta t=34.43 \log C+109.3$	0.9994	$\pm 2.1 (7.04\text{mequiv L}^{-1})$
			$\Delta S=2.53 \log C+7.4$	0.9790	$\pm 3.5 (7.04\text{mequiv L}^{-1})$

^a Δt =peak width/s; ΔS =peak area covered by the base line and the measured height

^b C =analyte concentration

Source: Reproduced with permission from the Royal Society of Chemistry [3]

Table 7.3 Determination of pH, alkalinity and total ionic concentration in natural and potable water by the Canate and conventional methods

Sample	Alkalinity/ $\mu\text{g mL}^{-1}\text{ CaCO}_3$			Total ionic concentration/ mequiv L^{-1}	
	pH	FIA	Conventional ^a	FIA Co	Conventional ^a
Bottled waters-					
Font-bella	7.99	194.79	195.47	4.856	4.760
Cabras	8.58	481.11	453.21	12.373	12.444
Unbottled waters-					
Córdoba (urban)	7.95	134.64	137.62	4.689	4.781

La Rambla (urban)	7.96	400.68	393.81	17.333	17.808
La Rambla (well)	7.51	366.79	366.29	13.145	13.340

^aSee text
Source: Reproduced with permission from the Royal Society of Chemistry [3]

Table 7.4 Determination of pH, alkalinity and total ionic concentration in synthetic samples

Sample position, ppm	pH	Alkalinity/ $\mu\text{g mL}^{-1}$ CaCO_3	Error, %	Total ionic concentration/ mequiv L^{-1}	Error, %
Cl^- , 5; SO_4^{2-} , 5; NO_3^- , 5; HCO_3^- , 10	6.74	15.84	-3.4	0.666	1.9
Cl^- , 25; SO_4^{2-} , 30; NO_3^- , 10; HCO_3^- , 30	7.34	46.59	-5.3	2.519	1.9
Cl^- , 60; SO_4^{2-} , 60; NO_3^- , 20; HCO_3^- , 60	7.65	99.95	1.5	5.363	2.6
Cl^- , 125; SO_4^{2-} , 150; NO_3^- , 40; HCO_3^- , 150	8.24	252.9	2.7	12.010	-1.5
Cl^- , 250; SO_4^{2-} , 250; NO_3^- , 50; HCO_3^- , 175	8.30	301.4	4.9	18.637	-0.7
Cl^- , 350; SO_4^{2-} , 350; NO_3^- , 50; HCO_3^- , 250	8.38	420.3	2.4	26.564	1.63

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measured by measurement of the decrease in absorbance of the indicator solution of 550nm.

7.2 Arsenate

7.2.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.2.2 and 12.6.6.

7.3 Arsenite

7.3.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 7.28.2 and 12.2.2.

7.4 Bicarbonate

7.4.1 Gas permeable membrane

Symanski and Bruckenstein [5,6] have described a simple method for the determination of bicarbonate/carbon dioxide based on a conductionmetric sensor with a gas permeable membrane. Although this method is very sensitive to bicarbonate/carbon dioxide, the detector response to concentration is not linear. Also, acidic or basic gases such as sulphur dioxide or ammonia interferes in the carbon dioxide determination.

7.4.2 Ion chromatography

This technique has been applied to the co-determination of carbonate and bicarbonate in natural and potable waters [7].

7.4.3 Ion exclusion chromatography

Tanaka and Fritz [8] have described a procedure for the determination of bicarbonate and carbon dioxide in water by ion exclusion chromatography using water as the eluent and an electrical conductivity detector. The sensitivity of detection is improved approximately 10 fold by the use of two ion exchange enhancement columns inserted in series between the separating column and the detector. The first enhancement column converts carbonic acid to potassium bicarbonate and the second enhancement column converts the potassium bicarbonate to potassium hydroxide.

The plastic separating column was 7.5×100mm and was packed with a cation-exchange resin in the H⁺ form TSK SCX 5μm (polystyrene divinyl benzene copolymer-based material with a high cation exchange capacity).

The first enhancement column was constructed of plastic (4.6×50mm) and packed with

a cation-exchange resin in the K^+ form (TSK SCX T μ m;

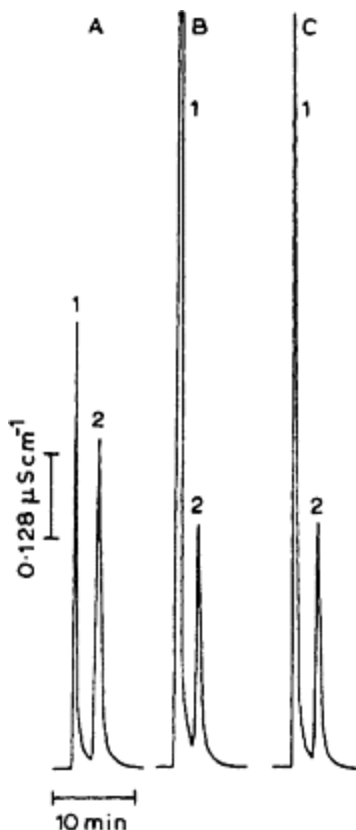


Fig. 7.5 Ion exclusion chromatograms of HCO_3^- in some tap waters: (A) raw tap water of City of Ames, IA, after 10-fold dilution ($0.653mM \times 10$); (B) potable water after softening treatment ($0.466mM$); (C) potable water (La Salle, IL) after 20-fold dilution ($0.470mM \times 10$). Peak 1 is strong acid anions and peak 2 is HCO_3^-

Source: Reproduced with permission from the American Chemical Society [8]

TSK IC-Cation for cation chromatographic use, $10\mu m$ silicon based material with low cation-exchange capacity).

The second enhancement column was constructed of plastic ($4.6 \times 50mm$) and packed with an anion-exchange resin in the OH^+ form TSK SAX ($5\mu m$). The precolumn was constructed of plastic ($7.5 \times 100mm$) and packed with an anion exchange resin in the OH^+ form (TSK SAX, $5\mu m$).

All samples were filtered with a $0.45\mu m$ polytetrafluoroethylene (PTFE) membrane filter before injection into the column.

Tanaka and Fritz [8] applied this procedure to the determination of bicarbonate or

carbon dioxide in some potable water samples. Fig. 7.5 shows the ion exclusion chromatograms obtained before and after a softening treatment. The results indicated that the method is useful in the field of water quality control of water treatment facilities.

Environmental waters such as river, lake and well waters were analysed for carbon dioxide and bicarbonate by the three column ion exclusion method without any difficulty. It may be possible to use the first peak to estimate the total salts of strong acids (such as chloride and sulphate) in water samples. The detection limit for bicarbonate was about $2\mu\text{M}$ and the relative standard deviation about 1%.

Strong acids and salts of strong acids, which are converted to acids by the separation column, pass rapidly through ion exchange columns and do not interfere with the carbon dioxide/bicarbonate peak which elutes later. The effect of weak acids or salts of weak acids was determined by adding various carboxylic acids to samples containing a known amount of sodium bicarbonate. Fig. 7.5 shows chromatograms obtained by the one-column, two-column and three-column ion exclusion methods. No interference was observed from equal molar amounts of formic, acetic or butyric acids. Propionic acid has almost the same retention time as carbonic acids and therefore constitutes an interference. Oxalic, tartaric, citric, lactic, malic and malonic acids elute before carbonic acid and therefore do not interfere.

7.5 Bromate

7.5.1 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.2.1.

7.6 Bromide

In studies of the formation of bromoform produced during the disinfection of water supplies it is necessary to have methods capable of determining bromide at the $\mu\text{g L}^{-1}$ level.

7.6.1 Spectrophotometric method

Moxon and Dixon [9] have described an automated method for the determination of $\mu\text{g L}^{-1}$ amounts of bromide in potable water which is based on the catalytic effect of the bromide ion on the oxidation of iodine to iodate by permanganate and colorimetric measurement of residual iodine in carbon tetrachloride. A Technicon AutoAnalyser 1 is used. The system is kept at $0\pm 0.2^\circ\text{C}$ using an insulated ice bath. An automatic chloride method of similar sensitivity, accuracy and reproducibility is used to estimate chloride interference. The detection limit of the method is $4\mu\text{g L}^{-1}$ and the precision is of the order of 6%.

For most potable waters the effects of interferences except for that of chloride will be

negligible. Some contaminated drinking waters can contain elements such as iron and manganese in amounts which could give substantial interference and these could be diluted to a level where the interference was removed.

Based on the bromine contents, bromide, and bromate give the same response in this technique indicating that bromide and bromate have a similar catalytic activity. Excellent precision data were obtained for this procedure, coefficients of variation ranging from 2.2% at the $100\mu\text{g L}^{-1}$ level to 7.0% at the $5\mu\text{g L}^{-1}$ bromide level. Spiking experiments gave recoveries between 98 and 103%, ie excellent accuracy.

7.6.2 Ion chromatography

Morrow and Minear [10] have developed an ion chromatographic procedure using a concentrator column to improve sensitivity. This analysis, which was carried out on a Dionex model 125 ion chromatograph equipped with concentrator column in place of an injection loop, coupled with an auto-sampler, allowed detection at the $\mu\text{g L}^{-1}$ level. A concentrator column is a short separator column used to strip ions from a measured volume of matrix leading to a lowering of detection limits by several orders of magnitude. The concentrated sample was flushed into the system using 0.003M sodium bicarbonate/0.0024M sodium carbonate eluant.

When using conventional ion chromatographic separation techniques, it is possible that other matrix anions also common to non saline waters may coelute with bromide. For example, bromide and nitrate elute simultaneously using a standard anion separator column (Dionex No. 30065), standard anion suppressor (Dionex No. 30366) and standard eluant (0.003M sodium bicarbonate/0.0024M sodium carbonate).

A representative chromatogram is shown in Fig. 7.6(a).

Separation of bromide from all other matrix anions was shown to be possible using a trace anion separator (Dionex No. 30827), a standard anion suppressor and slightly weakened standard eluent. A chromatogram is presented in Fig. 7.6(b).

Chloride, nitrate and sulphate were the only ions found to be present in any significant quantities in the representative raw waters analysed. To determine whether response for bromide remained the same regardless of the concentration of these anions, recovery tests were performed on bromide standard solutions of $80\mu\text{g L}^{-1}$ spiked with varying concentrations of chloride, nitrate and sulphate, using the concentrator found to have the highest μ -equivalent capacity. In the presence of 100mg L^{-1} chloride, there was 100% recovery of $80\mu\text{g L}^{-1}$ bromide. Chloride was not expected to interfere with the elution of bromide at any concentration since bromide is held preferentially over chloride by the concentrator column. In the presence of 100mg L^{-1} nitrate only 16.2% of the bromide was recovered, indicating the concentrator's preference for the nitrate

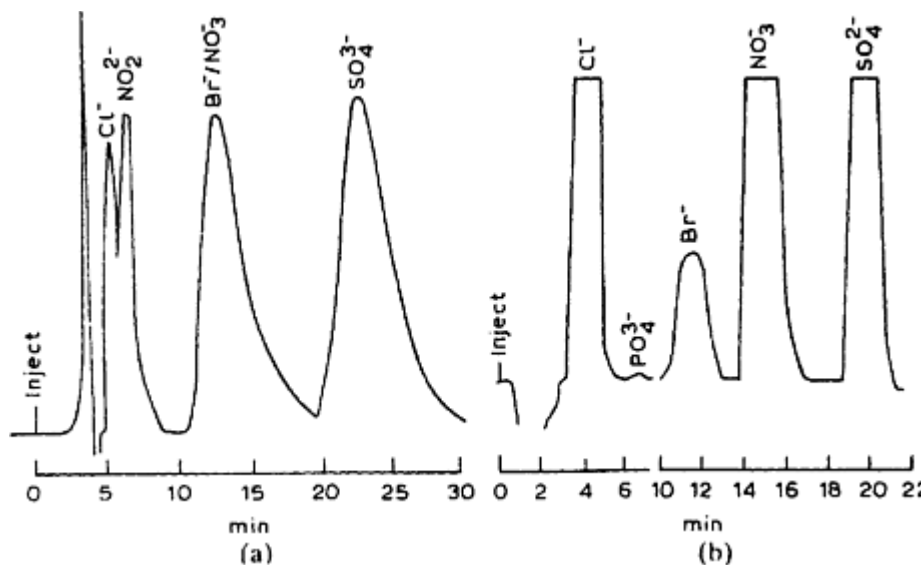


Fig. 7.6 Ion chromatography on anions in potable water, (a) Simultaneous elution of bromide and nitrate using standard eluant; (b) separation of bromide and nitrate using trace anion separator and standard eluant
Source: Reproduced with permission from Elsevier Science [10]

ion. There was no response for $80\mu\text{g L}^{-1}$ bromide in the presence of 1000mg L^{-1} sulphate, indicating 0% recovery.

Nitrate in excess of 17mg L^{-1} interfered with the elution of bromide and sulphate in excess of 25mg L^{-1} interfered with the elution of bromide.

The application of this technique is discussed under multianion analysis in sections 12.6.2 and 12.6.3.

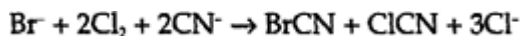
7.6.3 High performance liquid chromatography

Morrow and Minear [10] have described an ion chromatographic method for the determination of bromide in potable water.

The application of this technique is discussed under multianion analysis in section 13.1.2.1.

7.6.4 Gas chromatography

Nota *et al.* [11] have devised a simple and sensitive method for the determination of amounts of bromide down to 0.05mg L^{-1} in water. The procedure is in two stages. Cyanogen bromide is formed by the reaction between bromide, chlorine and cyanide,



Cyanogen bromide is then separated by gas chromatography and selectively detected with an electron capture detector.

It should be noted that the internal standard (nitromethane) must always be introduced after the addition of cyanide in order to prevent rapid darkening of the solutions, which causes non-reproducible results. No interferences are caused by oxidising or reducing substances or by mercury or cadmium at concentrations below 200mg L^{-1} . Mercury and cadmium are, among the metals, the strongest complex-forming agents with bromide.

Even small amounts of aromatic compounds are likely to produce some interferences owing to their tendency to bind bromine, which is formed by reaction with chlorine water.

Grandet *et al.* [12] have described a gas chromatographic method for the determination of μg levels of bromide in potable water.

The application of this technique is discussed under multianion analysis in sections 7.28.3 and 14.1.3.1.

7.7 Chromate and dichromate

7.7.1 Atomic absorption spectrometry

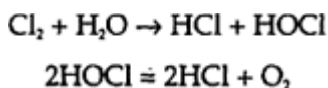
Posta *et al.* [13] have described a high performance flow flame atomic absorption spectrometric method for the determination of tri- and hexavalent chromium in potable water, and the preconcentration of hexavalent chromium.

A high performance liquid chromatographic integrator at the output of the flame atomic absorption spectrometer makes it possible to process simultaneously the signals of both oxidation states of chromium. Detection limits for tri- and hexavalent chromium are, respectively, 0.03 and $0.02\mu\text{g L}^{-1}$.

7.8 Chloride

7.8.1 Titration method

Levy [14] has described a titrimetric procedure for the determination of chloride ions in the presence of free chlorine. Previous workers have attempted to remove free chlorine by boiling the sample. This, however, leads to partial decomposition of hypochlorous acid to hydrochloric acid and oxygen:



Levy [14] overcame this problem by carrying out the reaction at a temperature close to 0°C and sweeping unhydrolysed chlorine out of solution with a purge of nitrogen before commencing the determination of chloride ions.

All solutions, except those to be added from burettes, are kept in an ice-bath

throughout the analysis. Nitrogen via a fine bleed or glass frit is bubbled for 20min through the cooled sample solution, which contains $0.5\text{--}10\text{mmol L}^{-1}$ total chloride, to displace unhydrolysed chlorine. 5ml aliquots are analysed for chloride by the addition of 0.01mol L^{-1} silver nitrate solution until one drop causes no further precipitation of silver chloride. Near the end-point, three drops of nitric acid (5mol L^{-1}) are added to ensure complete precipitation. Centrifugation enables the endpoint to be clearly distinguished. Separate 5ml aliquots are analysed for hypochlorous acid by the addition of 10mg of potassium iodide and titration with 0.01mole L^{-1} sodium thiosulphide solution. One drop of starch solution is added just before the end-point to clarify when it has been reached. The difference between two concentrations thus determined gives the concentration of chloride exclusive of that produced by chlorine hydrolysis.

7.8.2 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 7.28.2, 12.6.1 and 12.6.2.

7.8.3 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.2.1.

7.8.4 Gas chromatography

Bachmann and Matusca [15] have described a gas chromatographic method for the determination of $\mu\text{g L}^{-1}$ quantities of chloride, bromide and iodide in potable water. This method involves reaction of the halide with an acetone solution of 7-oxabicyclo-(4,1,0) heptane in the presence of nitric acid to form halogenated derivatives of cyclohexanol and cyclohexanol nitrate.

The column effluent passes through a pyrolysis chamber at 800°C and then through a conductivity detector. The solution is injected on to a gas chromatographic column (OV-10-Chromosorb W-HPL, 80–100 mesh, 150cm, 0.2cm dia.) operated at 50°C . Hydrogen is used as carrier gas. Chloride contents determined by this method were $5.0\pm 1.8\mu\text{g L}^{-1}$ chloride in potable water, $20.0\pm 1.5\mu\text{g L}^{-1}$ in drinking water. A typical gas chromatogram is shown in Fig. 7.7 showing peaks for the three halogens.

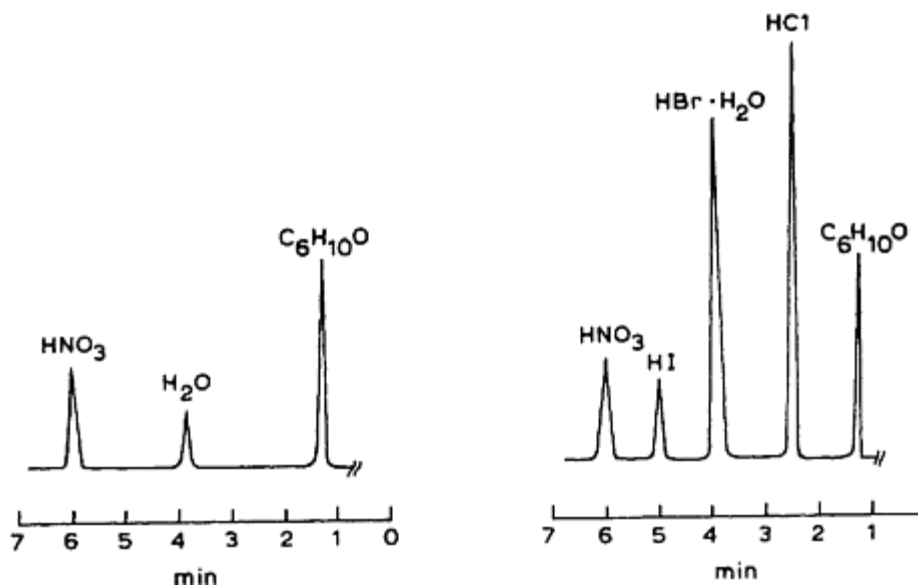


Fig. 7.7 Gas chromatogram of halogen mixture

Source: Reproduced with permission from Springer Verlag [15]

7.9 Chlorate

7.9.1 Titration method

The application of this technique is discussed under multianion analysis in section 14.3.1.1.

7.9.2 Flow injection analysis

Dietrich *et al.* [17] applied flow injection analysis and ion chromatography to the determination of chlorate and chlorite in potable water.

7.9.3 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.6.7.

7.9.4. High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.2.1.

7.10 Chlorite

7.10.1 Titration method

The application of this technique is discussed under multianion analysis in section 14.3.1.1.

7.10.2 Flow injection analysis

Deitrich *et al.* [17] applied flow injection analysis and ion chromatography to the determination of chlorite and chlorate in potable water.

7.10.3 Ion chromatography

Haufman and Bolyand [18] determined chlorite (ClO_2^-) in potable waters by ion chromatography.

7.11 Chlorolignosulphonate

7.11.1 Pyrolysis-gas chromatography

Van Loon *et al.* [19] have described a method of quantitative determination of macromolecular chlorolignosulphonates in potable water, river water and sulphite pulp mill effluents. The method is based on pyrolysis-gas chromatography-mass spectrometry. Down to $16\text{--}32\mu\text{g L}^{-1}$ chlorolignosulphonates can be determined, $18\text{--}310\mu\text{g L}^{-1}$ having been found in river water and $60\mu\text{g L}^{-1}$ in potable water.

7.12 Cyanide

7.12.1 Ion chromatography

The application of this technique to the determination of free cyanide is discussed under multianion analysis in sections 12.6.4 and 12.6.5.

7.13 Fluoride

7.13.1 Spectrophotometric method

Anosova [20] determined fluoride in highly demineralised water by separating fluoride ion as hydrofluoric acid by steam distillation of the sample (concentrated by evaporation and treated with silver nitrate solution to precipitate chloride ion) from sulphuric acid

medium. The distillate is treated with Alizarin Red S (C.I. Mordant Red 3) solution, buffered at pH 2.5–3.5, and then allowed to react with a known volume of standard thorium nitrate solution. After 30min, the colour is compared with those of a series of standards covering the range 0.0–0.1mg L⁻¹ fluoride.

One method is based on the bleaching effect of fluoride on the colour of the zirconium erichrome organic R complex [21]. This method is applicable over the range 2–25µg fluoride. Sulphate does not interfere in the determination. Lanthanum-alizarin complexan has been used to determine fluoride [22]. The main interfering ions are removed from the sample with a strongly acidic cation exchanger. The reagent (a buffered pH 4.3 mixture of 3-amino-methylalizarin-NN-diacetic acid and lanthanum nitrate with added acetone) is added, and the red chelate is allowed to develop in the dark for about 20min and the extinction determined against a reagent blank at 620nm. If very high sulphate and chloride concentrations are present in the sample, the results must be corrected by reference to a calibration graph. Water samples containing aluminium (greater than 0.1mg L⁻¹) must be adjusted to pH 9 with potassium hydroxide solution before analysis, to ensure quantitative ion exchange.

Wierzbicki and Pawlita observed that free chlorine [23] and ozone [24] interfere in the determination of fluoride by the zirconium-Alizarin Red-S-spectrophotometric method. Chlorine partially decolorises the lake formed; this is prevented by the addition of sodium thiosulphate in an equivalent amount to the concentration of free chlorine present. Ozone interferes at concentrations as low as 0.1mg L⁻¹ and its effect can also be overcome by the addition of a slight excess of sodium thiosulphate.

Mehra and Lambert [25] used a solid ion association reagent comprising Buffalo Black and Brilliant Green dyes supported on activated alumina. When this solid is added to the sample, Brilliant Green reacts with fluoride releasing an equivalent amount of Buffalo Black for spectrophotometric determination at 618nm. The test solution is passed through a column of the reagent and any Brilliant Green released is selectively decomposed by adding solid sodium bisulphite to the percolate before measurement of the extinction. The calibration graph is rectilinear for up to 10mg L⁻¹ fluoride and the detection limit is 1µg. Interfering ions, especially sulphate and bicarbonate must first be removed by adsorption on Amberlite IRA 400 (NO₃⁻ form) and preferential elution of fluoride with 0.1M sodium nitrate; this treatment also serves to concentrate fluoride.

Lei *et al.* [26] determined fluoride in potable water by adding a lanthanum-alizarin complex to the sample. The ternary fluorolanthanum-alizarin complex formed is extracted into isoamyl alcohol containing *N,N*-diethylaniline and is mixed with carbon disulphide and acetone to form a solution with a refractive index of 1.57 and the complex is determined with a total-reflection long capillary cell colorimeter. The detection limit for fluoride was 10ng L⁻¹ and recoveries were in the range 93–104%.

Cherian and Gupta [27] have described a method for determining fluoride which involves decomposition of the coloured thoriumchromotrope 2R complex to form the more stable fluoride-thorium complex which is measured spectrophotometrically at 570µm.

Capitan-Vallvey *et al.* [28] reacted fluoride with zirconium and xylenol orange to produce a charged complex which was preconcentrated in an ion exchange resin (Duvex 1-X8). Absorbance was measured directly at 580 and 750µm. The detection limit was

1 $\mu\text{g L}^{-1}$ fluoride in a 500ml sample.

7.13.2 Flow injection analysis

Flow-injection potentiometry using a combination fluoride-selective electrode was used to determine fluoride in potable water [29]. Sample throughput was 30–40 samples/h, based on triplicate injections at a rate of 120 samples/h. Recoveries after spiking potable water with fluoride concentrations ranging from 0.01 to 1mg L⁻¹ were in the range of 91–106%.

7.13.3 Atomic absorption spectrometry

A method for determining fluoride in potable water and seawater, based on the formation of aluminium fluoride in an electrothermal graphite furnace, followed by molecular absorption at 227.56nm was developed by Gomez Gomez *et al.* [30]. The detection limit was 8ng mL⁻¹ and the peak-height precision at 0.2 μg of fluoride mL⁻¹ was 5%.

7.13.4 Ion selective electrodes

Various workers have discussed the applications of ion selective electrodes to the determination of fluoride in potable water [16,31,32]. Reported detection limits are in the range 0.1 to 1mg L⁻¹. Nicolson and Duff [16] have carried out a detailed study of an optimum buffer system for use with a fluoride selective electrode. They examined 11 buffer systems to determine maximum complexing ability, with optimal reproducibility and sensitivity, in the determination of fluoride in water by the direct potentiometric electrode method. A buffer system containing triammonium citrate was found to have the best masking ability as well as satisfying the other criteria. Only aluminium and magnesium posed interference problems. It is recommended that a minimum decomplexing time of 20min (and preferably 24h) be allowed and fresh buffer solutions be prepared after a maximum storage period of 2 weeks.

The composition of TISAB 111 M buffer is as follows: 58g sodium chloride, 57ml glacial acetic acid, 4g EDTA, 2.43g tri-ammonium citrate.

Table 7.5 Interference limits (mg L⁻¹) of several species

Buffer	Ion	0.1mg L ⁻¹ F ⁻ Recovery limit		1.0mg L ⁻¹ F ⁻ Recovery limit	
		100%	95%	100%	95%
TISAB III M	Al	>500	>500	35	100
tri-ammonium citrate	BO ₂	>100	>100	>100	>100
	BO ₃	>100	>100	>100	>100
	Ca	>1000	>1000	>1000	>1000
	H ₂ BO ₃	>500	>500	>500	>500

Hg	>500	>500	100	1000
PO ₄	>500	>500	>500	>500

Source: Reproduced with permission from Marcel Dekker Inc [16]

The method employed in the determination of fluoride was that of direct potentiometry using a calibration curve constructed from standard solutions. Subsequent aliquots of the same standard or sample solution were analysed until two EMF readings within 0.5mV were obtained. A fresh calibration curve was constructed for each batch of buffer and each temperature of analysis.

After insertion of the electrode into the solution, the system was allowed to achieve equilibrium for 5min when the EMF readings was taken to the nearest 0.1mV. Further EMF readings were taken at 1min intervals until consecutive EMF readings did not differ by more than 0.5mV. This is considered to be the equilibrium EMF.

Table 7.5 shows interference limits for various ions in the determination of fluoride using the tri-ammonium citrate (TISAB III) buffer. Only aluminium, magnesium and borate give cause for concern.

Of all the buffer masking agent combinations examined, triammonium citrate buffer, employing CDTA and tri-ammonium citrate as complexing agents, was most efficient in terms of masking ability. At 1mg L⁻¹ fluoride, aluminium and magnesium up to 100mg L⁻¹ and 1000mg L⁻¹ respectively were tolerated for 95% fluoride recovery. This is greatly superior to TISAB II which, at the same fluoride concentration and recovery level, tolerated only 2.7mg L⁻¹ aluminium, 400mg L⁻¹ magnesium, and, additionally, 1000mg L⁻¹ calcium which is not a problem with the tri-ammonium citrate buffer.

The best temperature of analysis (20±0.1°C or 50±0.1°C) for maximum decomplexing was dependent upon the species involved and the buffer employed. This prevents the development of any simple method which would exploit the optimum decomplexing conditions for each individual species. However, while the maximum possible decomplexing may not be achieved in all cases, samples analysed at 20°C, 24h following buffer addition, will, for each species and each buffer, at 1mg L⁻¹ fluoride be beneficial in terms of an increased fluoride recovery over that obtained at 20°C soon after buffer addition.

Classic ion selection electrode methods for fluoride suffer from the disadvantages of excessive electrode drift, long response time and inadequate precision.

Ballcizo [33] carried out direct potentiometric determinations of fluoride in potable water. This was carried out with the aid of tiron (pyrocatechol 3,5-disodium disulphonate) as a decomplexing agent. This substance releases fluoride from a wide range of complex fluoride ions (eg aluminium, iron, titanyl, magnesium, silica and boric acid) and thus permits the determination of total fluoride content, even in the presence of appreciable amounts of aluminium. As the fluoride electrode is also highly sensitive to hydroxyl ions the pH value must be kept at or slightly below neutral, but not so low as to allow the formation of hydrochloric acid. The buffering action of tiron is also sufficient to enable the use of any additional buffers such as those for ionic strength adjustment, to be dispensed with.

Kissa [34] has described modifications to the determination of fluoride using the fluoride ion selective electrode, to enable the determination of concentration in the range $1\text{--}10\text{mg L}^{-1}$ fluoride with relative errors from 0.2 to 0.6%.

Kissa [34] overcame the aforementioned problems by

- (a) limiting the fluoride concentration to which the electrode is exposed to a $0.01\text{--}0.1\text{mg L}^{-1}$ fluoride or $0.05\text{--}1\text{mg L}^{-1}$ fluoride concentration range;
- (b) measuring the electrode potential in the analyte by approaching equilibrium in the same direction from a higher potential to a lower potential and
- (c) keeping the temperature of the solutions constant within $\pm 0.2^\circ\text{C}$. The fluoride concentration in the analyte is adjusted to the concentration range of the ion selective electrode by dilution or fluoride addition.

7.13.4.1 Determination of fluoride by the analyte addition method

Experimental details are as follows.

The fluoride ion selective electrode, Orion Model 94-09A, was used in combination with a double junction electrode, Orion Model 90-01. The cell potentials were measured with the Orion Ionalyzer, model 901. The Orion electrode holder (Catalog No. 13-641-814) was provided with a stop to keep the immersion depth of the electrodes constant. Two sets of electrodes were used, one set being exposed only to solutions containing $10\text{--}100\mu\text{g L}^{-1}$ fluoride and the other to solutions containing $50\text{--}100\mu\text{g L}^{-1}$ fluoride. All volumetric flasks and beakers used were made of 'nalgene'. Agitation was provided by a thermally insulated magnetic stirrer operating at a constant speed.

The standardising solutions were prepared by successive dilutions of a stock solution containing 11.10g L^{-1} of reagent-grade sodium fluoride (dried to a constant weight at 125°C). The standardising solutions and analytes contained an acetic acid-sodium acetate buffer (2 vol%) prepared by adding 2800ml of water, 480ml of acetic acid, reagent grade, and 500ml of 30% sodium hydroxide solution, made of ACS certified, electrolytic sodium hydroxide pellets, diluting to 3800ml with water and adjusting to pH 5.0-5.2 with sodium hydroxide.

TISAB II (without CDTA) or TISAB III were used for electrolyte containing analytes.

The equilibration time needed to attain a stable electrode potential decreases with increasing fluoride concentration and stirring rate and increases with the increasing concentration change resulting from successive immersions. If the concentration difference is small, the equilibrium time can be reasonably short even at low fluoride concentrations. Kissa [34] restricted therefore, the exposure of the fluoride ion selective electrode to solutions differing less than 10 or 20 times in fluoride concentration. By limiting the fluoride concentration range and using a programmed immersion sequence, the equilibration time in the analyte was reduced to 3-7min even at fluoride concentrations as low as $20\mu\text{g L}^{-1}$. This is the lower practical limit for determining fluoride conveniently, because the electrode response is no longer linear below this concentration.

If the millivolt reading indicates that the fluoride concentration in the analyte exceeds the concentration range of the fluoride ion selective electrode ($20\text{--}100$ or $100\text{--}1000\mu\text{g L}^{-1}$ fluoride) the electrode is withdrawn immediately from the analyte and the fluoride

concentration of the analyte adjusted by appropriate dilutions or additions. The concentration restriction applies also to rinsing of electrodes and their storage. The electrodes are stored in a buffer containing fluoride at a concentration corresponding to the lower limit of the fluoride concentrations measured.

Between immersions, the electrode stems are wiped and the electrode tips gently blotted with tissue paper to remove adhering liquid drops. The electrodes are not rinsed with water or a buffer solution. The electrodes are first immersed in 40ml of the solution to be measured (analyte or reference solution) which is agitated for 1min and discarded. A fresh 40ml portion of the solution is then used for electropotential measurement.

The precision of the electrode potential measurement by this procedure depends mainly on temperature constancy. The standard deviation of

Table 7.6 Sequential programme of fluoride determination

	<i>External standard method</i>		<i>Analyte addition method</i>	
	<i>Electrode A</i>	<i>Electrode B</i>	<i>Electrode A</i>	<i>Electrode B</i>
F ⁻ concn (mg of F-L ⁻¹) of standardising solution used for electrode storage	0.02	0.10	0.02	0.10
Sequential programme for F ⁻ concentration determination				
(I) Conditioning concn, mg of F-L ⁻¹ time, min	0.01	0.05	0.01	0.05
	3	3	3	3
(II) Reference solution concn, mg of F-L ⁻¹ time, min	0.02	0.10	0.025	0.10
	1+10	1+10	1+10	1+10
(III) Analyte time, min	1+10 ^a	1+10 ^a	record mV 1 0m in after adding analyte	record mV 10min after adding analyte
Concentration range of F ⁻ determined				
Lower limit, mg of F-L ⁻¹	0.02 ^b	0.10 ^b	0.025	0.10
Higher limit, mg of F-L ⁻¹	0.10 ^c	1.0 ^c	depends on analyte volume added	

^a1min in 40ml of solution, discard solution, 10min in another 40ml of solution, record mV reading

^bIf F⁻ concentration of the analyte is below this limit, add NaFi solution to increase F⁻ concentration

^cIf F^- concentration is above this limit, dilute analyte with diluted buffer (20ml L^{-1})
 Source: Reproduced with permission from the American Chemical Society [34]

temperature and the electrode potentials in a buffered solution containing $20\mu g L^{-1}$ fluoride were $0.16^\circ C$ and $0.18mV$ and $0.05^\circ C$ and $0.08mV$ respectively. If the temperature is kept within $\pm 0.2^\circ C$, the electrode can be operated for weeks without calibration drift.

It has been observed by previous workers [35] that the electrode response drifted while the fluoride solution was stirred, but, when stirring was stopped, the electrode assumed a stable potential within 5–30min, depending on the fluoride concentration. Kissa [34] examined this procedure and concluded that the apparently stable potential resulted from a reduced transport of fluoride ions to the electrode and did not always represent an equilibrium potential in the bulk of the solution. Under the conditions outlined in this modified method, a stable electrode potential can be obtained in a short time in stirred solutions as dilute as $20\mu g L^{-1}$ fluoride.

The modified test conditions proposed by Kissa [34] are outlined in Table 7.6.

7.13.5 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 7.28.2 and 12.6.1.

7.13.6 Miscellaneous

Crosby *et al.* [36] examined five spectrophotometric methods, titration with standard thorium nitrate, and an ion selective electrode method, for the determination of fluoride in potable water. The methods were examined for reproducibility, sensitivity, range, specificity, and, in the case of the spectrophotometric methods, for colour stability and temperature effects. Of the spectrophotometric methods, the alizarin complexan procedure is particularly suitable for samples containing only small amounts of fluoride. The electrode method surpasses all the colorimetric methods for speed, accuracy and convenience.

7.14 Hypochlorite

7.14.1 Titration method

The application of this technique is discussed under multianion analysis in section 14.3.1.1.

7.15 Iodate

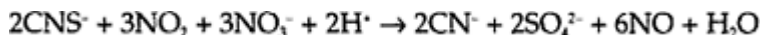
7.15.1 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.2.1.

7.16 Iodide

7.16.1 Spectrophotometric method

Manual [37] and automated [38] spectrometric methods have been described for the determination of iodide in potable water. Moxon [38] describes an automated procedure capable of determining iodide ion in potable water in amounts down to $0.4\mu\text{g L}^{-1}$ and total inorganic iodine (including iodate) in amounts down to $0.2\mu\text{g L}^{-1}$. The methods are based on the catalytic effect of iodide on the destruction of the thiocyanate ion by the nitrite ion:



The methods are applicable to normal drinking waters, with possible interfering ions having negligible effects. The system is easy to use and can handle 20 samples per h.

When series of drinking waters were run by this method, the peaks were found to be irregular and erratic. It was found that there was a relationship between the hardness of the waters and the peak irregularity, and this was removed when the alkaline earth metals were precipitated out with potassium carbonate. Subsequently, samples and standards were made up in 0.3% potassium carbonate solution. This addition of alkali prolonged the stability of the standard solutions from 6h to 8d, but led to a decrease in the sensitivity of the method. Chloride at a level of 400mg L^{-1} gave a 20% increase in the response to a $4\mu\text{g L}^{-1}$ of iodide standard solution. To overcome this interference, a large excess of chloride in the form of sodium chloride solution was introduced into the sample stream and it was found that, as well as removing the interference effect of chloride, the sensitivity of the method was greatly increased.

A considerable proportion of the total inorganic iodide present in water can consist of iodate. System A, illustrated in Fig. 7.8, recovered iodate quantitatively and gave measure of the total inorganic iodine in solution. In order to determine free iodide only, the oxidation-reduction potential of the reaction mixture was adjusted so that iodate was not reduced to iodine or iodide. This was achieved by:

(a) reducing the concentration of nitric acid in the ammonium iron(III) sulphate reagent;

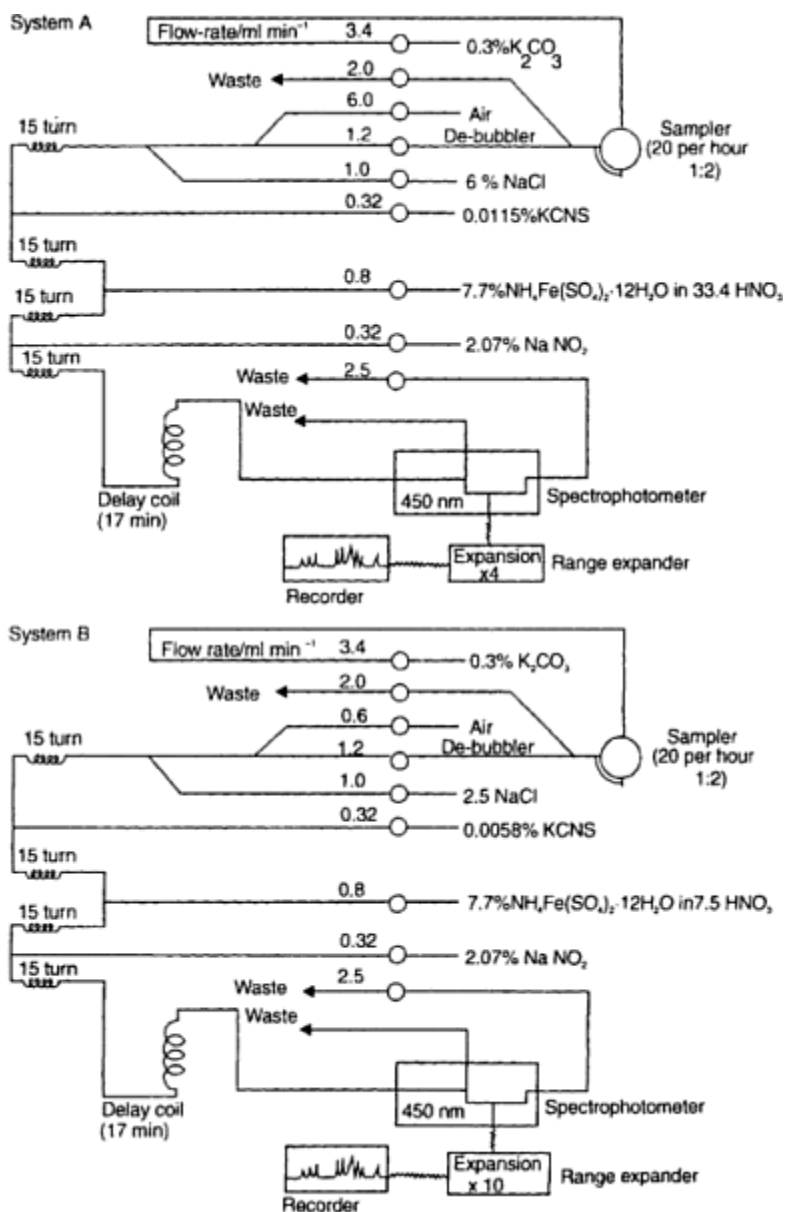


Fig. 7.8 Flow diagrams for the determination of total inorganic iodine in waters (system A) and free iodide in waters (system B)

Source: Reproduced with permission from the Royal Society of Chemistry [38]

Table 7.7 Amounts of free iodide and total inorganic iodine in a range of United Kingdom potable waters

<i>Sample source</i>	<i>Total iodine/$\mu\text{g L}^{-1}$</i>	<i>Free iodide/$\mu\text{g L}^{-1}$</i>
London (borehole)	28.0	28.0
Harrogate	2.2	0.9
File	7.8	7.8
Bristol	4.1	2.1
Nottingham	14	3.5
Amesbury	4.3	0.9
Oxford	4.3	1.3
Gloucester	3.2	3.2
Dunoon	1.1	0.9
Nuneaton	2.8	1.6

Source: Reproduced with permission from the Royal Society of Chemistry [38]

- (b) reducing the concentration of the sodium chloride reagent; and
- (c) reducing the concentration of the potassium thiocyanate reagent.

These changes caused a corresponding decrease in sensitivity. The manifold system shown in Fig. 7.8 has two different sets of reagents. Set A was used for the determination of total inorganic iodine in water over the range $0.2\text{--}5.0\mu\text{g L}^{-1}$ of iodide and set B was used for the determination of free iodide in water over the range $0.4\text{--}5.0\mu\text{g L}^{-1}$ of iodide. A comparison of the concentration of free iodide and total inorganic iodine in a range of potable waters determined by the methods described below is shown in Table 7.7.

The results in Table 7.8 show that it is necessary to adopt a standardised sampling procedure. Samples were made up in 0.3% potassium carbonate solution in polypropylene calibrated flasks, centrifuged and then stored in polystyrene bottles (30ml universal containers, Sterilin Ltd., Teddington, Middlesex). Fresh potable water was treated in the same way, but allowed to stand for 3 days before analysis.

Reagents for the determination of total inorganic iodine (System A)

All chemicals used should be of analytical-reagent grade and glass distilled water should be used in preference to deionised water.

Standard iodide solution— 4g L^{-1} . Dissolve 0.5232g of potassium iodide, previously dried in an oven at 105°C for 2h, in distilled water and dilute to 100ml in a calibrated flask.

Standard iodide solution— 40mg L^{-1} . Dilute 10ml of the standard iodide solution (4g L^{-1} of iodide) to 1000ml with distilled water in a calibrated flask (stable for 1 month).

Table 7.8 Changes in the iodine concentration of standards, blanks and drinking water solutions made up in 0.3% potassium carbonate in different containers over a period of days

<i>Test solution</i>	<i>Container</i>	<i>Iodine concentration $\mu\text{g L}^{-1}$</i>			
		<i>After 1h</i>	<i>After 1 day</i>	<i>After 3 days</i>	<i>After 8 days</i>
4 $\mu\text{g L}^{-1}$ solution	Glass calibrated flask	3.9	4.0	4.0	4.2
	Polyethylene bottle	3.9	3.9	4.0	4.0
	Polystyrene bottle	3.9	3.9	3.9	3.9
Blank solution	Glass calibrated flask	0.0	0.2	0.4	0.5
	Polyethylene bottle	0.0	0.1	0.2	0.3
	Polystyrene bottle	0.0	0.0	0.0	0.0
Laboratory drinking water straight from tap	Glass calibrated flask	4.7	5.5	5.7	5.8
	Polyethylene bottle	4.5	5.5	5.8	5.6
	Polystyrene bottle	4.5	5.4	5.7	5.7
Cambridge drinking water	Glass calibrated flask	5.4	—	5.8	6.1
	Polystyrene bottle	5.4	—	5.5	5.4
Hertford drinking water	Glass calibrated flask	4.4	—	5.0	5.0
	Polystyrene bottle	4.5	—	4.6	4.5
Oxford drinking water	Glass calibrated flask	5.6	—	6.0	6.0
	Polystyrene bottle	5.7	—	5.9	5.8

Source: Reproduced with permission from the Royal Society of Chemistry [38]

Standard iodide solution—200 $\mu\text{g L}^{-1}$ of iodide. Dilute 5ml of the standard iodide solution (40mg L^{-1} of I) to 1000ml with distilled water in a calibrated flask. Store in a polythene or polystyrene bottle (stable for 1 month).

Working solutions—into 200-calibrated flasks pipette 5, 4, 3, 2, 1 and 0ml of standard iodide solution (200 $\mu\text{g L}^{-1}$ of I). Add 2ml of 30% m/V potassium carbonate solution and dilute to 200ml with distilled water. These are the working standards. Store in polystyrene bottles and prepare freshly every 2 weeks.

Potassium carbonate solution—30% w/v. Dissolve 300g of potassium carbonate in distilled water and make up to 1L.

Potassium thiocyanate solution—0.0115% w/v. Dissolve 0.115g of potassium thiocyanate in distilled water and make up to 1L.

Sodium nitrite solution. Dissolve 4.14g of sodium nitrite in distilled water and dilute to 200ml (stable for 1 day only).

Sodium chloride solution—6% w/v. Dissolve 60g of sodium chloride in distilled water and dilute to 1L.

Ammonium iron(III) sulphate reagent. Dissolve 77g of ammonium iron(III) sulphate ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in approximately 300ml of distilled water. Add 334ml of concentrated nitric acid. (sp. gr. 1.42) and make up to 1L. Heat on a hot plate until all traces of solid dissolve.

Reagents for the determination of free iodide (System B).

Standard iodide solutions. These are exactly the same as those described for system A.

Potassium carbonate solution—30% w/v. Dissolve 300g of potassium carbonate in water and dilute to 1L.

Sodium nitrite solution—2.07% w/v. Dissolve 4.14g of sodium nitrite in distilled water and dilute to 200ml (stable for 1 day only).

Sodium chloride solution—2.5% w/v. Dissolve 25g of sodium chloride in distilled water and dilute to 1L.

Potassium thiocyanate solution—0.0058% w/v. Dissolve 0.058g of potassium thiocyanate in distilled water and dilute to 1L.

Ammonium iron(III) sulphate reagent. Dissolve 77g of ammonium iron(III) sulphate ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in approximately 400ml of distilled water. Add 75ml of concentrated nitric acid (sp. gr. 1.42) and make up to 1L. Warm until all traces of solid dissolve.

Sodium oxalate reagent. Dissolve 5g of sodium oxalate in 100ml of 5 vol. % sulphuric acid (this reagent is toxic).

Apparatus

Centrifuge speed of 50Hz, glass or polypropylene centrifuge tubes of 150ml capacity, Polystyrene bottles of 30–50ml capacity. AutoAnalyzer system for colorimetric analysis, eg the Technicon. AutoAnalyzer 1 system with a range expansion facility that was operated and maintained in accordance with the instructions given in the Operator Instruction Manual.

Procedure

Wash all glassware and polystyrene containers with concentrated nitric acid and rinse copiously with distilled water before use. Dispense 1.0ml of 30% w/v potassium carbonate solution into a 100ml calibrated flask. Make up to 100ml with a water sample and shake well. Centrifuge the resulting solution for 5min at 50Hz. Decant about half of the solution into polystyrene bottles. Allow fresh tap water to stabilise for 3 days before analysis.

Set up the manifold system shown in the flow diagram (Fig. 7.8) and use the appropriate set of reagents for either total inorganic iodine determination (A) or free

iodide determination (B). Load the sample tray with a set of working standards followed by 20 samples interspersed with a working standard every fifth sample. Complete the series with another set of working standards and run at a rate of 20 per h.

If deposits of iron(III) thiocyanate occur, these may be removed by running two sample cups of sodium oxalate reagent through the system at the end of a run.

Calculation

Plot a calibration graph of the mean standard peak heights against their respective iodine concentrations. The iodine concentration of a sample is obtained by comparing its peak height with the calibration graph. Multiply the result by 1.01 to compensate for the addition of potassium carbonate.

The effects of ions commonly occurring in drinking waters that could cause possible interference were tested and the results, representing a mean of three determinations, are shown in Table 7.9. The results show that interferences do not present any major problems in the analysis of drinking waters for either total inorganic iodide or free iodide.

Table 7.10 shows a comparison of total iodine determinations obtained by the above automated method of Moxon [38] and an automated method which is based on the method of Dubravcic (cerium(IV) sulphate-arsenious acid) modified for an AutoAnalyzer system. The mean recovery of iodide by the total inorganic iodine method are $100 \pm 5.4\%$ and $102 \pm 7.5\%$ respectively. The results show reasonable agreement with those of the automated method.

7.16.2 Polarography

The application of this technique is discussed under multianion analysis in section 14.10.2.1.

7.16.3 High performance liquid chromatography

Savov *et al.* [39] determined iodide, chloride, bromide, chlorate, bromate and iodate in potable water by high performance liquid chromatography with an inductively coupled argon plasma mass spectrometric detector.

The application of this technique is discussed under multianion analysis in section 13.1.2.1.

7.16.4 Gas chromatography

Bachmann and Matusca [15] have described a gas chromatographic method involving the formation of halogenated derivatives of cyclohexanol for the determination of iodide, chloride and bromide in potable water.

Table 7.9 Effect of added ions on the determination of (A) total inorganic iodine concentration and (B) free iodide concentration in a $4\mu\text{g L}^{-1}$ standard iodide solution

<i>Element added</i>	<i>Concn mg L⁻¹</i>	<i>Maximum concn. in drinking waters mg L⁻¹</i>	<i>(A) Total 1 found µg L⁻¹</i>	<i>(B) Free 1 found µg L⁻¹</i>
Zn ²⁺	1	0.69	4.0	3.9
Cu ²⁺	1	0.36	4.0	3.8
Li ²⁺	1	0.01	4.1	3.8
Pb ²⁺	0.1	0.046	4.0	3.9
Fe ³⁺	2	1.5	4.0	3.8
Mn ³⁺	1	0.06	3.9	3.9
Ni ²⁺	0.2	0.013	4.0	4.2
Hg ²⁺	0.005	0.001	3.9	4.2
Co ²⁺	0.2	0.011	4.0	4.2
Mg ²⁺	30	23	4.1	4.0
Cl ⁻	400	245	4.0	4.0
Br ⁻	1	—	4.0	4.1
F ⁻	1	—	4.1	4.3
IO ₃ ⁻	0.004	—	8.0	4.0
SO ₄ ²⁻	200	—	4.1	4.5
Humic acid	20	—	3.9	0.0
Iodoform	1	—	5.6	5.6
Methyl iodide	0.1	—	4.2	4.2

Source: Reproduced with permission from the Royal Society of Chemistry [38]

Table 7.10 Comparison of the proposed method for total inorganic iodine with automated spectrophotometric cerium(IV) sulphate-arsenious and method for a range of waters

<i>Sample source</i>	<i>Iodine concentration µg L⁻¹</i>	
	<i>Moxon method [38]</i>	<i>Keller's et al. [40] method</i>
Slough	11.5	12.7
Oakington	5.5	6.0
Catterick	0.7	0.7
Hexham	2.3	2.9
Royston	4.5	5.2
Harrogate	2.2	1.7

Braintree	13.7	13.9
Benson	5.8	6.5
London (borehole)	28.0	30.0
File	7.8	5.8
Nottingham	14.0	15.4
Dunoon	1.1	1.1
London (tap)	5.8	5.9

Source: Reproduced with permission from the Royal Society of Chemistry [38]

Grandet *et al.* [12] have described a gas chromatographic method for the determination of μg levels of iodide in potable water.

The application of this technique is discussed under multianion analysis in section 7.28.3.

7.17 Molybdate

7.17.1 Preconcentration

The preconcentration of molybdate is discussed in section 15.2.1.

7.18 Nitrate

Groundwaters provide almost 40% of the domestic water supply in England and Wales and the concentration of nitrate present has an important bearing on potability. The current WHO standard for European drinking water [41] recommends that levels of nitrate should not exceed 11.3mg L^{-1} of nitrate-nitrogen (50mg L^{-1} of nitrate). High levels of nitrate can give rise to harmful physiological effects, such as methaemoglobinaemia, particularly in infants, and at present there is concern over evidence that suggests that nitrate concentrations in some major aquifers are increasing to an undesirably high level. Analytical methods for nitrate therefore need to be accurate so that threshold values can be determined with confidence, and precise so that small trends in concentration can be detected quickly.

7.18.1 Spectrophotometric methods

Spectrophotometric methods employing brucine [42] and Devarda's alloy reduction to ammonia followed by Nesslerisation [43] and the use of dihydroxycoumarin [44] have all been employed for the determination of nitrate in water. Apart possibly, from the dihydroxycoumarin [44] method, which employs an ethyl acetate extraction step, none of these methods is sufficiently sensitive for the determination of nitrate in potable water.

More recent spectroscopic methods for measurement of nitrate are based on measurements in the ultraviolet region.

Spectrophotometric methods based on the use of resorcinol [45] and 2, 4-xylenol [46] have been described for the determination of nitrate in mineral waters and ground waters.

Miles and Espejoi [46] compared results for nitrate in ground waters of low salinity obtained by the 2, 4-xylenol Spectrophotometric method and by ultraviolet spectroscopy. The ultraviolet procedure is not subject to interference from the major cations present in typical ground waters, and interference by high levels of nitrite can be overcome by addition of sulphamic acid. There was good agreement between nitrate levels determined by both methods on a number of ground water samples.

The samples are filtered through 0.45µm membrane filters on collection and acidified by addition of 2ml of 50 vol% Arister sulphuric acid per L of sample.

Ultraviolet spectrophotometric procedure

Dilute the samples as necessary to bring their concentrations of nitrate into the range 0–1.00mg L⁻¹ of nitrate-nitrogen and add sufficient 1% sulphamic acid solution to give a final sulphamic acid concentration of 0.1% w/v if the concentration of nitrite in the final solution is likely to exceed 20µg L⁻¹ of nitrite-nitrogen. Measure absorbances at 200nm in 1.0cm cells.

2, 4-xylenol method

To 10ml of sample, or an aliquot containing not more than 300µg of nitrate-nitrogen, in a 100ml conical flask, 2ml of 2% mercury(II) sulphate and 0.5ml of 1% sulphamic acid solutions are added; and the flask allowed to stand for 5min, then 1ml of 1% 2, 4-xylenol is added to the solution and mixed. 24.5ml of 85 vol% sulphuric acid is added, while cooling the flask in running water. The flask is placed in a water bath at 30°C for 30min, then the contents are transferred to a 125ml separating funnel and rinsed in the flask and the funnel shaken with two successive 25ml volumes of water. 10ml of toluene phases are left for 3min. The phases are left to separate and the aqueous layer run to waste. 10ml of sodium hydroxide (40g L⁻¹) is added to the toluene extract, measured and shaken for 1min to separate. The sodium hydroxide layer is run into a 1.0cm cell and the absorbance measured at 445nm. A set of standards in the range 1–20mg L⁻¹ of nitrate-nitrogen are run in parallel.

Nitrate, which absorbs in a similar part of the ultraviolet region, is a potential source of interference in this method. A solution containing 1mg L⁻¹ of nitrite-nitrogen was scanned between 190 and 260nm and the spectrum is shown in Fig. 7.9 together with that of a 1mg L⁻¹ solution of nitrate-nitrogen for comparison. The nitrite absorption maximum is at about 211nm and it absorbs less strongly than nitrate at a similar concentration. Solutions containing 0.5mg L⁻¹ of nitrate-nitrogen and up to 100µg L⁻¹ of nitrite-nitrogen were prepared and the interference from nitrite is significant only at concentrations above 20µg L⁻¹. Interference by higher concentrations of nitrite can be removed by the addition of 0.1% w/v of sulphamic acid.

Iron does not interfere at concentrations below 1000µg L⁻¹ and chloride is without effect at concentrations below 100mg L⁻¹.

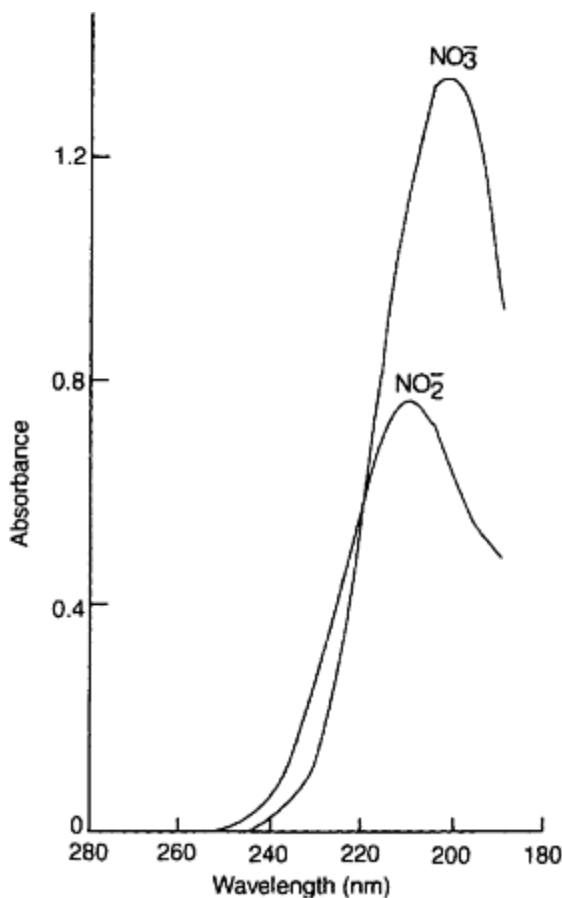


Fig. 7.9 Absorption spectra of nitrate and nitrite standard solutions containing 1 mg L^{-1} of nitrogen

Source: Reproduced with permission from the Royal Society of Chemistry [46]

Results obtained for nitrate by ultraviolet spectroscopy and spectrophotometry are compared in Table 7.11. Good agreement was obtained for all ground water samples analysed.

7.18.2 Ultraviolet spectroscopy

This technique has been investigated by several workers [47–49].

Rennie *et al.* [48] describe a method for determining down to $6\mu\text{g L}^{-1}$ nitrate nitrogen in raw and potable waters which uses an activated carbonfilter, at an elevated pH, to eliminate interference from organic matter. Interference from several cations that are precipitated out of solution is also removed by this system. The results obtained using the

technique show that the method is precise.

Table 7.11 Nitrate concentrations determined by ultraviolet and 2, 4-xenol methods

Type of water	Absorbances measured in 1cm cells	
	Nitrate-nitrogen/mg L ⁻¹	
	Ultraviolet method	2, 4-Xenol method
Bunter sandstone	0.04	0.04 ^a
Bunter sandstone	8.3	8.2
Bunter sandstone	0.005 ^a	0.04 ^a
Bunter sandstone	0.54	0.55
Bunter sandstone	4.5	4.6
Lincolnshire limestone	7.9	7.9
Lincolnshire limestone	5.8	5.5
River Thames, Chiswick	11.0	10.9

^a4cm cell

Source: Reproduced with permission from the Royal Society of Chemistry [46]

Rennie *et al.* [48] utilised absorbances at 210 and 275nm to indicate the presence of nitrate and organic matter respectively. The absorbance at 275nm was used as an indicator of the presence or absence of organic matter that could absorb also at 210nm.

Although some workers have corrected measurements of nitrate made at 210nm for organic absorbance based on measurements at or near 275nm, this method of correction becomes decreasingly reliable when low nitrate contents are being measured. Hence, in the method described by Rennie *et al.* [48], organic matter is completely removed from the sample prior to ultraviolet spectroscopy. This method is based on the observation that at pH values above 12 one particular grade of carbon black ADC 33 (Sutcliffe Speakman Co) will adsorb 98–100% of organic compounds from the water sample and, unlike many other grades of carbon black, will retain no nitrate. An analytical grade carbon filter paper (Schleicher and Schill No. 58) was also satisfactory in this respect and permitted organics removal from the alkaline sample to be conducted in a filtration assembly. Nitrite interference is overcome by the presence of sulphamic acid in the mixed reagent.

The effects of certain concentrations of the adventitious contaminants are summarised in Table 7.12 and the concentration that gave an absorbance at 210nm equivalent to 0.02mg L⁻¹ N is defined as the interference limit for the method (denoted by a superscript 'a') in Table 7.12. The lack of an interference effect, compared with that found by direct ultraviolet spectrophotometry, of the sodium salt of dodecylbenzene-sulphonic acid is due to the effectiveness of removal of organic matter by the filter. Whereas iron(II) and iron(III) interfere significantly in

Table 7.12 Interference effects

<i>Interfering substance</i> <i>Species</i>	<i>Interference effect (mg L⁻¹ N)</i>		
	<i>Concentration (mg L⁻¹)</i>	<i>With carbon filtration</i>	<i>Without carbon filtration</i>
Chloride	2500 ^a	0.02	0.02
	5000	0.06	0.06
Bromide	1.0 ^a	0.02	0.02
	2.0	0.04	0.04
Iodide	0.65 ^a	0.02	0.02
	1.30	0.05	0.05
Iron	13.5	<0.02	<0.02
	27	<0.02	0.08
	1000 ^b	<0.02	1.4
Iron	0.2	<0.02	>0.02
	0.4	<0.02	0.08
	1000 ^b	<0.02	1.75
Dichromate	0.15 ^a	0.02	0.02
	0.30	0.08	0.08
Manganese	100	<0.02	>0.02
	1000 ^b	<0.02	0.4
Dodecylbenzenesulphonic acid, sodium salt	3.5	<0.02	>0.02
	7.0	<0.02	0.06
	1000 ^b	<0.02	1.8

^aIndicates 'interference limit'^bIndicates highest concentration investigated

Source: Reproduced with permission from the Royal Society of Chemistry [48]

direct ultraviolet methods, such interference is eliminated in this method as a result of the formation of insoluble hydroxides at the elevated pH, the precipitates being removed by the GF/C paper on the filter. It is apparent that the interference effects of anions are not reduced by carbon treatment.

De Fulvio and Olori [50] determined nitrate in drinking water by ultraviolet spectrophotometry at 210nm, and matrix interferences were overcome by control of the ionic strength.

7.18.3 Continuous flow analysis

Thompson and Blankley [49] have described an automatic ultraviolet continuous flow determination of nitrate in raw and potable water. The method has a linear calibration range of 0–30 $\mu\text{g L}^{-1}$ nitrate N and a detection limit of 0.01 $\mu\text{g L}^{-1}$.

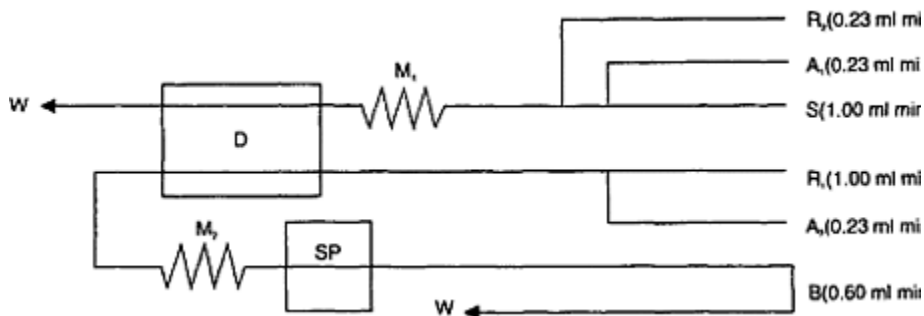


Fig. 7.10 Diagram of the continuous flow manifold Air (A_1) is used to segment the flow of sample (S) that is mixed with reagent R_1 in a four-turn 20mm diameter mixing coil M_1 , and pumped through one half of the 150mm diameter (D) to waste (W). Reagent R_2 is segmented with air (A_2) pumped through the other half of the dialyser and mixed in coil M_2 with dialysed sample. Mixing coils M_1 and M_2 are identical. Nitrate absorbance at 210nm is measured by spectrophotometer SP where part of the flow is pulled through a 1.0mm silica flow cell by pump tube B

Reagent R_1 Dissolve 100g of sulphamic acid in about 500ml of water, carefully add 5.0mol of sulphuric acid (98 wt%) followed by 4.00g of hydroxylamine sulphate and 3 drops of a 30% w/v Brij 35 solution (BDH Chemicals). Dilute to 1L with water. Prepare freshly every 2 weeks. The hydroxy-amine sulphate was added to reduce any chromium(VI), iron(III), chromium(III) and iron(II) respectively. The lower oxidation states of these elements do not significantly absorb at 210nm at the maximum concentrations likely to be encountered.

Reagent R_2 Dissolve 10g of anhydrous sodium sulphate in approximately 500ml of water, add 3 drops of 30% w/v Brij 35 solution and dilute to 1L

Source: Reproduced with permission from the Royal Society of Chemistry [49]

The incorporation of a dialysis membrane minimised the effect of humic acid type substances that did not freely diffuse through the membrane, and also avoided the necessity to filter water samples prior to measurement.

The method requires no sample pre-treatment or dilution. It utilises a conventional dialysis membrane to minimise interference effects from suspended, colloidal and

organic matter.

Absorbance measurements were made at 210nm with a Cecil Instruments 272 ultraviolet visible spectrophotometer, fitted with a 10nm path length Spectrosil silica micro-flow cell (Type 75, Starna Ltd). The output trace was monitored on a Smiths Industries Servoscribe recorder. A Chemiab Instruments 15 channel peristaltic pump and 40 position autosampler were used. The continuous-flow manifold is depicted in Fig. 7.10.

Excellent precision is obtained by this procedure (Table 7.13).

The dialysis membrane minimised the ultraviolet absorption interference from organic matter present in water, as the efficiency of transfer

Table 7.13 Precision of analytical results

Solution	Standard deviation/mg L ⁻¹ of N			Mean concn. found/mg L ⁻¹ of N
	Sw.	S _b	S _t	
0.00µg mL ⁻¹ of N	0.032 (5)	—	—	0.031
2.00µg mL ⁻¹ of N	0.10(5)	ns(4)	0.11(8)	2.30
15.00µg mL ⁻¹ of N	0.17(5)	ns(4)	0.17(8)	14.95
18.00µg mL ⁻¹ of N	0.16(5)	0.25 (4)	0.30 (8)	18.04
River Dove water	0.061 (5)	ns(4)	0.071 (7)	4.58
River Dove water ⁺				
9.55µg mL ⁻¹ of N	0.11 (5)	ns(4)	0.16(6)	14.08 ^b

^aNumbers in parentheses correspond to the number of degrees of freedom, ns indicates that the result is not statistically significant at the 0.05 level of significance

^bRecovery of added nitrate was 99.48%

Source: Reproduced with permission from the Royal Society of Chemistry [49]

Table 7.14 Comparison of methods for the determination of nitrate in some coloured raw Pennine water samples

Sample no.	Apparent colour	Nitrate concentration/mg L ⁻¹ of N		
	A m ^{-a}	Reduction method	Manual UV method ^b	Proposed method ^c
1	10.0	0.81	2.19	0.85
2	12.2	0.64	2.19	0.65
3	10.4	1.33	2.98	1.34

^aMeasured on unfiltered sample at 400nm; A=absorbance units

^bNo correction at 275nm was applied to the manual method

^cCalibration range 0–25µg mL⁻¹ of N

Source: Reproduced with permission from the Royal Society of Chemistry [49]

of this matter through the membrane was significantly lower than that of nitrate ions. The nitrate concentrations of three highly coloured raw Pennine waters were determined by the conventional continuous-flow reduction method [51], the manual nitrate method [52] (using unfiltered samples), and the above dialysis method. The results (Table 7.14) show that the dialysis method eliminates the ultraviolet absorption contribution from organic matter observed with the manual method and that there is good agreement between the dialysis method and the continuous-flow

Table 7.15 Effect of other substances on nitrate. If other substances did not interfere, the results would be expected (95% confidence) to be in the following ranges:
10.00 ± 0.33µg mL⁻¹ and 0.00 ± 0.05µg mL⁻¹. Negligible interference was observed from the presence of Ca (200µg mL⁻¹), Mg (100µg mL⁻¹), K (200µg mL⁻¹) and NH₄⁺ (1 00µg mL⁻¹ NO, all present as chlorides

<i>Substance</i>	<i>Concn mg L⁻¹</i>	<i>Added as mg L⁻¹</i>	<i>Measured nitrate concentration ^a of N</i>	
Cl	1000	NaCl	10.19	0.02
SO ₄	1000	Na ₂ SO ₄	10.09	0.00
PO ₄ (as P)	5	KH ₂ PO ₄	9.74	0.01
F	5	NaF	9.70	0.00
Humic acid	250	–	10.15	0.33
Fulvic acid	250	–	11.58	1.36
Fe(II)	10	FeSO ₄	10.27	0.06
Fe(III)	10	FeCl ₃	9.89	0.00
NO ₂ (as N)	50	NaNO ₂	10.01	0.00
Cr(VI)	10	K ₂ Cr ₂ O ₇	9.85	0.13
Persil ^b	10	–	9.76	0.00
Al	2	Al ₂ (SO ₄) ₃	9.92	0.00
Mn	2	MnSO ₄	10.03	0.02
I	5	KI	10.17	0.00
Br	5	KBr	9.98	0.00
Glucose	100	–	10.25	0.00
Acetate	100	CH ₃ COONa	10.25	0.00

Benzoate	100 $\text{C}_6\text{H}_5\text{COONa}$	14.80	4.62
Acetone	100 –	10.75	0.45

^aResults in the first column have an added nitrate concentration of 10mg L^{-1} of N

^bProprietary detergent

Source: Reproduced with permission from the Royal Society of Chemistry [491]

reduction method. The manual method (no dialysis) is prone to very significant positive interference from the naturally occurring organic matter.

The interference effect of other substances is given in Table 7.15, and it can be seen that the method is relatively free of interference effects for its intended uses. There was a small positive bias from chromium(VI), acetone and humic acid, and a somewhat larger bias from fulvic acid and the benzoate ion. However, the interference tests were carried out at concentrations of these determinands considerably in excess of levels likely to be encountered in potable waters.

7.18.4 Flow injection analysis

Al Wehaid and Townshend [53] describe flow injection spectrophotometric system similar to that described by Van Staden *et al.* [54] for the determination of nitrate in potable waters using titanous chloride as reducing agent.

7.18.5 Polarography

The application of this technique is discussed under multianion analysis in section 14.10.2.1.

7.18.6 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 7.28.2, 12.6.1, 12.6.2 and 12.6.3.

7.18.7 High performance liquid chromatography

Schroeder [55] determined nitrate in potable water using high performance liquid chromatography with a reversed phase octadecyl C18 column using aqueous phosphoric acid and dihydrogen phosphate as a mobile phase and ultraviolet detection. Detection limits were $7\mu\text{g L}^{-1}$.

7.18.8 Ion exchange chromatography

Sherwood and Johnson [56] have described an ion exchange chromatographic determination of nitrate and amperometric detection at a copperised cadmium electrode. The chromatograms obtained in this procedure resolve nitrate from dissolved oxygen.

7.18.9 Miscellaneous

Nitrate has been determined by a nitrate selective electrode [57] consisting of a porous polymer wick sealed with liquid ion exchanger tris(4, 7-diphenyl)-1, 10-phenanthroline nickel(II) in 2-nitro-p-cymene). Chloride and bicarbonate interferences are overcome by the addition of silver sulphate and 0.5M phosphate buffer, pH 2 respectively.

Maracek *et al.* [58] investigated the feasibility of using a hanging drop electrode for the determination of nitrate, perchlorate and iodide in potable water. A 3-electrode system was used with a polarographic analyser. The potential range of the method was increased by using crystal violet dicarbollylcobaltate electrolyte in the nitrobenzene phase and magnesium sulphate in the aqueous phase, with a lead/lead sulphate reference electrode.

A nitrogen-15 isotopic tracking method has been used [59] to identify the origin of nitrates of some aquifers in the Paris basin.

Clifford and Weber [60] have discussed the application of anion exchange resins to the commercial scale removal of nitrate from potable water supplies.

7.19 Nitrite

See also section 7.20.

Nitrite in the environment is derived from biological denitrification, acid rain and industrial waste. Nitrite can induce methaemoglobinemia and react with secondary and tertiary amines forming carcinogenic nitrosamines. Such nitrosation reactions can take place *in vivo*. Even though saliva is the primary source of human exposure to nitrite, it is desirable to monitor the nitrite level in the environment, particularly in drinking water.

7.19.1 Spectrophotometric method

The current standard method for nitrite analysis in water is based upon Spectrophotometric determination of an azo dye formed by coupling diazotised sulphanilamide with *N*-(1-naphthyl)ethylenediamine dihydrochloride (Griess reaction). It takes about 30min; however, a parallel determination of multiple samples is possible. The detection limit is about $10\mu\text{g L}^{-1}$ as nitrite if a 1cm light path is used. The problem of this chemical method is that it is subject to interference by some reducing compounds and metal ions or colour.

One such method [61] claims a detection-limit of 0.001mg L^{-1} nitrite (as N) with a standard deviation of 0.018mg L^{-1} at the 0.04mg L^{-1} nitrite level and 0.04mg L^{-1} at the 1.6mg L^{-1} nitrite level.

3, 3' dimethylbenzidine has been used as a chromogenic reagent for the determination of down to $5\mu\text{g L}^{-1}$ nitrite N in potable water. Spectrophotometric measurements are carried out at $437\mu\text{m}$ [62]. Iron and copper interfere in this procedure. Two modifications have been described [63] of the Griess-Ilosvay method for determination of nitrites in drinking water. The first is based on modification of the reaction between the diazonium salt of aniline-4-sulphonic acid with *N*-phenyl-1-naphthylamine-8-sulphonic acid. The second is based on the reaction of the diazonium salt of aniline-4-sulphonic acid with *N*-

ethyl-1-naphthylamine. The first produces a red violet coloration measured photometrically at 554nm and the second a red coloration measured at 537nm. Absorbance increased linearly over the range 1–3 $\mu\text{g L}^{-1}$ of sample. Both methods were equally suitable for the determination of nitrites.

7.19.2 Ion chromatography

Kim and Kim [64] determined nitrite in potable water by ion exclusion chromatography with electrochemical detection. The application of ion chromatography is also discussed under multianion analysis in sections 7.28.2, 12.6.1 and 12.6.3.

7.20 Nitrate and nitrite

7.20.1 Spectrophotometric method

Zhou and Xie [65] give details of a rapid spectrophotometric method for the determination of traces of nitrite and nitrate in water. In this method, nitrate is quickly reduced to nitrite at pH 3.0 in 5min with freshly prepared cadmium sponge, which is produced *in situ* by the action of zinc powder in a dilute solution of cadmium chloride in the presence of ammonium chloride. At pH 2.0, nitrous acid diazotises with p-aminoacetophenone, which is then coupled with *N*-(1-naphthyl)-ethylene-diamine. The azo dye formed is extracted into *n*-butanol at pH 2.0 in the presence of β -naphthyl sulphonic acid and aluminium nitrate.

The absorbance is measured at 550nm. The molar absorptivity of the extract is about $4.8 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$. The ions normally present in water do not interfere when sodium metaphosphate is added as a masking agent.

In this method 20ml or less of the sample containing 0.5–10 μg nitrate-nitrogen are transferred to a 25ml graduated flask. 1.0ml of ammonium chloride is added followed by 1.0ml of potassium chloride-hydrochloric acid buffer (50ml 0.2mol L⁻¹ KCl plus 17ml 0.2mol L⁻¹ HCl, diluted to 200ml and adjusted to pH 1.8) 1.0ml of 0.1% w/v of cadmium chloride and 1.0ml 5% w/v sodium metaphosphate. The pH is adjusted to pH 3.0, the solution diluted to the mark with water and again mixed thoroughly. After addition of 100mg of zinc powder through a small glass funnel, the contents of the flask are mixed by inverting three times within 5min (stand for 2min for clarification). Aliquots of the clear solution are pipetted for determination of nitrite as follows.

A portion of sample solution containing 0.1–2.0 μg nitrite-nitrogen is transferred in a 60ml separatory funnel. 1.0ml of p-aminoacetophenone hydrochloride solution (0.5% w/v in 1+99 HCl) and adjusted to pH 2.0 with either 30% w/v sodium acetate solution or hydrochloric acid. After 15min standing at room temperature, 1.0ml of *N*-(1-naphthyl)-ethylenediamine dihydrochloride solution (0.5% w/v in 1+99 HCl) is added. 1.0ml of β -naphthyl sulphonic acid 0.5% w/v and 3g of powdered aluminium nitrate are added. Extract the azo compound into 5.0ml of *n*-butanol by shaking mechanically for 3min. After clarification, the absorbance of the *n*-butanol layer is measured at 550nm in a 1cm cell against a reagent blank.

7.20.2 Differential pulse polarography

Barsotti *et al.* [66] determined nitrate in amounts down to $0.4\mu\text{g L}^{-1}$ N and nitrite by this technique. Nitrate is reduced on a cadmium column to diphenylnitrosamine and then determined polarographically. Cadmium interference is removed by adjustment of pH and complexing with EDTA. Nitrite is determined directly as the diphenylnitrosamine.

In order to separate the cadmium(II) peak from that of diphenyl nitrosamine, advantage was taken of the fact that organic polarograms are usually pH dependent, while those of reversible inorganic ions are not. Changing the pH from 1.0 to 4.0 shifts the diphenyl nitrosamine peak, without loss of peak height, hence sensitivity, but causes no change in the cadmium(II) peak. A pH of 1.0 is used for the formation of diphenyl nitrosamine since the rate is fast at that pH with no decomposition. At a pH of 4.0 a peak separation of 140mV occurs which is sufficient to determine nitrite ion in the presence of cadmium (II) to a level of approximately $200\mu\text{g L}^{-1}$. At this pH the EDTA complex of cadmium(II) has a stability constant of approximately 10^{16} . Thus, the addition of EDTA at a pH of 4.0 results in the complete disappearance of the cadmium(II) peak and total removal of any interference. Therefore, by an adjustment of pH and the addition of EDTA to the nitrite ion procedure, nitrate could be determined.

7.20.3 Ion chromatography

Various workers [67–70] have discussed the application of this technique to the determination of nitrite and nitrate (Table 7.16).

7.20.4 Ion exchange chromatography

Gerritse [71] separated nitrate and nitrite on a cellulose anion-exchanger column and detected them in a spectrophotometric flow through cell at 210 nm. The detection limit was $1\text{--}5\mu\text{g L}^{-1}$ as nitrogen with a sample volume of 100–200 μL and the linear range extends up to 20mg L^{-1} as nitrogen.

Table 7.16 Determination of nitrite and nitrate in rain water by ion chromatography

Type of water sample	Co-determined anions	Ref
Rain	Cl, PO_4 , SO_4	[67]
Rain	Cl, PO_4	[68]
Rain	Cl, F, Br, SO_4 , SO_3 , PO_4	[69]
Rain	Cl, Br, F, PO_4 , BrO_3 , SO_4	[70]

Source: Own files

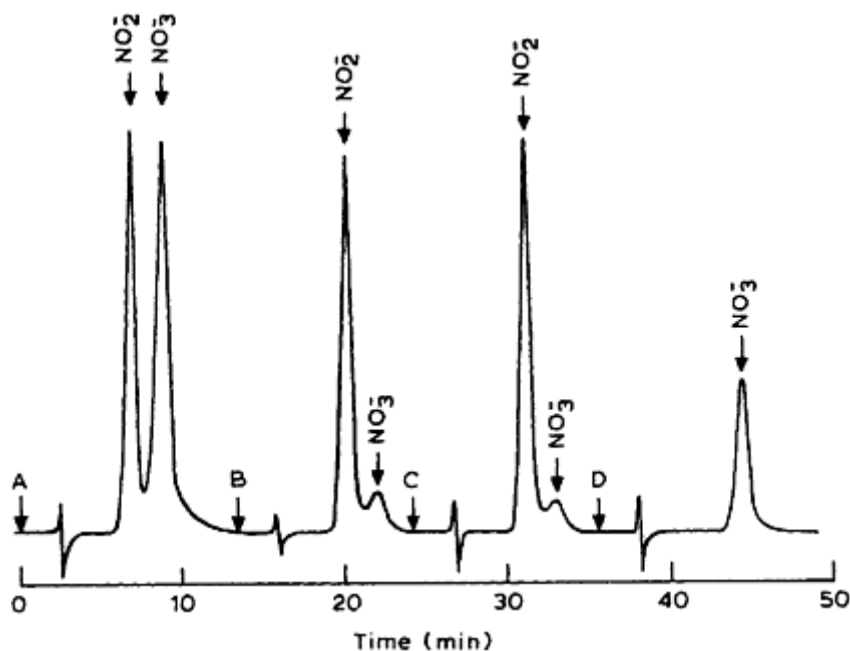


Fig. 7.11 Chromatograms resulting from the injection of samples containing nitrate and nitrite into a mixed bed column containing Kieselguhr and Ecteola ET 41 cellulose anion exchanger

Eluant: $0.03\text{M K}_2\text{SO}_4$, 0.01M Tris buffer (pH 7); A. Standard mixture containing 1.4mg L^{-1} as nitrogen of both nitrite and nitrate (attenuated 0.1); B, sewage sludge sample, diluted 1:100 containing 2.7mg L^{-1} as nitrogen of nitrite and 0.35mg L^{-1} as nitrogen of nitrate (attenuation 0.2); C, sewage sludge sample, diluted 1:100 containing 1.4mg L^{-1} as nitrogen of nitrite and 0.1mg L^{-1} as nitrogen of nitrate (attenuation 0.11); D, potable water containing 0.45mg L^{-1} as nitrogen of nitrate (attenuation 0.1)

Source: Reproduced with permission from Elsevier Science [71]

A stainless steel column (SS 316) of length 30cm and i.d. 0.3cm was filled with a mixture of Kieselguhr and Ecteola ET 41 cellulose anion exchanger (Whatman: W & R Balston, Maidstone, UK). The eluent used was 0.03M potassium sulphate solution and 0.01M Tris buffer at pH 7 in water.

A ratio of Kieselguhr to Ecteola of 1:2 (by weight) was used. The column was operated at a pressure of 40 bar. The eluant was monitored with a Cecil CE-212 spectrophotometric flow through detector at a wavelength of 210nm. The temperature of the column was ambient. Samples were injected with the aid of a sample injection valve (Valvo C20) using a sample loop of $60\mu\text{L}$.

Examples of chromatograms of potable water and of sludge solution resulting from

aeration of anaerobically digested sewage sludge are shown in Fig. 7.11. The sludge was centrifuged at 40000g for 1h, then the supernatant was diluted 1:100 with distilled water and injected into the column. Potable water was injected undiluted. Without dilution, samples with concentrations of up to 20mg L^{-1} each (as nitrogen) of nitrite and nitrate could be injected.

Davenport and Johnson [72] used ion exchange chromatography on Amberlite IRA-900 strongly basic resin to determine nitrate and nitrite in water. Perchloric acid (0.01mol L^{-1}) was used as eluent and an electrochemical cadmium electrode detector was used.

7.20.5 Gas chromatography

A method has been described [73,74] for determining aqueous nitrates by conversion to nitrobenzene followed by electron capture gas chromatography. The procedure can also be used to determine aqueous nitrites and gaseous oxides of nitrogen if they are first converted to nitrates. The procedure was evaluated by analysing drinking water for nitrate over a period of one month. The method is sensitive and capable of measuring typical environmental levels of nitrogen compounds. The detection limit for nitrobenzene is about 10^{-12}g .

For the determination of nitrate, use a 1 dram vial with a polyethylene stopper (Kimble No. 60975-L) as a reaction vessel. Introduce a 0.20ml aliquot of aqueous sample into the vial, followed by 1.0ml of thiophen free benzene. Catalyse the reaction by addition of 1.0ml of concentrated sulphuric acid. Shake the vial for 10min. Remove the benzene layer immediately from the reaction vial with a Pasteur pipette, place it in a separate vial and analyse by gas chromatography with electron capture detection for the nitrobenzene concentration generated. Treat standard solutions of potassium nitrate in the same manner to generate a standard calibration plot relating nitrobenzene concentration to peak height. If higher precision is desired (approximately 4% relative standard deviation), add 2, 5-dimethylnitrobenzene to the benzene prior to reaction as an internal standard (concentration $5 \times 10^{-7}\text{gm L}^{-1}$ to correct for differences in injection size, detector sensitivity, fluctuations, etc. When this internal standard is used, normalise the peak heights of nitrobenzene to the peak heights of the standard before further data reduction.

Determine nitrite by difference, treating a second identical sample with an oxidant to convert nitrite to nitrate. Consequently, the concentration of nitrite plus nitrate is subsequently measured, so nitrite must be determined by difference. Specifically, the procedure used was to introduce 0.15ml of the sample into the reaction vial, followed by addition of 0.05ml of 0.1N hydrogen peroxide. The rest of the procedure is the same as that for nitrate.

The results of applying the microtechnique to the analysis of nitrate in several samples of drinking waters are summarised in Table 7.17. In no cases were detectable amounts of nitrite found (the limit of detection for nitrite depends on the nitrate concentration, since nitrite is determined by

Table 7.17 Comparison of analyses of drinking waters for NO_3^- concentration by GC-ECD and ISE. Numerical designations refer to selected municipal water supplies in Crowley County, Colo., USA. Unless otherwise specified concentrations are expressed in ppm (w/w)

Site	Concentration NO_3^- (mg L^{-1})	
	GC-ECD ^a	ISE ^b
Boulder, Colo.	0.40	–
TW0011	44	48
TW0012	42	46
TW0013	51	52
TW0014	16	16
TW0015	35	36
TW0016	12	13

^aElectron capture gas chromatography

^bIon selective electrode measurement

Source: Reproduced with permission from Elsevier Science [73]

difference, generally a nitrate concentration which is 5% of the nitrite concentration can be detected). In Table 7.17 the results are shown of a comparative study of the electron capture gas chromatographic microtechnique vs ion selective electrode measurements. The close agreement (usually within 5%) of the totally independent methods used for the analysis of identical samples is an excellent demonstration of the efficacy of the methods.

7.21 Perchlorate

7.21.1 Polarography

The application of this technique is discussed under multianion analysis in section 14.10.2.1.

7.22 Phosphate

7.22.1 Spectrophotometric method

Matsubara *et al.* [75] determined trace amounts of phosphate (and arsenate) in potable water by Spectrophotometric detection at 627nm of their heteropoly-malachite green aggregates following preconcentration by nitrocellulose membrane filtration.

7.22.2 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 7.28.2 and 12.6.1.

7.23 Selenate/selenite

7.23.1 Spectrofluorometric method

Selenate has been determined in potable water fluorometrically using naphthalene-2, 3-diamine [76]. The complex is extracted into cyclohexane and evaluated at 521nm (excitation 389nm). The calibration graph is rectilinear in the range 0.02–1.0µg of selenium. The coefficient of variation for samples containing 0.5 and 1.0ng of selenium was 6.3% and a 1000-fold excess of nitrate, barium, cadmium, calcium, chromium(III), cobalt, copper(II), iron(III), magnesium, manganese(II), nickel(III) or zinc did not interfere.

7.23.2 Ion chromatography

The application of this technique to the determination of selenate and selenite is discussed under multianion analysis in sections 7.28.2, 12.2.2 and 12.6.6.

7.24 Silicate

7.24.1 Polarography

Iyer *et al.* [77] converted trace amounts of silica in potable water to silicomolybdate by addition of ammonium molybdate, followed by methylethylketone to ensure that only the beta form of silicomolybdate was present. Buffering with citrate masked any phosphate or excess molybdate. The initial potential of the hanging mercury drop electrode was kept at –0.2V for 2min and silicomolybdate accumulated by adsorption in the interface. Its bulk concentration was determined by measuring the peak height at –0.36V. The reduction of the silicomolybdate gives a well defined peak at –0.36V, followed by reduction of the molybdate ion at –0.52kV. With increasing the concentration of silica only the first peak at –0.36V increased linearly unlike that of the second peak.

A typical voltammogram of silicomolybdate at the hanging drop mercury electrode obtained by following the standard procedure is given in Fig. 7.12. The reduction of the silicomolybdate gives a well defined peak at –0.36V, followed by reduction of the molybdate ion at –0.52V. With increasing concentration of silica only the first peak at –0.36V increased linearly unlike the second peak.

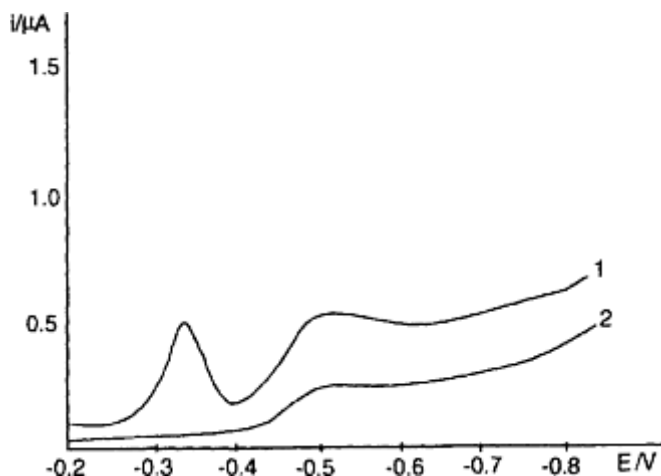


Fig. 7.12 Voltammogram of silicomolybdate at the HMDE in the presence of methylethylketone, 0.2 mol L^{-1} citrate buffer, pH 2.5, $3 \times 10^{-7} \text{ mol L}^{-1}$ SiO_2 , 10% ketone. MMDE surface area $2.8 \times 10^{-2} \text{ cm}^2$, scan rate v 100 mV s^{-1} , adsorption time t 120s at the starting potential $E_2 = -0.2 \text{ V}$. Curve 1—supporting electrolyte, curve 2—silico-molybdate

Source: Reproduced with permission from Marcel Dekker Inc [77]

Table 7.18 Determination of silica (SiO_2) in potable water

Nature of water samples		Voltammetric method $\mu\text{g L}^{-1}$ SiO_2	Spectrophotometric method
Drinking water	1	140	130
	2	150	155
	3	190	180
	4	110	130
	5	130	140

Source: Reproduced with permission from Marcel Dekker Inc. [77]

Results obtained on applying the procedure to samples of potable water are summarised in Table 7.18. For comparison the samples were analysed by the spectrophotometric molybdenum blue method. The values obtained by voltammetry agree satisfactory with this method, confirming the accuracy of the voltammetric determination.

7.25 Sulphate

7.25.1 Nephelometric method

Regnet and Quentin [78] describe a nephelometric method for determining up to 50mg L⁻¹ sulphate in potable waters in which a suspension of barium sulphate is produced by addition of a specially prepared barium chloride reagent, and the turbidity measured at 490nm after a reaction time of 45min. The calibration curve can be considered as made up of two linear portions of different slope, which intersect at about 30mg L⁻¹ sulphate ion. The procedures for calibration and determination, taking about 2h, are outlined. Other ionic constituents do not interfere at concentrations normally encountered, although nitrate can cause discrepancies if present in excess of 100mg L⁻¹.

7.25.2 Turbidimetric method

Van Staden [79] reported the application of an active pre-valve carbon filter, for the turbidimetric determination of sulphate in potable waters. The filter is incorporated into an automatic flow injection system, between the sampler and the sampling valve system, to remove suspended and coloured materials which interfere with the spectrophotometric determination of turbidity. The method has been applied to the analysis of sulphate at concentrations up to 200mg L⁻¹ at a sampling rate of up to 60 samples per h, with a coefficient of variation less than 1%. The accuracy is similar to that of a standard automated segmented method and standard flow injection methods.

Krug [80] and Van Staden *et al.* [79,81] have also described a turbidimetric method in which the sample is injected into an inert carrier stream which is mixed with barium chloride solution to form a barium sulphate suspension. Intermittent pumping of a disodium ethylenediamine tetraacetate wash solution is used to inhibit a precipitation of barium sulphate in the lines of the system.

7.25.3 Continuous flow analysis

Archer [82] has described a method in which sulphate is precipitated as 2-aminoperimidine sulphate under acidic conditions, the excess of 2-aminoperimidine is diazotized and coupled with ethanolamine to give a red coloured solution the intensity of which is inversely proportional to the sulphate concentration. Down to 2mg L⁻¹ sulphate can be determined by this method with a standard deviation of 0.5mg L⁻¹ at the 32mg L⁻¹ sulphate level and 3.4mg L⁻¹ at the 96mg L⁻¹ sulphate level. The layout of the apparatus required to perform this analysis is illustrated in Fig. 7.13.

7.25.4 Flow injection analysis

Koch [83] modified the standard ASTN 15/84 (Tecator) flow injection method for the determination of sulphate in potable water by adding methyl thymol blue to barium ions in an alkaline alcoholic solution to

Table 7.19 Comparison of results of sulphate determinations with three different methods

Sample no	Sulphate ion (mg L ⁻¹)		
	Gravimetric n=1	Atomic absorption spectrometry n=5 (±1s)	Turbidimetric n=2
10000-1	926	1077 (±31)	1180, 1168
6891-1	2800	2640 (±87)	2897, 2885
7036-1	52	57 (±4)	62.4, 60.5
7062-1	40	32 (±2.7)	29.0, 28.0

Source: Reproduced with permission from the Society for Applied Spectroscopy [85]

directed at precipitation of the sulphate with a metal ion followed by determination of the metal retained on a porous graphite filter after washing off excess precipitant. Siemer *et al.* [85] discovered that non-resonance atomic absorption at 405.7nm of the lead in a lead sulphate precipitate served the purpose.

At a furnace temperature of 1550°C lead sulphate gives reasonable absorbance values for the amounts of sulphate in potable water. From 50 to 75% of ethyl alcohol was incorporated during the lead sulphate precipitation and washing steps to decrease solubility errors. An excess of lead ions was added to the sample in this medium and excess lead ions determined.

In Table 7.19 sulphate determinations obtained by this technique are compared with those obtained turbidmetrically and gravimetrically.

7.25.6 Ion selective electrodes

Sun *et al.* [86] measured sulphate in mineral and drinking waters using a selective electrode potentiometric titration method. They reported a detection limit of 5×10^{-5} M and relative standard deviations $\leq 3.7\%$.

7.25.7 Ion chromatography

Various workers [67,68,69,87-93] have discussed the application of this technique to the determination of sulphate (Table 7.20).

The application of this technique is discussed under multianion analysis in sections 7.28.2, 12.6.1, 12.6.2 and 12.6.3.

Table 7.20 Determination of sulphate in potable water by ion chromatography

<i>Type of water sample</i>	<i>Co-determined anions</i>	<i>Ref.</i>
Rain	Br, F, Cl, NO ₂ , PO ₄ , BrO ₃ , NO ₃	[87]
Rain	Cl, PO ₄ , NO ₃	[88]
Rain	Cl, Br	[89]
Rain	Cl, F, NO ₃ , PO ₄	[90]
Rain	Cl, PO ₄ , NO ₂ , NO ₃	[67]
Rain	Cl, NO ₃	[68,91,92]
Rain	F, Cl, Br, NO ₂ , NO ₃ , SO ₃ , PO ₄	[69]
Rain	None	[93]

Source: Own files

7.26 Sulphite

7.26.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.6.5.

7.27 Sulphide

7.27.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.6.4.

7.28 Multianion analysis

7.28.1 Electrophoresis

Choi and Cho [94] determined mg L⁻¹ levels of anions in potable waters by capillary electrophoresis and compared results obtained with those obtained by ion chromatography.

7.28.2 Ion chromatography, chloride, fluoride, nitrate, nitrite, phosphate, sulphate, arsenite, selenate and selenite

This technique has been applied to the determination of fluoride and other anions (nitrate,

phosphate and sulphate) [90] and arsenite, selenate and selenite [95].

The Environmental Protection Agency US [96] has issued a detailed standard procedure for the determination of chloride, fluoride, nitrate, nitrite, phosphate and sulphate in potable waters. For more detail see section 6.1.13.1.

7.28.3 Gas chromatography, bromide and iodide

Grandet *et al.* [12] have described a method for the determination of traces of bromide and iodide in potable water which permits determination of $50\mu\text{g bromide L}^{-1}$ and $5\mu\text{g iodide L}^{-1}$, without preconcentration of the sample or $0.5\mu\text{g bromide}$ and $0.2\mu\text{g iodide L}^{-1}$ after preconcentration. The method is based on the transformation of the halides into 2-bromo- or 2-iodo-ethanol. These derivatives are extracted with ethyl acetate and determined with an electron capture detector. The difference in the retention periods enables both halides to be determined simultaneously in one sample. The method is substantially free of interferences and is suitable for use on many types of water.

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Chapter 8

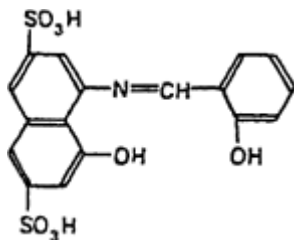
Anions in wastewaters

8.1 Borate

The level of boron in raw waters has tended to increase, resulting from its greater use in cleansing materials and in industrial processes [1]. As sewage treatment does not significantly reduce this level the increase is passed to surface waters, which may then be utilised for crop irrigation or potable water supply. Many varieties of fruit can tolerate no more than 0.5mg L^{-1} of boron [2] in irrigation water. The US Environmental Protection Agency [3] recommends limits of 0.75mg L^{-1} for most fruits, 1.0mg L^{-1} for most cereals, potatoes, peas and tomatoes and 2.0mg L^{-1} for tolerant species including sugar beet, turnips and cabbage. The Anglian Water Authority [4] apply criteria such that the 'maximum desirable' limit for crop irrigation is 0.5mg L^{-1} and the 'maximum permissible' limit is 1.0mg L^{-1} . They also apply criteria of 0.8 and $1.0\text{--}1.2\text{mg L}^{-1}$, respectively, to potable water abstractions.

8.1.1 Spectrophotometric method

Several reagents have been developed for the routine determination of boron, but most require a final stage in concentrated sulphuric acid. Apart from the hazards involved in pumping the concentrated acid the procedures are difficult to automate, principally because of density effects resulting from small changes in acid concentration. These methods include the carminic acid procedure, which has been automated by the Water Pollution Research Laboratory [5]. This method is not very precise.



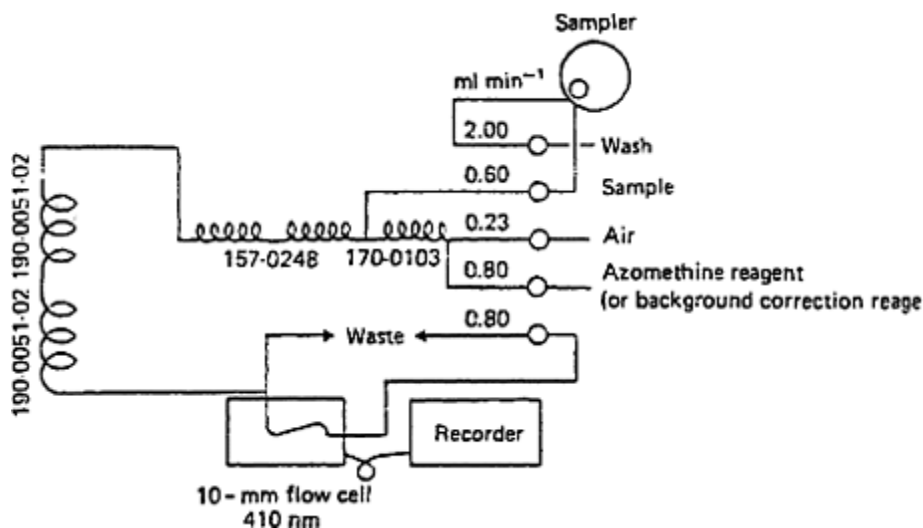


Fig. 8.1 Manifold arrangement for AutoAnalyzer 2

Source: Reproduced with permission from the Royal Society of Chemistry [7]

The curcumin procedure does not involve these dangers, but includes an evaporation stage unsuitable for automation. A method employing ferroin has been developed [6] involving extraction into chloroform but this method suffers from interference by anionic detergents.

Edwards [7] has developed a method employing azomethine-H (a condensation product of H-acid, (8-aminonaphthyl-1-ol-3, 6 disulphonic acid and salicylaldehyde) in aqueous medium, for the determination of boron in raw waters and effluents. This reagent is very sensitive to borates, forming, in aqueous medium, a yellow ion associated compound by reversible reaction. The method is capable of a limit of detection of 0.1 mg L^{-1} and the response is essentially linear to 4.0 mg L^{-1} , although a calibration graph is required above this level. A wide range of possible interferences was tested, but none proved of practical importance except sample colour, for which adequate correction is provided. Recovery after spiking a typical range of raw and waste waters was adequate.

A Technicon Auto Analyser 2 system is fitted with the manifold shown in Fig. 8.1. A sample cam of 30 h^{-1} is employed, with a 2:1 sample to wash water ratio; 410 nm wavelength filters are fitted.

The Azomethine-H reagent is prepared as follows: dissolve 18 g of H-acid in 1 L of water with gentle heating, neutralise to $\text{pH } 7.5 \pm 0.5$ with $10\% \text{ w/v}$ potassium hydroxide solution and filter if necessary. Add concentrated hydrochloric acid, to $\text{pH } 1.5 \pm 0.1$, while still warm. Add 20 ml of salicylaldehyde and stir vigorously while heating gently (not

Table 8.1 Recovery of boron from real samples spiked at 20mg L⁻¹

<i>Sample description*</i>	<i>Colour/ Hazen units mg L⁻¹</i>	<i>Boron concn. in sample %</i>	<i>Recovery 100 ±5%</i>	<i>Significance†</i>
Clean river water 1	200	<0.1	106.1	N.S.
Clean river water 2	70	<0.1	103.7	N.S.
Clean peaty stream water	500	<0.1	101.5	N.S.
Good sewage effluent	40	0.89	103.3	N.S.
Poor sewage effluent	60	0.74	99.6	N.S.
Septic tank effluent	40	1.45	99.4	N.S.
industrial makings effluent	500	<0.1	102.1	N.S.
Detergent manufacture effluent	50	0.16	104.4	N.S.
Surface water from detergent manufacture	30	0.64	99.7	N.S.
Poor petrochemical treatment plant effluent	50	0.25	109.8	S.

*See Table 8.2

†N.S.=not significant at 95% confidence level. S=significant at 95% confidence level

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exceeding 40°C) for 1h. Allow the azo-methine-H to settle for 16h. Centrifuge and discard the supernatant liquid, slurry the residue with ethanol and filter through a Whatman grade C glass-fibre filter paper. Dry at 105 °C for 3h and store in a desiccator. The yield of azomethine-H should be approximately 18g.

Dissolve 900 ± 10mg of azomethine-H and 2g of L-ascorbic acid in 70ml of water while heating gently (not exceeding 70°C) and dilute to 100ml. Add 100ml of buffer solution and mix thoroughly. The reagent is stable for 2 days only. The solution without buffer will keep for 14 days provided that it is filtered prior to use.

Buffer solution: Dilute 500ml of glacial acetic acid to 750ml with water. Add 10g of EDTA and 300g of ammonium acetate and warm to dissolve. Adjust to pH 5.2 ± 0.1 with acetic acid or ammonia solution if necessary. Add 1ml 1% Brij 35, polyoxyethylene lauryl ether). Absorbance occurs over a wide peak at 410–420nm, and was linear over the range 0–4mg L⁻¹ of borate.

Determination of boron in a range of raw waters and sewage effluents was found to be satisfactory relative to the standard carmine method [8], which involves destruction of organic matter at 500°C. The river waters tested gave a mean of 0.2mg L⁻¹ with a recovery of 105.3% relative to the standard method and the effluents gave a mean of 1.3mg L⁻¹ with a relative recovery of 102.9% (Table 8.1).

Table 8.2 Analysis of samples used for spiking recovery tests

Sample	BOD/ mg L ⁻¹	Suspended solids at 105°C/ mg L ⁻¹	Ammonia (as N)/ mg L ⁻¹	Total oxidised nitrogen (as N)/ mg L ⁻¹	pH	Electrical conductivity/ μS cm ⁻¹	Anionic detergent (Manoxol OT)/mg L ⁻¹
Clean river water 1	1.5	5	0.14	0.35	6.6	90	–
Clean river water 2	0.3	1	0.41	1.8	7.2	475	–
Peaty stream water	2.1	7	0.29	0.8	6.6	100	–
Good sewage effluent	9.6	17	2.6	28.0	6.8	580	–
Poor sewage effluent	30.0	31	14.8	17.1	7.0	560	–
Septic tank effluent	–	56	17.2	0.2	7.4	800	–
Maltings effluent	234	80	1.8	0.1	7.2	1200	–
Detergent manufacture effluent	8.0	13	0.2	0.6	7.5	720	0.16
Surface water from detergent manufacture	1.2	2	0.8	17.0	7.5	3000	0.37
Petrochemical treatment plant effluent	270	84	28.8	0.1	6.5	760	–

Source: Reproduced with permission from the Royal Society of Chemistry [7]

Table 8.3 Species producing interference

Interfering species	Level producing interference/ mg L ⁻¹	Interfering species	Level producing interference/ mg L ⁻¹
Chromium(VI)	10	Hydrogen carbonate	1000

Iron(III)	25	Carbonate	1000
Nitrite (as N)	50	Calcium	3000
Aluminium	100	Colour	According to absorbance
Iron (II)	300		at 4 10nm. Adequately corrected by re-run

Source: Reproduced with permission from the Royal Society of Chemistry [7]

Table 8.4 Species not indicating interference

<i>Species</i>	<i>Highest concentration tested/mg L⁻¹</i>	<i>Species</i>	<i>Highest concentration tested/mg L⁻¹</i>
Cadmium	100	Nickel	1000
Lead(II)	100	Nitrate (as N)	1000
Sulphide	100	Orthophosphate (as P)	1000
Ammonia (as N)	1000	Silica (SiO ₂)	1000
Anionic detergent (Manoxol)		Zinc	1000
OT, sodium lauryl sulphate)	1000	Chloride	10000
Chromium(III)	1000	Magnesium	10000
Copper(II)	1000	Potassium	10000
Fluoride	1000	Sodium	10000
Manganese	1000	Sulphate	10000
Non-ionic detergent (Lissapol NX)			1000

Source: Reproduced with permission from the Royal Society of Chemistry [7]

There was no evidence of bias in any of the effluents or raw waters tested except for the effluent containing substantial petrochemical industry waste. Results of analyses of the samples used in spiking recovery tests are given in Table 8.2.

The method was tested for interferences by specific factors and Table 8.3 illustrates the level at which interferences became possibly significant for a recovery of boron of 100 ±5% at a 95% confidence level. Table 8.4 shows the highest concentrations tested for those factors that do not produce interference.

Table 8.5 Ion chromatographic conditions

Eluent	0.003mol L ⁻¹ NaHCO ₃ /0.004mol L ⁻¹ Na ₂ CO ₃
Flow rate	138ml/h, 30%
Analytical column	3×500mm brine anion separator
Suppressor column	6×250mm anion suppressor
Detector sensitivity	3μmho full scale
Injection volume	100μL

Source: Reproduced with permission from the American Chemical Society [9]

8.1.2 Ion chromatography

Hill and Lash [9] have described an ion chromatographic method for the determination of down to 0.05mg L⁻¹ of borate in environmental waters, nuclear fuel dissolvent solutions and effluents.

Borate is selectively concentrated on Amberlite XE-243 ion exchange resin and converted to tetrafluoroborate using 10% hydrofluoric acid. Tetrafluoroborate is strongly retained by the resin, thus allowing excess fluoride to be eluted without loss of boron. The tetrafluoroborate is eluted with 1mol L⁻¹ sodium hydroxide and is determined in the eluent by ion chromatography. Boron is quantified to a lower limit of 0.05mg L⁻¹.

A Model 14 ion chromatograph (Dionex Corporation) was used in this work. Clear polymethylpentane plastic ware (Nagel Company) was used in the preparation of all reagents and standards. Separating columns; standard 3×150 and 3×500mm anion separator columns, as well as a 3 ×500mm brine anion separator were used [10]. Suppressor column-standard; 6×250mm anion suppressor column, from Dionex Corporation.

Samples and calibration standards containing between 1 and 20mg L⁻¹ tetrafluoroborate are injected into the ion chromatograph using the conditions shown in Table 8.5. Results are calculated on a peak height ratio basis.

The effects of the common anions on the standard procedure are shown in Table 8.6. As can be seen, none of these ions interferes at a 100 to 1mole ratio to boron. In addition, at least a 280 to 1mole ratio of fluoride to boron, as well as a 100 to 1mole ratio of chloride to boron, can be tolerated. Fig. 8.2 shows an ion chromatogram of a sample which initially contained all of the above anions at a 100 to 1mole ratio and which was prepared according to the standard procedure. As shown, tetrafluoroborate peaks are well resolved from all the residual amounts of those anions not completely removed by the XE-243 column treatment.

Five water samples prepared to contain boron at levels ranging from 500 to 0.05mg L⁻¹ were analysed according to the standard procedure. Recoveries ranged from 99.3% to 94.6%.

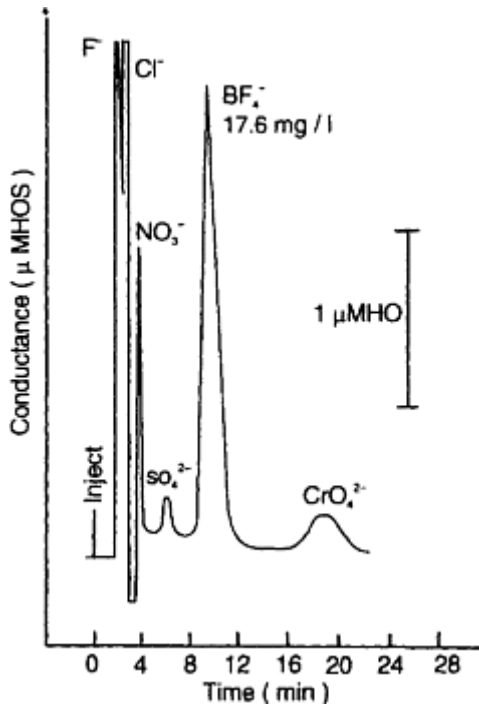


Fig. 8.2 Effects of diverse ions on IC determination of tetrafluoroborate ion
Source: Reproduced with permission from the American Chemical Society [9]

Table 8.6 Effect of diverse ions

<i>Ion</i>	<i>Added as</i>	<i>Mole ratio to boron^b</i>	<i>% recovery</i>
CrO ₄ ²⁻	K ₂ CrO ₄	100 to 1	101.4
NO ₃ ⁻	NaNO ₃	100 to 1 ^a	
SO ₄ ²⁻	Na ₂ SO ₄	100 to 1a	99.1
HPO ₄ ²⁻	Na ₂ HPO ₄ ·9H ₂ O	100 to 1 ^a	

^aAdded as a mixture of NO₃⁻, SO₄²⁻ and HPO₄²⁻

^b10⁻³M boron

Source: Reproduced with permission from the American Chemical Society [9]

8.2 Bromide

8.2.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.7.1.

Table 8.7 Typical results: 10 samples of coal mine waste water were analysed in triplicate

<i>Sample No</i>	<i>Result in mg L⁻¹</i>	<i>Sample No</i>	<i>Result in mg L⁻¹</i>
1	3.21	6	2.64
2	2.89	7	2.57
3	2.79	8	3.01
4	1.86	9	2.56
5	2.85	10	3.43

Relative standard deviation for all samples is between 0.5 and 3% for three analyses.

Approximate time of analyses is 2.8min.

Source: Reproduced with permission from Orion Research Inc. [12]

8.3 Chloride

8.3.1 Titration method

Barrera and Martinez [11] compared two methods, the Mohr procedure based on precipitation of silver chloride with a chromate indicator and the mercuric nitrate method based on the formation of soluble, slightly ionised mercuric chloride, for the volumetric determination of chlorides in waste waters. Results are in agreement. The mercuric nitrate method is preferred because the end-point is sharper, a magnetic stirrer is not required, the range of concentrations is 0–700mg L⁻¹ (against 5–300mg L⁻¹) and it is less expensive for both high and low chloride concentrations.

Workers at Orion Research Inc. [12] have described a method for the determination of chloride in mine waste water using the KAP analysis technique of multiple known addition. Although the samples could be measured by titration with silver nitrate, use of the KAP technique offers some advantages; it is more reliable at low levels (at few mg L⁻¹) of chloride, especially when there may be interfering ions such as phosphate present, which also react with silver; and the KAP technique can be used over a very wide range of sample concentration, without the need to adjust the standard concentration (Table 8.7).

8.3.2 Spectrophotometric method

Greenberg *et al.* [13] and Williams [14], recommend a method for the determination of chloride in waste waters in the ranges 0.5mg L^{-1} [13] and $0\text{--}500\text{mg L}^{-1}$ based on reaction of chloride with mercuric thiocyanate to form the sparingly ionised mercuric chloride complex. An equivalent amount of thiocyanate is released which with the addition of iron(III) forms a red coloured ferricthiocyanate complex which is evaluated spectrophotometrically.

8.3.3 Flow injection analysis

Van Staden [15] monitored chloride levels in waste waters using flow injection analysis coupled to a double membrane analyser.

8.3.4 Ion selective electrode

An ion selective electrode determination of chloride in wastewater from the leather industry ($\sim 10.000\text{mg L}^{-1}$) was described by Chen [16]. This method had a recovery of 99% and a detection limit of 5mg L^{-1} .

8.3.5 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.7.1 and 12.7.2.

8.3.6 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.2.1.

8.4 Chlorite

8.4.1 Spectrophotometric method

The application of this technique is discussed under multianion analysis in section 14.2.3.1.

8.5 Carbonate

8.5.1 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section 13.2.2.1.

8.6 Chromate (dichromate)

8.6.1 Spectrophotometric methods

Wei *et al.* [17] described a Spectrophotometric method for the determination of chromium(VI) in electroplating waste waters and total chromium(III) and (VI) in industrial waste waters using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. This was found to be the most sensitive reagent for chromium. The complex formed was very stable.

In this method a portion of sample containing not more than 15µg of chromium is transferred into a 100ml flask. 2ml of acetate buffer (pH 4.7), 1ml of 10% w/v hydroxylamine hydrochloride solution, and 2ml of 2(5-bromo-2-pyridylazo)-5-diethylaminophenol solution are added and 5ml water added. The flask is fitted with a stopper which carries a funnel. The flask is placed on an electric plate having a surface temperature of 100–105°C. The contents of the flask are heated until the volume of the solution is reduced to 3–5ml. The walls of the flask are rinsed with 5ml of ethanol and reflux continued for 40min. The flask is removed from the hot plate, and after cooling to room temperature 5ml of ethanol is added to dissolve the reagent and reaction product. The solution is transferred to a 25ml volumetric flask and made up to the mark with distilled water. The absorbance of the coloured solution is measured at 600nm, using a reagent blank as reference.

The effect of foreign ions on the determination of 10µg of chromium(III) was examined. The following ions (when present in the amounts in mg shown in brackets) do not interfere:

Na⁺, K⁺, NH₄⁺, Cl⁻, Br⁻, I⁻, NO₃⁻, SO₄²⁻, Ac⁻ (10);
 Li⁺, Ca²⁺, Mg²⁺, Sr²⁺, Al³⁺, Mn²⁺, Cd²⁺, SCN⁻, SiO₃²⁻, PO₄³⁻ (1);
 Be²⁺, Pb²⁺, As³⁺, La²⁺, La³⁺, Ce³⁺, Y³⁺, Ge⁴⁺, Sc⁴⁺, UO₂²⁺ (0.1);
 Zn²⁺, Th⁴⁺, F⁻ (0.05) and Ag⁺, Au³⁺, Hg²⁺, Sc³⁺, WO₄²⁻, VO₃⁻ (0.01).

Equal amounts of Fe³⁺, Cu²⁺, Co²⁺, Ni²⁺, Ga³⁺ and Tl³⁺ produce positive errors.

Table 8.8 shows the results of determination of chromium by the above method in comparison with the diphenylcarbazide method, o-toluidine [18], o-nitrophenylfluorone acid [19], and 2(5-bromo-2-pyridylazo)-5-diethylaminophenol have been used as chromogenic reagents in the determination of hexavalent chromium (chromate) in waste waters. Qi and Zhu [19] have reacted chromium(VI) with o-nitrophenylfluorene in the presence of acetyltrimethyl ammonium bromide to form a purple red complex at pH 4.7–6.6 by heating at 50°C for 10min. The wavelength of maximal absorbance was 582nm. Beer's law is obeyed up to 0.2µg L⁻¹ chromium(VI). Interference due to copper(II), iron (III) and aluminium(III) was eliminated by the addition of a masking agent containing potassium fluoride, trans-1, 2-diaminocyclohexane tetraacetic acid and potassium sodium tartrate.

8.6.2 Atomic absorption spectroscopy

Martin and Riley [20] used this technique to determine hexavalent chromium in waste waters.

8.6.3 Differential pulse polarography

Harndorf and Janner [21] applied this technique to waste water samples and investigated interference by other cations.

Table 8.8 Results of analysis by present method in comparison with diphenylcarbazide method

Sample No.	Water taken ml	Chromium found by present method μg	Chromium content in water sample mg L^{-1}	Chromium found by diphenylcarbazide method mg L^{-1}
1	20.0	2.30	0.115	0.1 10
2	10.0	6.00	0.600	0.550
3	2.0	5.56	2.78	2.65
4	4.0	7.40	1.82	1.73
5	2.5	9.1	3.64	3.76

Source: Reproduced with permission from Springer Verlag [17]

8.6.4 Miscellaneous

Pavel *et al.* [22] examined the behaviour and persistence of trace amounts of chromium (VI) in waste water samples as a function of pH, container material, initial concentration and temperature. Based on these results they devised a method for preserving the hexavalent form of chromium; following adjustment to pH 7–8, addition of 10% v/v of a solution containing 0.5M sodium bicarbonate and 0.1M EDTA (disodium salt) reduced losses of chromium(VI) to less than 20% after 7 days, compared with a 60–80% loss in unprotected samples.

8.7 Cyanate

8.7.1

Spectrophotometric method

The application of this technique is discussed under multianion analysis in section 14.2.3.2.

8.7.2 Paper chromatography

Thieleman [23] attempted the separations of cyanate, thiocyanate and cyanide ions by thin-layer and paper chromatography.

The three ions were successfully separated by paper chromatography using methanol:pyridine:dioxan (7:2:1) as solvent in 8h.

Cyanate was identified using a bromocresol purple spray reagent. Carbonate ions interfered.

Cyanate and cyanide in waste water have also been separated by paper chromatography [24]. Separation was achieved by the use of isopropyl alcohol:ethanol:water (9:4:3) as solvent with Filtrak FN8 paper. Bromo-cresol green solution was used as spray reagent which produced clear green spots on a blue background with cyanate and cyanide.

8.7.3 Miscellaneous

See section 14.12.5.1.

8.8 Cyanide (free)

8.8.1 Titration method

Workers at Orion Research Inc. US [25] have described a method for the determination of free cyanide in wastewaters from a cyanide extraction process of gold by a first derivative titration technique using an Orion 960 autochemistry system, equipped with an Orion silver/sulphide electrode and Orion Sure-Flow Reference electrode. One mL of 10N sodium hydroxide is added to 50ml of sample and titration is carried out using 0.1N silver nitrate to the single end-point indicated on an automatic recorder. Chloride, thiocyanate and thiosulphate have no effect on cyanide determination. Sulphide when present will cause two end points, the first for sulphide and the second for cyanide.

8.8.2 Spectrophotometric method

Fu-Sheng *et al.* [26] applied the copper-cation 2B-Triton A-100 system to the Spectrophotometric determination of micro accounts of free cyanide in waste water.

Nagashima and Ozawa [27] have given details for the determination of cyanide in aqueous samples by spectrophotometry, using isonicotinic acid and barbituric acid as reagents. Cyanide reacts with chloramine-T, and then the reagent is added to form a soluble violet-blue product, which is measured at 600nm. Maximum absorbance is achieved in 15min at 25°C and remains constant for about 30min. This method is applicable to water samples containing 0–5mg L⁻¹ cyanide. Results obtained on several plating waste waters are reported and show good agreement with those obtained by the conventional pyridine-pyrazolone method [28].

Details of the isonicotinic acid-barbituric acid procedure are given below.

In a dried reaction tube is placed 10ml of sample solution (pH 5–8) containing less than $-5\mu\text{g}$ of cyanide and free from sulphide and thiocyanate ions. 3.0ml of potassium dihydrogen phosphate solution (1mol L^{-1}) and 0.2ml of 1% (w/v) chloramine-T solution are added, the tube stoppered and shaken. After 1–2min, 5.0ml of isonicotinic acid-barbituric acid reagent is added and the tube stoppered again,

Table 8.9 Comparison of effect of diverse ions on the determination of $2.0\mu\text{g CN}^-/10\text{ml}$ by the isonicotinic acid-barbituric acid method

<i>Ion</i>	<i>Added as</i>	<i>Amount added ($\mu\text{g}/10\text{ml}$)</i>	<i>CN^- found (μg)</i>	<i>Error (μg)</i>
Cl^-	NaCl	1000	2.0	0.0
NO_2^-	NaNO_2	1000	1.9	-0.1
NO_3^-	KNO_3	1000	2.0	0.0
SO_3^{2-}	Na_2SO_3	100	2.0	0.0
		1000		
SO_4^{2-}	Na_2SO_4	1000	2.0	0.0
CH_3COO^-	$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$	100	2.0	0.0
OCN	KOCN	1000	1.9	-0.1
S^{2-}	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	1	2.0	0.0
		10	2.0	0.0
		100	0.9	-1.1
		1000		
SCN^-	KSCN	2	2.9	+0.9
		5	4.3	+2.3
Fe^{3+}	FeCl_3	100	2.1	+0.1
$\text{Fe}(\text{CN})_6^{4-}$	$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	100	2.0	0.0
$\text{Fe}(\text{CN})_6^{3-}$	$\text{K}_3[\text{Fe}(\text{CN})_6]$	10		
		100	2.0	0.0

Source: Reproduced with permission from Gordon AC Breach [27]

keeping the mixture at 25°C for 15min. The absorbance is measured at 600nm against a reagent blank.

The effect of diverse ions on the determination of 2mg L^{-1} cyanide by the above method is shown in Table 8.9. A large amount of sulphide caused a negative error and 1mg of sulphide did not develop colour. In the pyrazolone method, sulphite and ferricyanide also led to a negative error. Thiocyanate led to a significant positive error when sulphide or thiocyanate ions were present in a sample solution, and a suitable pretreatment is necessary for the removal.

The large positive error caused by thiocyanate suggested that the method could be used

for determining this ion. This method can be used, as described above, for the determination of free cyanide or, with a suitable sample pretreatment, to the determination of total cyanide. The pretreatment involves distillation with phosphoric acid and an alkaline 10% EDTA solution, using 2% sodium hydroxide or 2% sodium acetate as absorbent. For the sodium hydroxide solution (2%) absorbent, the receiving solution was neutralised with acetic acid.

Table 8.10 Determination of cyanide in plating waste waters by the isonicotinic acid-barbituric acid method and the pyridine-pyrazolone method in comparison

Sample	CN^- concentration (mg L^{-1})			
	<i>Isonicotinic acid-barbituric add method</i>		<i>Pyridine– pyrazole method</i>	
	2% NaOH	2% CH_3COONa	2% NaOH	2% CH_3COONa
I	0.04	0.04	0.03	0.04
II	0.11	0.12	0.10	0.12
III	0.19	0.18	0.19	0.18
IV	0.26		0.26	
V	0.35	0.34	0.34	0.35

Source: Reproduced with permission from Gordon AC Breach [27]

Table 8.10 shows the good agreement in results for total cyanide obtained on wastewater samples obtained by this method and by the spectrophotometric pyridine-pyrazolone method [28].

Tan [29] also reported a spectrophotometric method for determining cyanide in wastewater and non saline water using isonicotinic acid and barbituric acid as the colour-forming system with an absorption maximum at 600nm. The method had a detection limit of $0.6\mu\text{g L}^{-1}$ and recoveries >90%.

Another indirect spectrophotometric method for determining cyanide in wastewaters is based on its reaction with the complex mercury(II)– tetrakis(4-triammoniumphenyl)-porphyrin; decrease in the absorbance of the complex at 449nm is proportion to the cyanide concentration [30]. In another study cyanide was reacted with copper(II) and cetyltrimethylamine bromide to form a stable ternary complex which was extractable into butanol and determined by atomic absorption spectrophotometry [31]. This method has a detection limit of $3\mu\text{g L}^{-1}$ and the coefficient of variation was in the range of 1.77–1.81%. Another spectrophotometric method for determining cyanide was based on its reaction with bromine to form cyanogen bromide followed by reaction of the latter with pyridine [32]. The gluconaldehyde so formed is coupled with phloroglucinol to form a red violet dye, the absorbance of which is measured at 540nm. Beer's law was obeyed over the range of 400–300 $\mu\text{g L}^{-1}$.

The application of this technique is also discussed under multianion analysis in section

14.2.3.2.

8.8.3 Flow injection analysis

Zhu and Fang [33] used an automated flow-injection system with gas-diffusion separation and preconcentration, coupled with spectrophotometric detection, to determine cyanide in wastewaters. An unstable red intermediate product of the reaction of cyanide with isonicotinic acid 3-methyl-1-phenyl-2-pyrazolin-5-one is measured in the determination. The sampling frequency was 40 samples/h and the detection limit was $0.6\mu\text{g L}^{-1}$ with a 2mL sample; the relative standard deviation was 1.4% ($n = 22$) at the 0.5mg L^{-1} level

8.8.4 Atomic absorption spectrometry

Rosentreter and Skogerboe [34] have used this technique to study the trace determination of speciation of free cyanide in wastewaters.

By utilising a high selective reaction between silver metal and cyanide ions, these workers developed an apparatus and procedure for the analytical determination of aqueous cyanide species. The rapid analysis of free cyanide was achieved through the use of pure silver filters as the reaction medium and atomic absorption spectroscopy as the detection method. This methodology has allowed for the quantitative detection of cyanide ions down to the sub-parts-per-billion level. By incorporating selective oxidation, kinetic equilibria, and photo-dissociation techniques, the silver-cyanide reaction technique has been adapted to provide a means of categorically speciating aqueous cyanide compounds. The complete system has been shown to be free from common chemical interferences, including thiocyanate. This detection system provides high-speed cyanide determinations with little to no sample preparation or instrument supervision.

8.8.5 Chronopotentiometry

Procopio *et al.* [35] carried out an indirect determination of cyanide in waste waters by this technique. Cyanide was determined by measuring the displacement of the quarter wave potential of the chronopotentiometric graph of formaldehyde. After separation of the cyanide by distillation into alkaline media, formaldehyde solution was added and the resultant solution transferred to the cell of a constant current coulostat. A constant potential of -1.4V was applied for 5min while nitrogen flowed through continuously. The potential was removed and the solution allowed to become quiescent, before applying a constant current to the working gold electrode. A transition time of 30s was obtained. From the displacement of the formaldehyde curve with and without cyanide present, a detection limit of $10\mu\text{g L}^{-1}$ cyanide was obtained with a relative error of less than 2% and a relative standard deviation of 1%.

8.8.6 Ion selective electrodes

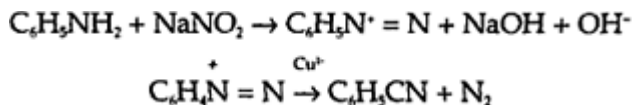
Ion selective potentiometry in alkaline solution provides a suitable finish for the

determination of cyanide [36–39]. Sulphide ion is an interferent, a cadmium nitrate treatment has been found to remove sulphide without influencing the response of the silver iodide-silver sulphide electrode. If both the precipitate and solution from this treatment are colourless (sulphide absent) filtration of the mixture before the potentiometric measurement is unnecessary. Since the electrode response of the electrode is pH dependent, standards and samples must be brought to the same pH. It is noteworthy that the silver/silver sulphide electrode (eg Orion 94–16) is more sensitive to cyanide than the silver iodide-silver sulphide one [38,40], but the response is affected by cadmium ion.

Fraut *et al.* [40] have described an electrode indicator technique for the determination of low levels of free cyanide in waste waters. Concentrations of cyanide down to $30\mu\text{g L}^{-1}$ are determined with the use of the Ag^+ selective electrode and $10\mu\text{M Ag}(\text{CN})_2^-$ as indicator solution. The pH of the sample is adjusted to between 11 and 12 and an addition procedure is used, the concentration of cyanide in the sample being obtained by use of a Gran plot; samples containing more than 260mg L^{-1} of cyanide must be diluted initially. Copper and nickel are masked with EDTA and any sulphide removed by addition of lead ions in slight excess. Ammonia does not interfere even in a 1000-fold excess.

8.8.7 Gas chromatography

Funazo *et al.* [41] have described a method for the determination of cyanide in water in which the cyanide ion is converted into benzonitrile by reaction with aniline, sodium nitrite and cupric sulphate. The benzonitrile is extracted into chloroform and determined by gas chromatography with a flame ionisation detector. The detection limit for potassium cyanide is 3mg L^{-1} . Lead, zinc and sulphide ion interfere at 100mg L^{-1} but not at 10mg L^{-1} .



More recently, Funazo *et al.* [42] have described a more sensitive gas chromatographic procedure capable of determining down to $3\mu\text{g L}^{-1}$ total cyanide in waste waters. The method is based on the derivatisation of cyanide to benzonitrile, which is extracted with benzene and determined

Table 8.11 Results of interference study CN^- concentration: $0.5\mu\text{g/mL}$

<i>Ion</i>	<i>Concentration Added as (mg L⁻¹)</i>	<i>Peak area^a</i>
None		100.0±2.0
F^-	500 NaF	99.2±1.7
Cl^-	500 NaCl	99.4±0.2
Br^-	500 NaBr	100.2±1.8
I^-	500 KI	98.6±1.3
SO_4^{2-}	500 Na_2SO_4	100.4±3.2
NO_3^-	500 NaNO_3	100.8±2.5
HCO_3^-	500 KHCO_3	99.9±1.9
H_2PO_4^-	500 KH_2PO_4	99.4±0.8
SCN^-	500 NaSCN	86.0±2.1
SCN^-	100 NaSCN	99.0±3.0
CNO^-	500 KCNO	104.1±0.7
CNO^-	100 KCNO	102.8±1.7
S^{2-}	0.1 $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	90.9±4.6
S^{2-}	0.05 $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	100.2±2.3
NH_4^+	500 $(\text{NH}_4)_2\text{SO}_4$	101.8±1.7

^aMean±S.D. of five replicate analyses

Source: Reproduced with permission from Elsevier Science [42]

by flame thermionic gas chromatography. In the derivatisation reaction, aqueous cyanide reacts with aniline and sodium nitrite in the presence of copper(II) sulphate and forms benzonitrile.

Funazo *et al.* [42] tested this method in the presence of several ions normally found in environmental samples (Table 8.11). The peak area of benzonitrile derivatised from the standard cyanide solution (0.5mg L^{-1}) was arbitrarily assigned a value of 100.

None of the ions except thiocyanate, cyanate and sulphide interfered at a concentration of 500mg L^{-1} . At this concentration, thiocyanate interferes negatively and cyanate positively. However, these interferences are not observed at the 100mg L^{-1} level. Sulphide ion interferes at relatively low concentrations, even at 0.1mg L^{-1} , a negative interference is observed. Similar interferences of sulphide are well known in the pyridine pyrazolone method and in the method using a cyanide ion selective electrode. However, sulphide can be removed from the sample solution by treating the alkaline sample at pH 11.0 with small amounts of powdered lead carbonate.

Funazo *et al.* [42] analysed several wastewater samples from various factories using cyanide, such as metal refining and plating factories by the gas chromatographic and by the spectrophotometric pyridine pyrazolene

Table 8.12 Comparison of spectrophotometric and gas chromatographic methods for the analysis of waste water samples

Sample	Cyanide concentration (mg L ⁻¹)	
	Spectrophotometric method ^a	Gas chromatographic method ^b
A	0.48	0.51±0.015
B	0.20	0.20±0.006
C	0.13	0.16±0.002
D	0.08	0.03±<0.0005
E	0.08	0.09±0.002

^aPyridine-pyrazolone method

^bMean=S.D. of five replicate analyses

Source: Reproduced with permission from Elsevier Science [42]

methods. Instantly after collection, sodium hydroxide was added to the samples and the solution was adjusted to pH 12–13 in order to prevent the evolution of hydrogen cyanide. The results show that the values measured by the two methods agree well (Table 8.12).

Nota and Improta [43] determined cyanide in coke oven waste water by gas chromatography. The method is based on treatment of the sample with bromine and direct selective determination of the cyanogen bromide by gas-solid chromatography using a BrCN⁻ selective electron capture detector. No preliminary treatment of the sample to remove interferences is necessary in this method, and in this sense it has distinct advantages over many of the earlier procedures. Bromine also oxidises thiocyanate to cyanogen bromide. Previous treatment of the sample with aqueous formaldehyde destroys thiocyanate and prevents its interference.

Some typical results of cyanide analysis of coke oven water and coke oven water effluents are reported in Table 8.13, and are compared with the results obtained following the procedure suggested by the Standard Methods [44].

Generally, results obtained by the APHA standard method [44] are some 15% lower than those obtained by gas chromatography.

Nota *et al.* [45] have made the cyanogen bromide technique for determining cyanides and thiocyanate more sensitive and reproducible by adopting the headspace technique. This technique lends itself to automation.

Nota *et al.* [46] have also described a gas chromatographic headspace method based on different principles for the determination of 0.01–100mg L⁻¹ of cyanide and thiocyanate in coke oven waters and waste effluents. This method involves first transforming the

cyanides, or the thiocyanates,

Table 8.13 CN^- determination in some typical samples of coke-oven water (A–E) and coke-oven water effluent into the sea (F–J)

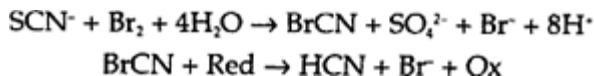
Sample	mg L ⁻¹				
	Standard methods	Gas chromatographic method	CN^- added	Standard methods	CN^- recovered gas chromatographic method
A	39.0	44.0	20.0	18.6	20.2
B	50.0	55.0	20.0	17.5	20.3
C	62.0	70.0	25.0	23.0	25.1
D	47.0	53.0	5.0	4.6	4.91
E	46.0	52.0	5.0	4.5	4.93
F	0.27	0.295	0.150	0.134	0.147
G	0.27	0.307	0.150	0.137	0.154
H	0.31	0.353	0.175	0.150	0.178
I	0.25	0.263	0.050	n.d.	0.047
J	0.37	0.414	0.50	n.d.	0.048

To each sample a known amount of KCN was added to check the recovery. Concentrations are expressed in ppm

Source: Reproduced with permission from Elsevier Science [43]

into hydrogen cyanide by acidification with 85% phosphoric acid, then removing hydrogen cyanide from the aqueous sample by the headspace technique, and finally separating hydrogen cyanide by gas solid chromatography and selective detection with a nitrogen phosphorus detector. Any oxidising agents present in the sample must be reduced with sodium sulphite prior to heating the sample.

A similar procedure is adopted for the determination of thiocyanate, the only difference being the quantitative transformation of thiocyanate into hydrogen cyanide according to the reactions:



(where Red=SO₂ or I⁻ and Ox=SO₄²⁻ or I₃⁻). If cyanide is present prior to the oxidation step, it must be transformed into unreactive cyanohydrin by an excess of formaldehyde or removed by boiling the solution previously acidified to pH 2.

The headspace conditions were as follows: needle temperature, 100°C; flushing of

sampling capillary, 15s; pressurisation of sample vial, 60s; sample withdrawal from headspace, 5s; 20ml vials thermostated at 80°C for 10min were used. Under these conditions the retention time of hydrogen cyanide was 5min.

Table 8.14 Influence of sodium chloride concentration on the HCN response

<i>Amount of CN⁻ (mg L⁻¹)</i>	<i>NaCl added (%)</i>	<i>Peak height (cm)</i>	<i>Increase(%)</i>
1.00	0	7.4	–
1.00	10	8.2	11
1.00	20	8.8	19
1.00	30	9.4	27

Source: Reproduced with permission from Elsevier Science [43]

Table 8.15 Standard additions method applied to a 2mg L⁻¹ CN⁻ sample

<i>Aliquot No.</i>	<i>Amount of CN⁻ present (μg)</i>	<i>Sample volume (ml)</i>	<i>CN⁻ added (μg)</i>	<i>Peak height (cm)</i>
1	10	5.00	0.00	5.5
2	10	5.00	1.00	6.1
3	10	5.00	2.00	6.5
4	10	5.00	4.00	7.7
5	10	5.00	5.00	8.3

Source: Reproduced with permission from Elsevier Science [43]

A F42 gas chromatograph (Perkin Elmer) equipped with a headspace device or equivalent and a nitrogen phosphorus detector were employed. The column (2m×0.3cm id) was made of borosilicate glass and packed with Poropak Q. Methods were developed to determine cyanide alone, thiocyanate in the absence of cyanide and thiocyanate in the presence of thiocyanate.

Table 8.14 shows the effect of the salt concentration on the response for hydrogen cyanide. The matrix effect can be avoided by making use of the method of standard additions, as illustrated by the results in Table 8.15 for a solution containing 2mg L⁻¹ of cyanide. The presence of iron(II), iron(III) and copper(II) in the sample decreases the response for hydrogen cyanide. The greatest effect is caused by copper(II). Reducing agents do not interfere in the analysis of cyanide but oxidising substances have to be reduced prior to heating of the sample. Oxidants and reducing agents do not interfere in the determination of thiocyanate.

Typical results for the analysis of cyanide in some coke oven waste waters and coke

oven waste effluents are reported in Table 8.16.

The results for samples A–D analysed by the headspace method [44] and the cyanogen bromide method [43] are in good agreement. Samples E–H show good agreement when analysed by the headspace method and

Table 8.16 Comparison with BrCN method and accuracy of proposed procedure

Sample	CN– determined (mg L ⁻¹)			CN– recovered by HS method (mg L ⁻¹)		
	BrCN method	HS method		By calibration graph	By standard additions method	
A	53	52	–	25.0	25.1	–
B	65	65	–	20.0	20.0	–
C	42	43	–	20.0	25.2	–
D	58	57	–	5.00	5.04	–
E	0.20	0.23	0.21	0.150	–	0.150
F	0.37	0.41	0.38	0.150	–	0.150
G	0.25	0.28	0.25	0.150	–	0.149
H	0.30	0.34	0.30	0.020	–	0.021

Source: Reproduced with permission from Elsevier Science [43]

the standard additions method. The results obtained by using a calibration graph are appreciably higher owing to the different matrix of the standards and the samples.

The accuracy of the procedure was tested by spiking samples A–H with a known amount of cyanide; the recoveries, reported in the last two columns in Table 8.16 are excellent.

8.8.8 Miscellaneous

da Nascimento and Schwedt [47] have compared several methods for the determination of cyanide in waste waters. See also section 14.12.5.1.

8.9 Cyanide (total)

Total cyanide includes free cyanide ions plus complexed metal cyanides, eg

ferrocyanides. The methods discussed in the previous section determine only free uncomplexed cyanide. To determine uncomplexed plus complexed cyanide, ie total cyanide, it is necessary prior to analysis to decompose the complexed cyanides to free cyanide.

Overbach [38] discussed problems encountered in the determination of low concentrations of cyanide in photographic processing waste waters. Determination of both total and free cyanide in the same sample differentiates between the toxic free cyanide and the complexed ferrocyanide. Because of possible instability of the cyanide, he recommended that samples should be analysed on site, for instance by the microdiffusion technique.

The determination of concentrations of total and labile cyanide is very important for many environmental and industrial applications. The sample pretreatment to obtain free cyanide is perhaps the most important aspect in cyanide analysis. The standard methods for cyanide analysis use acid distillation procedures to decompose metal cyanide complex. The standard methods have several drawbacks. The distillation procedure is very time-consuming and labour-intensive. The methods also suffer seriously from a number of interferences such as sulphide and thiocyanate. A different approach of sample pretreatment based on the photo-dissociation reactions of metal-cyanide complexes under ultraviolet-visible irradiation has been studied for the determination of total cyanide. Those studies have shown that complete decomposition of stable complexes such as $\text{Fe}(\text{CN})_6^{3-}$ can be obtained in a few minutes when the sample solution is exposed to intense irradiation from high pressure mercury lamps of several hundred watts. However, thiocyanate interferes since it is converted to cyanide under ultraviolet irradiation when quartz tubings or vessels are used as reactors. The Pyrex glass reactor avoids the photoconversion of thiocyanate to cyanide.

The separation of cyanide ion from interferences is required in the determination of cyanide because the measurement methods are usually prone to interferences such as sulphide and thiocyanate. The tedious procedures such as precipitation and extraction are used in standard methods. Gas diffusion methods using hydrophobic porous membranes have also been studied. Cyanide is separated as hydrogen cyanide gas from the acidic solution and hydrogen cyanide gas is collected in the basic solution on the opposite side of the membrane. The gas diffusion method separates cyanide from most ionic species in the sample solution. The drawback of the method is that it does not separate cyanide from sulphide since hydrogen sulphide gas also diffuses across the membrane, ion chromatography methods have been shown to be advantageous in the separation of cyanide from sulphide (see section 8.10.1). However, these methods may be subject to interferences.

8.9.1 Spectrophotometric method

Kollau and Reidt [48] determined total cyanide and cyanogen chloride in amounts down to 0.1 ml L^{-1} in waste water. To determine total cyanide, hydrogen cyanide is liberated by distillation with sulphuric acid and collected in aqueous sodium hydroxide. Cyanide is determined spectrophotometrically at 578nm after chloramine-T oxidation of cyanide to cyanogen chloride and formation of the coloured complex with pyridine and barbituric

acid.

Hartzinger [49] critically examined the D 13/3 German standard method the determination of free and complexed cyanides in waste water. He points out that interfering substances causing high results in the determination of cyanide in effluents by this pyridine-benzidine method (usually carried out at pH 7) appear to be unknown N-containing heterocyclic compounds, which, in the presence of cyanide, yield polymethine dyes. In cases of doubt the analysis is repeated after adjustment of the pH to 5.5–5.0 by use of an ion exchanger, thus avoiding the involved distillation procedure. The extinction at 480nm is decreased by 70–75% at the lower pH, so that errors of greater than 0.1mg L⁻¹ in the cyanide concentration can be avoided.

Goulden *et al.* [50] determined simple and complex cyanides in waste water by modifying the APHA standard distillation colorimetric method [51] to ensure accurate results for less than 100µg L⁻¹ cyanide. In the manual procedure, the sample is distilled under reflux with sulphuric acid in the presence of aqueous magnesium chloride and mercuric chloride, the absorption system being modified by recirculating the absorbent (0.2mol L⁻¹ sodium hydroxide) by a peristaltic pump through a column packed with glass helices. The lower limit of detection is 5µg L⁻¹ cyanide but this is lowered to 1µg L⁻¹ by using an AutoAnalyser system in which is included a ultraviolet irradiation cell to decompose complex cyanides, eg those of iron and cobalt; this cell is by-passed when only simple cyanides are being determined. The hydrogen cyanide is evolved in a continuous distillation apparatus, a mixture of phosphoric acid (1.2N) and dilute H₃PO₂ being used, because these acids also inhibit oxidation of cyanides during irradiation or by any free chlorine present etc. The absorbent is 2% aqueous sodium acetate (pH 6.5), use of which eliminates one stage in the pyridine-pyrazolone colorimetric procedure. With a 7ml sample the automated method has a detection limit of 7ng, the coefficient of variation was 1.2% at the 40µg L⁻¹ cyanide level.

Royer *et al.* [52] determined total cyanide in waste water by an Autoanalyser procedure. They used magnesium chloride and mercuric chloride in the carrying solution to decompose complex metal cyanides. Down to 10µg L⁻¹ total cyanide could be determined by this procedure.

A spectrophotometric method has been described for the determination in waste waters of total cyanide, including free cyanide, complex cyanides and thiosyanates [53]. Thiocyanates, together with simple and complex cyanides, are reacted with acid cuprous chloride and the hydrogen cyanide formed is absorbed in a sodium hydroxide solution which is then made slightly acidic to prevent hydrolysis to cyanate. Chloramine-T is added to produce cyanogen chloride, a pyridine/ pyrazolone reagent is added, and the optical absorbance of the resulting blue dye is measured at 620nm. Volatile aldehydes and ketones interfere in the final colour development.

Csikai and Barnard [54] used EDTA at pH 4 to displace cyanide from metal complexes and to avoid converting thiocyanate to free cyanide where oxidants are present. Sulphamic acid is added to prevent nitrite interference, sulphides are removed from the sample with calcium carbonate and from distillates with cadmium nitrate. Evolved cyanide is determined by pyridine-barbiturate photometry or potentiometrically with ion selective electrodes.

Czikai and Barnard [54] evaluated their procedure by adding both free cyanide and

complex metal cyanides to both deionised water solutions and wastewater samples containing or spiked with nitrate and thiocyanate. The recovery of cyanide was virtually complete.

For the cyanide complexes of chromium, copper, iron, and nickel, the recovery of cyanide was usually greater than 95%. As mentioned previously, the failure to disrupt hexacyanocobaltate(III) due to its kinetic inertness, is a limitation of most total cyanide procedures.

Leschber and Schlichting [55] discussed the decomposability of complex metal cyanides in the determination of cyanide in waste water. These workers found that complex cyanides of zinc, cadmium, copper, nickel, iron(II) and iron(III) corresponding to 1–100 mg L⁻¹ cyanide are easily decomposed by distilling the sample in the presence of dilute sulphuric acid and total cyanide can be determined in the distillate. However, K₃(Co(CN)₆) (hexacyano cobalt(III)) is only partially decomposed by this treatment.

Drikas and Routley [56] have described a spectrophotometric method for the determination of total cyanide in waste water samples.

8.9.2 Flow injection analysis

Zhu and Fang [33] have described a spectrophotometric determination of total cyanide in waste waters in a flow injection system with a gas diffusion separation. The method is based on the formation of the unstable red intermediate product of the reaction of cyanide with isonicotinic acid and pyrazolone. A detection limit of 0.6 µg L⁻¹ was achieved. Cobalt interfered in this method.

8.9.3 Atomic absorption spectroscopy

Rameyer and Janauer [57] have described a method using reactive ion exchange for the determination of complex iron cyanides in water in the mg L⁻¹ range. The cyanide complexes are preconcentrated on shallow beds of sulphonated cation-exchange resin in the copper(II) form by precipitation as copper hexacyanoferrate(II) or copper hexacyanoferrate(III). Other cations, including contaminant iron species, are eluted with hydrochloric acid. Aqueous ammonia relatively releases and elutes the hexacyanoferrate by the formation of the copper amine complex. Finally the complex cyanides are determined as iron by atomic absorption spectrometry.

8.9.4 Ion selective electrodes

A procedure has been developed for determination of cyanide [58] in concentrations down to 2 mg L⁻¹ by manual or automated potentiometry using a cyanide ion selective electrode. Distinction is made between simple and complex cyanides by irradiation with ultraviolet light.

Csikai and Barnard [54] used EDTA at pH 4 to displace cyanide from metal complexes and to avoid converting thiocyanate to free cyanide from metal where oxidants are present. Sulphamic acid is added to prevent nitrite interference, sulphides are removed from the sample with calcium carbonate and from distillates with cadmium nitrate.

Evolved cyanide is determined by pyridine-barbiturate photometry or potentiometrically with ion selective electrodes.

The initial sample (600ml) is preserved by the addition of 5ml 50% sodium hydroxide. To remove sulphide 0.2g cadmium carbonate is added to 600ml of preserved sample and the solution filtered. A portion of this

Table 8.17 Total cyanide values for waste water samples by high-acidity and EDTA displacement procedures

Sample nature ^a	Thiocyanate present mg L ⁻¹	Nitrate present mg L ⁻¹	Total cyanide found, mg L ⁻¹			
			High-acidity procedure		EDTA displacement procedure	
			Not added	Added	Sulphamic acid Not added	Added
WW H	<0.2	71	<0.02		<0.02	
WW I	<0.2	97	0.02		0.01	
WW J	<0.2	105	<0.02		<0.02	
WW K	<0.2	173	<0.02		<0.02	
WW L	1.2	90	0.37		0.07	
WW M	2.0	31	0.66		<0.02	
WW N	3.0	294	0.40		0.02	
WW O	4.0	9	0.60		0.07	<0.02
WW P	4.2	100	1.5		0.12	
WW Q	4.6	105	1.10		0.02	
WW R	5	102	2.2		<0.02	
WW S	5	33	1.20		0.02	
WW T	6	66	3.4		0.01	
WW C	6	127	2.0	0.26	0.12	0.02
WW F	9	140	2.8	0.16		<0.02
WW U	12	64	4.9		0.03	
WW V	15	91	4.7		0.18	<0.02
WW W	17	139	0.8		0.02	

^aWW=wastewater

Source: Reproduced with permission from the American Chemical Society [54]

sample is treated with sulphamic acid and disodium ethylene diamine tetraacetic acid,

then 2.5mole L⁻¹ sulphuric acid is added drop-wise until the solution becomes just red coloured to methyl red indicator. The solution is then rendered just alkaline (ie yellow colour) and buffered to pH 4.0. The solution is then heated and purged with air to liberate hydrogen cyanide which is collected in cadmium nitrate solution. Cyanide is then determined in this solution using a cyanide electrode (silver iodide silver sulphide, Orion 94-06 or equivalent) and a reference electrode (Orion 94-02 double junction or equivalent).

In many of the previously described procedures for total cyanide, high acidity is used as a means of decomposing complex cyanides prior to the determination of free cyanide ion. Csikai and Barnard [54] used a low acidity decomposition procedure (EDTA displacement at pH 4) and, in so doing, avoid interference by thiocyanate as illustrated in Table 8.17.

Table 8.18 Recovery of cyanide from complex metal cyanides by EDTA displacement procedure without sulphamate added

Sample nature ^a	Thiocyanate nitrate (present+added)		Cyanide (total)			
	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹ present	mg L ⁻¹ added	mg L ⁻¹ found	% Cyanide added Recovered as complex ^c of
DIW	0	0	0	1.00	1.00	100 Fe
DIW	0	0	0	1.00	1.00	100 Fe
DIW	0	0	0	1.00	0.99	99 Fe
DIW	0	0	0	1.00	0.96	96 Fe
DIW	0	0	0	5.00	4.95	99 Fe
DIW	0	0	0	5.00	4.85	97 Fe
DIW	0	0	0	1.00	1.00	100 Fe
DIW	0	0	0	1.04	1.07	103 Ni
DIW	10	100	0	1.04	0.81	78 Ni
DIW	10	100	0	5.00	4.95	99 Fe
DIW	10	100	0	1.00	1.01	101 Fe
DIW	10 ^b	100	0	1.00	0.91	91 Fe
DIW	10	100	0	1.00	1.01	101 Fe
DIW	10	100	0	5.00	5.04	101 Fe
DIW	10	100	0	5.00	5.17	103 Fe
DIW	50	200	0	1.00	1.00	100 Fe
DIW	50	1000	0	1.00	1.00	100 Fe

WW AA	<0.2	131	<0.02	1.00	0.98	98 Cr
WW AB	<0.2	74	<0.02	1.00	<0.02	<2 Co
WW AB	<0.2	74	<0.02	1.00	1.00	100 Cu
WW AC	<0.03	120	<0.02	2.00	1.84	92 Fe+Ni
WW AD	1.0	41	0.02	2.00	2.02	100 Fe+Ni
WW AE	5.0	11	<0.02	1.00	1.01	101 Fe
WW AF	10	100	0.04	1.04	0.96	96 Ni
WW AF	10	100	0.04	1.04	0.96	96 Ni
WW AG	19	55	<0.02	0.40	0.37	93 Fe
WW AG	19	55	<0.02	0.40	0.36	90 Fe
WW AG	19	55	<0.02	0.40	0.37	93 Fe
WW AG	19	55	<0.02	0.40	0.38	95 Fe
WW AG	19	55	<0.02	0.40	0.36	90 Fe

^aDIW=deionised water; WW=waste water

^b10 mg L⁻¹ sulphide also added

^cAdded as Fe(CN)₄³⁻, Ni(CN)₄²⁻, Cu(CN)₄³⁻, Cr(CN)₄³⁻ and Co(CN)₄³⁻

Source: Reproduced with permission from the American Chemical Society [54]

Table 8.18 presents typical results for wastewater samples containing thiocyanate. The values clearly indicate that the thiocyanate interference encountered in high-acidity procedure is avoided with the EDTA displacement procedure.

Table 8.19 Total cyanide values by photometric and ISE-potentiometric finishes for samples treated by EDTA displacement procedure (values expressed in terms of original samples taken for distillation)

Nature of sample distilled ^a	Total cyanide found, mg L ⁻¹	
	by photometry	by ISE-potentiometry
DIW	0.07	0.07
DIW	0.40	0.50
DIW	0.50	0.43
DIW	0.70	0.80
DIW	0.95	0.80
DIW	1.01	1.02
DIW	1.08	1.20

DIW	1.30	1.10
DIW	5.1	5.2
DIW	5.1	5.1
WW CA	0.06	0.06
WW CB	0.13	0.10
WW CC	0.31	0.29
WW BE	0.41	0.33
WW CD	0.66	0.64
WW CE	0.93	0.95
WW CF	0.96	0.97
WW CG	1.9	2.2

^aDIW=deionised water; WW=wastewater

Source: Reproduced with permission from the American Chemical Society [54]

Czikai and Barnard [54] evaluated their procedure by adding both free cyanide and complex metal cyanides to both deionised water solutions and wastewater samples containing or spiked with nitrate and thiocyanate. The recovery of cyanide was virtually complete. Typical findings for complex metal cyanides are presented in Table 8.18. For the cyanide complexes of chromium, copper, iron and nickel, the recovery of cyanide was usually greater than 95%. As mentioned previously, the failure to disrupt hexacyanocobaltate(II) due to its kinetic inertness is a limitation of most total cyanide procedures.

In Table 8.19 some results obtained by both the spectrophotometric and the cyanide electrode potentiometric finishes are presented. The similarity of cyanide determinations obtained by these two different procedures confirms that cyanide only is being determined.

8.9.5 Gas chromatography

Complex cyanides have been determined gas chromatographically in amounts down to $100\mu\text{g L}^{-1}$ [59]. The complex cyanides are broken down by ultraviolet radiation, reacted with bromine water and the cyanogen bromide formed is separated and determined selectively by means of an electron capture detector.

8.9.6 Miscellaneous

Overbach [38] discussed problems encountered in the determination of low concentrations of cyanide in photographic processing waste waters. Determination of both total and free cyanide in the same sample differentiates between the toxic free cyanide and the complexed ferrocyanide. Because of possible instability of the cyanide, he recommended that samples should be analysed on-site, for instance by microdiffusion

technique.

Bakensky [60] discussed inaccuracies in complex formation methods used to determine free and bound cyanide.

Pohlandt *et al.* [61] have critically evaluated 92 methods applicable to the separate determination of free cyanides and complex cyanides in waste waters and process streams. These include titrimetric, spectrophotometric, potentiometric, amperometric, polarographic, voltammetric, ion selective electrodes, indirect atomic absorption spectrometric, gas chromatographic and automated techniques. From this work it appears that most titrimetric, colorimetric and electrochemical methods (including potentiometry and the use of cyanide-selective electrodes) for the determination of ionic cyanide are liable to interference from ionisable metal cyanide complexes, eg $\text{Zn}(\text{CN})_4^{2-}$. These methods can therefore be employed only if such complexes are known to be absent. Potentially accurate methods for the determination of ionic cyanide include ion chromatography (because of its ability to effect separations) and indirect atomic absorption spectrophotometry based on the selective formation of $(\text{Ag}(\text{CN})_2)^-$.

Similarly, none of the methods mentioned gives a reliable result for the total amount of cyanide present in a sample. The decomposition of stable complexes and the separation from interfering substances by distillation is therefore necessary. However, most distillation procedures cannot effect the decomposition of all the metal cyanide complexes and they suffer from interferences. The most useful distillation procedure appears to be the ligand displacement technique [61]. With this method, interference from sulphide and thiocyanate can be avoided and all the ionic and coordinated cyanide—except cyanide from $(\text{Co}(\text{CN})_4)^{3-}$ —present in a sample can be distilled out.

Because of the speed in decomposing cyanide complexes, irradiation with ultraviolet light warrants further attention. A combination of this method with the separation, by ion chromatography, of interfering species might result in a fast method for the determination of total cyanide.

8.10 Cyanide, free and total

8.10.1 Ion chromatography

This is emerging as the method of choice for the determination of cyanides. Nonomura [62] determined free cyanide and metal cyanide complexes in wastewaters by ion chromatography with conductivity detection.

The cyanide is not detected by the conductivity detector of the ion chromatograph due to its low dissociation constant ($pK=9.2$). Nonomura [62] described an ion chromatographic method for the determination of free cyanide and metal cyanide complexes that uses a conductivity detector. It is based on the oxidation of cyanide ion by sodium hypochlorite to cyanate ion ($pK=3.66$). Therefore, cyanide ion can now be measured indirectly by the conductivity detector. In this procedure, optimum operating conditions were examined. In addition, the interferences from anions and reducing agents were investigated. The method was applied to the determination of metal cyanide complexes. The coefficients of variation (%) for CN^- (1.05mg L^{-1}), $\text{Zn}(\text{CN})_4^{2-}$ (CN^- ,

0.80mg L⁻¹) and Ni(CN)₄²⁻ (CN⁻, 0.96mg L⁻¹) were 1.1%, 1.5% and 0.5%, respectively.

Lui *et al.* [63] have described an automated system for determination of total and labile cyanide in water samples. The stable metal-cyanide complexes such as Fe(CN)₆³⁻ are photo-dissociated in an acidic medium with an on-line Pyrex glass reaction coil irradiated by an intense mercury lamp. The released cyanide is separated from most interferences in the sample matrix and is collected in a dilute sodium hydroxide solution by gas diffusion using a hydrophobic porous membrane separator. The cyanide ion is then separated from remaining interferences such as sulphide by ion exchange chromatography and is detected by an amperometric detector. The characteristics of the automated system were studied with solutions of free cyanide and metal-cyanide complexes. The results of cyanide determination for a number of wastewater samples obtained with this method were compared with those obtained with the standard method. The sample throughput of the system is eight samples per h and the detection limit for total cyanide is 0.1µg L⁻¹.

8.11 Ethylene diamine tetraacetate

8.11.1 Liquid chromatography

Dai and Helz [64] carried out a liquid chromatographic determination of ethylene diaminetetraacetate using an amperometric detector. Down to 0.15mg L⁻¹ of this anion can be determined in waste water.

8.12 Fluoride

8.12.1 Microdiffusion method

Microdiffusion has been applied [65] to the determination of down to 50µg L⁻¹ fluoride in waste waters, effluents and river waters. The sample (1ml containing <25µg of fluoride ion) is placed in the outer compartment of a polypropylene Conway-type diffusion cell containing 1ml of 0.5N sodium hydroxide in a polystyrene cup in the inner compartment, then 1ml of 70 vol% sulphuric acid is rapidly added to the sample and a polystyrene lid, greased with silicone, is placed on the cell, which is then heated in an oven at 65°C for 5h. To the dried residue in the centre cup is added 1 drop of phenolphthalein solution and the contents are washed with water into a volumetric flask. Fluoride is then determined by the lanthanum complexan or spectrophotometric procedure [66,67],

8.12.2 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.7.1 and 12.7.2.

8.13 Iodide

8.13.1 Titration method

Erdey and Kozmutza [68] used xenon difluoride as a reagent for the determination of mg L⁻¹ quantities of iodide and iodine in nuclear reactor cooling waters. The test solution is made IN in sulphuric acid and excess solid xenon difluoride added to convert iodide to periodate which is then determined by standard iodometric procedures.

8.14 Nitrate

8.14.1 Spectrophotometric method

Nitrates have been determined [69] in waste water in the presence of nitrites by a spectrophotometric method using salicylane as the chromogenic agent. Nitrites interfere in the determination of nitrates using the salicylane method but can be removed by amino sulphonic acid. The spectrophotometric method with salicylane may be used for determining nitrate levels of up to 20mg L⁻¹ nitrate-nitrogen in the presence of equimolar concentrations of nitrite-nitrogen.

The application of this technique is also discussed under multianion analysis in section 14.2.3.1.

8.14.2 Electrophoresis

The application of this technique is discussed under multianion analysis in section 7.28.1.

8.14.3 Ion selective electrodes

Hua [70] used an ion selective electrode to determine nitrate in wastewater; EDTA was added to prevent electrode contamination and improve reproducibility. The detection limit was 0.1mg L⁻¹ and the linear range was 1–1000mg L⁻¹ as nitrate nitrogen; the relative standard deviation was 0.10–2.6% and recoveries were 102–108%.

8.14.4 Roman spectroscopy

Furaya *et al.* [71] have used resonance Raman spectroscopy to determine nitrite in waste waters. They also proposed a method for simultaneous determination of nitrite and nitrate. These workers [72] have also discussed a laser Raman spectroscopic method for the determination of down to 1mg L⁻¹ nitrate in waste waters.

Raman Spectra were recorded on a JASCO Model J-800 Laser Raman Spectrophotometer. A Spectra-Physics Model 164 argon ion laser was used as an exciting source. As a detector, an HTC-R-464 photomultiplier was used. The spectral data were processed by a data processor containing a microcomputer, supplied with the

spectrophotometer. In order to improve the S/N ratios of the spectra, the data were accumulated and the number of repetitive scans was determined according to the noise levels for each of the samples. The sample solutions were illuminated with the 488nm line at 200mW output. A mirror served to double pass the laser beam through a cylindrical sample cell (0.3ml) Pyrex glass. In order to obtain the largest and most reproducible intensities, it is important that the mirror system is adjusted carefully in such a way that the scattering lights focus into a clear image on the entrance slit. As a key band, the most intense Raman line at 1045cm^{-1} was used.

In the case of waste and treated waters, the detection limit becomes about an order of magnitude higher than that in the case of pure water because of the strong luminescence of water samples. Furaya *et al.* [71] demonstrated that the addition of potassium iodide as a quencher makes the background markedly smaller. By this procedure, the sensitivity becomes comparable to that obtained in the case of pure water samples.

A plot of the background intensifies against the time of laser beam irradiation after the addition of various inorganic salts shows the effectiveness of potassium iodide.

Furaya *et al.* [71] recommended that Raman spectra were measured on sample solutions which were then exposed to the laser beam for about 30min.

8.15 Nitrite

8.15.1 Spectrophotometric method

Various Spectrophotometric procedures have been described for the determination of nitrite in waste waters [73–75]. In the Spectrophotometric method [73] based on the reaction between Griess Romijn reagent (ie the reaction of nitrite with a primary aromatic amine to form a diazonium salt, which is then coupled with another aromatic compound to form an azo dye whose absorbance is measured) and nitrite, interference by iodide, sulphide thiosulphate, sulphite or tetrathionate is avoided by the addition of mercuric chloride solution.

Nakamura and Mazuka [74] extracted nitrite in an ethyl acetate solution of 4, 5-dihydroxycoumarin. Beer's law was obeyed up to 0.75mg L^{-1} . Only iodide, sulphide, iron(III) and chromium ions interfered seriously at the $10\mu\text{g L}^{-1}$ level. Results agreed well with those obtained using the diazotising coupling method.

Koupparis *et al.* [75] have described procedures for the determination of nitrite using an automatic microprocessor-based stopped-flow analyser. The reaction is based on diazotisation of sulphanilamide, the product being coupled with *N*-(1-naphthyl) ethylenediamine dihydrochloride to form a coloured azo dye which is measured at 540nm. The analysis should be carried out on fresh samples to avoid bacterial conversion of nitrite to nitrate or ammonia. However, samples can be preserved for 1–2 days, either by freezing at -20°C or by addition of mercuric chloride and storage at 4°C . The methods are fast, sensitive, accurate and precise, and without serious interference. The sample throughput for routine analysis can be up to 360 samples per h in the range $0.025\text{--}2.00\text{mg L}^{-1}$ of nitrite-nitrogen.

The automated microprocessor-based stopped flow analyser has been described by

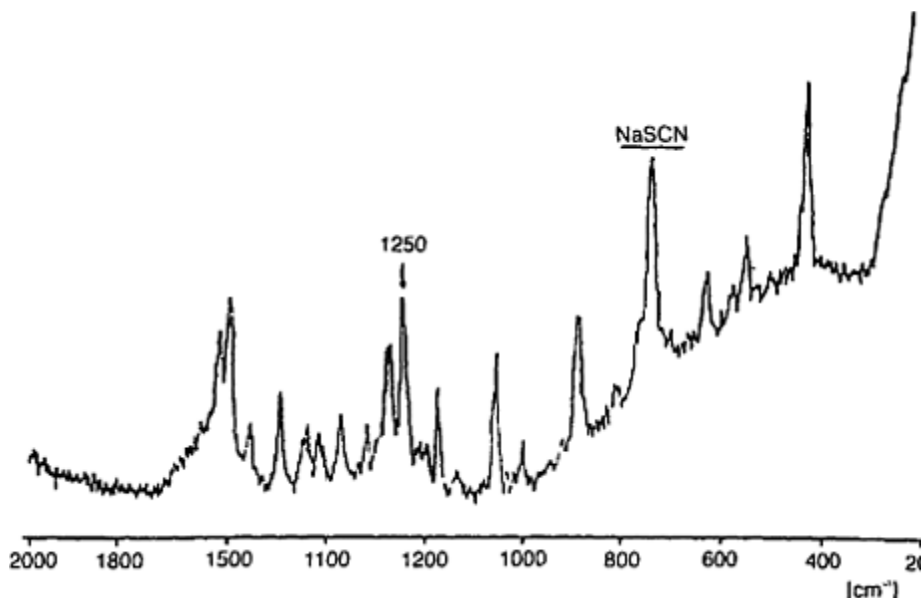


Fig. 8.3 Resonance Raman spectrum of the coloured product. Concentration of nitrite 0.2 mg L^{-1}

Source: Reproduced with permission from Elsevier Science [71]

Raman spectra were recorded on a JASCO Model J-800 Laser Raman Spectrophotometer. A Spectra-Physics Model 164 Argon Ion Laser was used as an exciting source. A HTC 464 photomultiplier was used as a detector. The spectral data were processed by a data processor containing a microcomputer in conjunction with the Spectrophotometer. In order to improve the S/N ratios of the spectra, the data were accumulated and the number of repetitive scans was determined according to the noise levels for each of the spectra. The sample solutions were illuminated with the 488.0nm line at 200mW output. In order to minimise the effect of local heating of samples due to the laser beam irradiation and the possible decomposition of the coloured product, the sample cell was rotated using a JASCO Model R-10 Cell Rotator (2500 rpm^{-1}). Moreover, the sample solutions were irradiated very close to the cell wall to minimise the reabsorption of scattering lights.

In this method a portion of the sample containing up to $7 \mu\text{g L}^{-1}$ nitrite is diluted with water and treated with acidic sulphanilic acid and acidic α -naphthylamine then the pH adjusted to 2–2.5 with 28% sodium acetate solution.

The coloured product obtained has a broad adsorption band with the maximum absorption at 520nm ($\lambda_{\text{max}} = 41,000 \text{ cm}^{-1}$, 1 mol^{-1}). The coloured product exhibits the resonance Raman effect against the 488.0nm line of argon ion laser. In Fig. 8.3 the resonance Raman spectrum

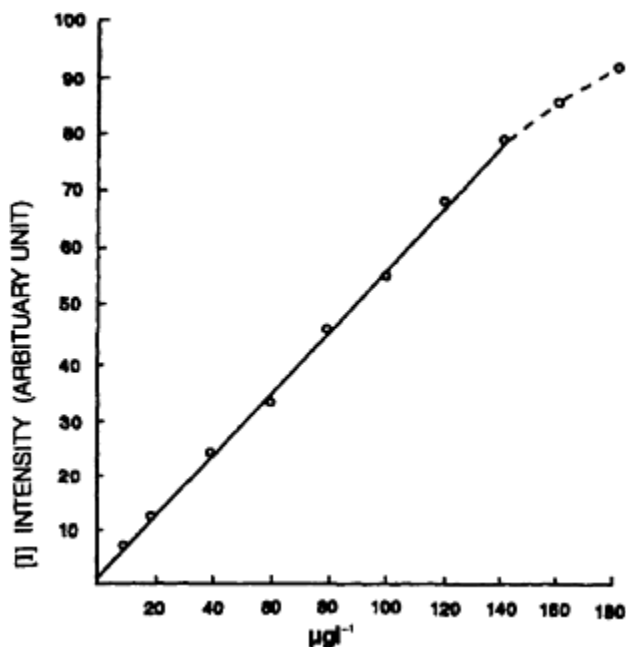


Fig. 8.4 Analytical curve obtained for the aqueous solutions of NO_2^- in the concentration range from 10 to 180 mg L^{-1} . The empirical formula was determined by the least squares method: $I = 1.45 + 0.55C$, $S_c = 2.70 \mu\text{g L}^{-1}$ (for the concentration)
Source: Reproduced with permission from Elsevier Science [71]

of this product solution is shown. The concentration of the solution is 0.2 mg L^{-1} ($4 \times 10^{-6} \text{ mol L}^{-1}$). As is seen from this figure, the solution of the azo dye obtained gives a lot of bands in the $2000\text{--}200 \text{ cm}^{-1}$ region in spite of remarkably low concentration. Of these bands, the one at 1250 cm^{-1} was used as a key band corresponding to nitrite since the band has the maximum peak intensity, and the background intensity in the vicinity of this band is comparatively low.

The sample solutions produced by the above mentioned reaction exhibit a comparatively strong background, which probably comes mainly from the fluorescence due to the laser beam irradiation, and, because of this, the required sensitivity cannot be attained unless this background intensity is made considerably lower by the addition of an inorganic salt as a quencher of fluorescence.

The addition of sodium thiocyanate leads to a marked decrease of the background. Moreover, it is seen that no distinct change of the reduced background is observed in this case, which means that the reduction rapidly reaches the equilibrium state.

In Fig. 8.4 the analytical curve obtained for aqueous solutions of nitrite in the concentration range $10\text{--}180 \mu\text{g L}^{-1}$ is shown. The curve can be fitted to a straight line in the concentration range below $140 \mu\text{g L}^{-1}$. When the concentrations of the added nitrite are smaller, that is, from 0 to $10 \mu\text{g L}^{-1}$ the relation obtained is also linear in this range.

However, the line does not go through the origin and there is a blank value that comes from the contamination of the distilled water, probably in the atmosphere, etc. This blank value is calculated to be about $1.3\mu\text{g L}^{-1}$. The existence of this blank causes no trouble in practice because, in the case of the analysis of nitrite in waste and untreated waters, the concentrations of nitrite are usually larger than $10\mu\text{g L}^{-1}$.

8.15.4 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.7.1.

8.15.5 Miscellaneous

8.15.5.1 Nitrite and nitrate

A method has been described for determining both of these anions in amounts down to $5\mu\text{g L}^{-1}$ in wastewaters [78,80,81]. In this method nitrate is reduced to nitrite in a cadmium column. Ammonium chloride is added as a buffer to prevent further reduction of nitrite. The nitrite reacts with sulphanilamide, forming a diazonium salt, which is coupled with *N*-(1-naphthyl)ethylene diamine forming a red-purple coloured complex which is evaluated spectrophotometrically at 650nm. Nitrite is determined separately on a further portion of the sample which is not subjected to cadmium reduction.

8.15.5.2 Nitrogen

Haga *et al.* [82] and Goto *et al.* [83] respectively, have reported flow injection analysis and continuous flow methods for the determination of total nitrogen in wastewaters.

8.16 Nitroacetate

8.16.1 Liquid chromatography

Dai and Helz [64] employed liquid chromatography to determine down to 0.1mg L^{-1} nitroacetate in wastewaters.

8.17 Phosphate

Recently, eutrophication in lakes and reservoirs has become an important problem. Phosphorus is a critical nutrient aiding the eutrophication process. The principal sources of phosphorus in environmental waters are agricultural effluents, municipal waste waters, industrial waste waters, etc. The determination of phosphorus is important.

8.17.1 Spectrophotometric method

Buchanan and Easty [84] showed that the official methods [85,86] for determining orthophosphate and total phosphorus (ie phosphate after digestion with persulphate) in waste water as reduced molybdophosphosulphate are subject to interference when applied to waste samples. Thus sulphide interferes in the determination of orthophosphate but not in that of total phosphorus because they are oxidised by the persulphate. Ligninsulphonates interfere in the determination of total phosphorus and somewhat less in the determination of orthophosphate. Addition of excess of aqueous bromine to the sample prevents interference from sulphide and greatly reduces that from lignin-sulphonates; in the determination of orthophosphate the unconsumed bromine is removed by a stream of air before further steps in the determination. It is also shown that the precipitation of alkali lignin and other substances which occurs when the solution, after the persulphate oxidation is neutralised according to the official procedure, can be eliminated by, instead, filtering the solution while it is still acidic (the amount of acid used in the reagent solution being reduced to compensate for that already present).

8.17.2 Ultraviolet spectroscopy

The automated ultraviolet Spectrophotometric method [87] for the determination of ortho and ortho plus hydrolysable or total phosphate involves the use of two independent flow systems, which are flow-charted, concurrently allowing these phosphates to be measured colorimetrically as orthophosphate. Features of the method include compensation of the bias effect of turbidity during orthophosphate determination, and the elimination of the need to neutralise acidified samples in hydrolysable and total phosphate determinations prior to colour development. The method and equipment both allow continuous operation for up to 24h.

Standard deviations over the ranges 0–3mg of L^{-1} phosphate and 3–30mg L^{-1} phosphate were 0.03 and 0.2 respectively. Up to 100mg of silicate, iron or nitrate $^{-1}$ did not interfere in the determination of 30mg L^{-1} phosphate.

8.17.3 Atomic absorption spectrometry

In the atomic absorption inhibition titration method [88] the phosphate in the sample is treated with incremental amounts of magnesium solution

Table 8.20 Major environmental factors affecting the hydrolytic degradation of condensed phosphates

<i>Factor</i>	<i>Approximate effect on rate</i>
Temperature	10^5 – 10^6 faster from freezing to boiling
pH	10^3 – 10^4 slower from strong acid to base

Enzymes	As much as 10^5 – 10^6 faster
Colloidal gels	As much as 10^4 – 10^5 faster
Complexing cations	Very many-fold faster in most cases
Concentration	Roughly proportional
Ionic environment in the solution	Several-fold change

Source: Reproduced with permission from Elsevier Science [88]

and magnesium determined by atomic absorption spectrometry. The endpoint is indicated by a sharp rise in the magnesium absorption; features of the titration curve after the endpoint are related to species formed in the flame. Some observations on polyphosphate titrations are presented, and the method was applied to the determination of phosphate in surface and waste waters.

Condensed phosphate is a generic title for all phosphates which are formed by the removal of one or more water molecules from orthophosphoric acid, which may be represented as $3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$. These include metaphosphoric acid ($\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$), pyrophosphoric acid ($2\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$), ultraphosphoric acid (general formula $m\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$) where $0 \leq m < 1$), and polyphosphoric acid (general formula $m\text{H}_3\text{PO}_4 - (m-1)\text{H}_2\text{O}$ where $1 \leq m < \infty$). The most common condensed phosphates are pyro- and tripolyphosphate which have dissociable protons and behave as typical polyprotic acids. The pyrophosphate and tripolyphosphate each occur in three forms

pyrophosphates ($\text{H}_3\text{P}_2\text{O}_7^-$, $\text{H}_2\text{P}_2\text{O}_7^{2-}$ and $\text{HP}_2\text{O}_7^{3-}$)
tripolyphosphates ($\text{H}_3\text{P}_3\text{O}_{10}^{2-}$, $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ and $\text{HP}_3\text{O}_{10}^{4-}$)

A number of factors affect the rate at which condensed and organic phosphates undergo hydrolytic degradation in aqueous solution. The major environmental factors in decreasing order of effectiveness are listed in Table 8.20. Consideration of Table 8.20 indicates that pH is one of the factors which exerts a considerable influence on the rate of hydrolysis.

In a domestic waste water, all these factors may influence the hydrolysis of condensed phosphate to orthophosphate. Thus if the sample is not analysed immediately, changes in the concentrations of condensed and orthophosphates will occur. If the forms of phosphate are to be determined rather than total phosphate, hydrolysis must be prevented.

8.17.4 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.7.1 and 12.7.2.

8.17.5 Ion exclusion chromatography

The application of this technique is discussed under multianion analysis in section

13.2.2.1.

8.17.6 High performance liquid chromatography

The methods developed by Sakurai *et al.* [89] and Morgan and Danielson [90] are also applicable to the determination of respectively, phosphates in waste waters and in sewage effluents.

8.17.7 Sample preservation

Rossin and Lester [91] evaluated some of the methods available for the preservation of condensed phosphates in samples of domestic waste waters, ie the prevention of the hydrolysis of condensed phosphate to orthophosphate. They showed that mercuric chloride at 40 mg L^{-1} at normal pH is the most effective preservative examined for samples stored at 20°C for 6 days (Table 8.21). Samples should be filtered as soon as possible after they have been taken. Mercuric chloride at high pH was not a satisfactory preservative. Addition of sodium hydroxide to raise the pH increases phosphatase activity but lowers the rate of spontaneous hydrolysis and, on balance, is not a satisfactory treatment. Formaldehyde at elevated pH was less efficient than mercuric chloride at normal pH.

The samples treated with mercuric chloride at normal pH presented the smallest difference from the mean with a range between -0.07 and $+0.06$. When formaldehyde was used at high pH, the range was between -0.16 and 0.00 . The samples containing mercuric chloride at pH 10 showed a range between -0.15 and $+0.21$. A variation between -0.21 and $+0.35$ was found when pH was increased in the filtered samples. The use of formaldehyde at normal pH resulted in a variation between -0.25 and $+0.34$.

8.18 Phosphite**8.18.1 X-ray fluorescence spectroscopy**

Taira *et al.* [92] reported an X-ray fluorescence spectrometric determination of phosphite (HPO_3^{2-}) in electrodeless plating process wastewater in which the phosphite was precipitated with iron(III), followed by collection on a

Table 8.21 Concentration of orthophosphate in settled sewage samples, filtered and unfiltered, with different preservatives, analysed at different times

Sample		Orthophosphate as P mg L^{-1} after storage				
		0	1 day	3 days	6 days	Mean
Settled	unfiltered	5.26	5.96	6.33	6.33	—
Sewage	filtered	4.28	4.20	4.48	4.74	—

	D.M. ^a	-0.15	-0.25	+0.05	+0.31	4.43
Settled	unfiltered	4.19	5.35	6.04	6.44	—
Sewage	filtered	4.19	4.03	4.14	4.59	4.24
pH 10	D.M. ^a	-0.05	-0.21	-0.10	+0.35	
Settled	unfiltered	4.89	4.77	5.34	5.85	—
Sewage	filtered	4.09	4.16	4.14	4.24	4.16
HgCl ₂	D.M. ^a	-0.07	0.00	-0.2	+0.06	
Settled	unfiltered	5.11	5.24	5.49	5.53	—
Sewage	filtered	3.46	3.54	3.76	3.90	3.69
HgCl ₂ +pH 10	D.M. ^a	-0.13	-0.15	+0.07	+0.21	
Settled	unfiltered	5.00	5.52	6.20	6.48	—
Sewage	filtered	4.15	4.16	4.54	4.74	4.40
Formaldehyde	D.M. ^a	-0.25	-0.24	+0.14	+0.34	
Settled	unfiltered	5.11	5.43	5.43	5.46	—
Sewage	filtered	3.84	4.09	4.04	4.00	4.00
Formaldehyde						
pH 10	D.M. ^a	-0.16	+0.09	+0.04	0.00	

^aD.M.=Derivation from the mean concentration in filtered samples

Source: Reproduced with permission from Sulpher Ltd, Chiswick [91]

membrane filter. The detection limit was $4.2\mu\text{g L}^{-1}$ and H_2PO_2^- , cobalt and nickel did not interfere.

8.19 Polysulphide

8.19.1 Anodic stripping voltammetry

The application of this technique is discussed under multianion analysis in section 14.8.1.1.

8.20 Sulphate

8.20.1 Spectrophotometric method

The application of this technique is discussed under multianion analysis in section 14.2.3.3.

8.20.2 Column coupling isotachoelectrophoresis

The application of this technique is discussed under multianion analysis in section 14.6.1.1.

8.20.3 Ion selective electrodes

Ion selective electrodes are suitable sensors for activity measurements in process control, continuous ion flow analysis and in industrial wastes. Inorganic gels possessing ion exchange properties may be developed as membrane electrodes selective to various ions. There have been several attempts to construct electrodes selective to sulphate ions. Fischer and Babcock [93] discussed a heterogeneous sulphate membrane consisting of powdered barium sulphate dispersed in paraffin. Rechnitz *et al.* [94], Rechnitz and Mohan [95], Ross [96] and Nagy and Fjeldly [97] prepared precipitate-based membranes from lead sulphate, lead sulphide and silver sulphide etc. All these are susceptible to interference by sulphide and sulphite etc. anions and a number of cations. Numerous other investigations made in this direction are summarised by Buck *et al.* [98] in the literature they have compiled for membrane electrodes.

Srivastava and Jain [99] investigated the performance of a sulphate ion selective solid state membrane electrode prepared from hydrous thorium oxide gel with polystyrene as binder. The membrane showed good selectivity for sulphate ions in the range $0.1\text{--}100\mu\text{mol L}^{-1}$ and there was practically no interference from a large number of anions and cations. The electrode could be used at pH 6–10 and could be used in partially non-aqueous systems. This electrode was used to determine sulphate in waste waters from the pulp and paper and leather processing industries.

The electrode is non-Nernstian in nature. The useful pH range for this assembly is 6–10. The membrane electrode shows good selectivity to sulphate ions and there is practically no interference from a large number of anions and cations.

The electrode has also been used as an end-point indicator in potentiometric titrations involving sulphate ions. The titration of potassium sulphate (20ml , 10^{-3}mol L^{-1}) was performed with barium chloride solution ($5\times 10^{-3}\text{mol L}^{-1}$). The break in the curve is quite sharp and represents a perfectly stoichiometric end-point (Fig. 8.5). Compared with direct potentiometric methods (based on Nernst equation) potentiometric titrations offer substantial improvement in accuracy and precision. The standard deviation (10 replicates) of this particular titration was 0.01ml .

Kotek [100] used barium chloride to determine sulphate in wastewaters at concentrations in excess of $0.5\text{g SO}_4\text{L}^{-1}$ by titration with barium chloride using a barium-selective electrode. This method was more accurate than

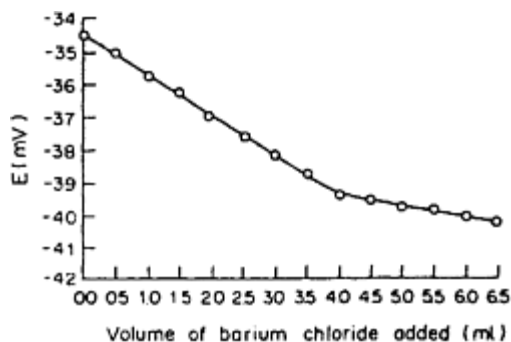


Fig. 8.5 Titration curve of 20ml, 10^{-3}M SO_4^{3-} ions with $5 \times 10^{-3}\text{M}$ BaCl_2
 Source: Reproduced with permission from Elsevier Science [99]

gravimetry in the presence of high concentrations of aluminium(III) and iron(III).

8.20.4 Ion chromatography

Cao and Luo [101] reported a relative standard deviation of <3% and a detection limit $\geq 40\mu\text{g L}^{-1}$ for the determination of sulphate in wastewater by ion chromatography. They also determined fluoride, chloride, bromide, nitrite and phosphate by this method.

The application of this technique is discussed under multianion analysis in sections 8.26.2, 12.7.1 and 12.7.2.

8.20.5 Column chromatography

This technique has been used [102] to determine sulphate in waste water. A post-column solid phase reaction detector was employed in conjunction with an anion exchange separation column to determine 5 to 40mg L^{-1} sulphate.

8.21 Sulphide

8.21.1 Spectrophotometric method

Kuban *et al.* [103] used nitroprusside and methylene blue spectrophotometric methods for a silicone membrane differential flow injection determination of sulphide in waste waters. In this method the hydrogen sulphide evolved from an acidified sample was collected in alkali prior to spectrophotometric evaluation. A detection limit of $2\mu\text{g L}^{-1}$ was achieved by the nitroprusside procedure.

Reaction with p-amino dimethylaniline to form a complex with an absorption maximum at 660nm is the basis of a further spectrophotometric procedure capable of determining down to 0.1 mg L^{-1} sulphide in wastewaters [104,105]. Broderius and Smith [106] have developed a procedure for the determination of traces of hydrogen sulphide in

water and waste waters. Compressed nitrogen is bubbled through the sample to displace hydrogen sulphide, which is collected in a glass-bead concentration column and measured colorimetrically.

The application of this technique is discussed under multianion analysis in section 14.2.3.3.

8.21.2 Cathodic stripping voltammetry

Xi *et al.* [107] report that a cathodic stripping oscillographic polarography method for determining trace sulphide in wastewater has recoveries $\geq 94\%$ for $10\text{--}560\mu\text{g L}^{-1} \text{S}^{2-}$ and a linear relationship between current peak height and sulphide concentration over the range of 5pg L^{-1} to 5mg L^{-1} . The anions chloride, bromide, iodide, phosphate, sulphate and thiocyanate do not interfere.

8.21.3 Ion selective electrodes

Both sulphide [108] and iodide-selective [109] electrodes have been used to determine sulphide in waste water. Papp and Havas [108] used a sulphide ion selective electrode as an indicator electrode in the potentiometric titration of sulphide with mercuric chloride. Novkirishka *et al.* [109] used an iodide-selective electrode in an indirect potentiometric titration procedure to determine sulphide in industrial waste waters. Sulphide is first precipitated as cadmium sulphide by addition of cadmium acetate in an alkaline medium. The isolated cadmium sulphide is dissolved in excess standard iodine solution and excess iodine estimated by potentiometric titration using the iodide selective electrode.

8.21.4 Ion chromatography

Goodwin *et al.* [110] determined trace sulphides in turbid waters by a gas dialysis/ion chromatographic method. The sulphide is converted to hydrogen sulphide which is then isolated from the sample matrix by diffusion through a gas dialysis membrane and trapped in a dilute sodium hydroxide solution. A $200\mu\text{L}$ portion of this solution is injected into an ion chromatograph for determination with an electrochemical detector. Detection limits were $\geq 1.9\text{ng/mL}^{-1}$.

8.21.5 Ion interaction chromatography

Haddad and Heckenberg [111] determined sulphide in wastewaters by reversed-phase ion-interaction chromatography following precolumn reaction of sulphide with *N,N*-dimethyl-*p*-phenylenediamine giving a detection limit of $0.8\mu\text{g L}^{-1}$.

8.22 Sulphite

8.22.1 Spectrophotometric method

The application of this technique is discussed under multianion analysis in section

14.2.3.3.

8.22.2 Polarography

Sulphite in wastewaters has been determined by dc polarography with a detection limit of $10^{-6} \text{ mol L}^{-1}$ and by ac polarography with a detection limit of $10^{-7} \text{ mol L}^{-1}$ [112].

8.22.3 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 8.26.2 and 12.7.2.

8.23 Silicate**8.23.1 Spectrophotometric method**

Greenberg *et al.* [113] and Babulak and Gildenberg [114] in official methods have determined silicate down to 0.1 mg L^{-1} (as Si) spectrophotometrically by the molybdosilicate method in which the extinction of the silicomolybdate complex is measured at 810nm. Ascorbic acid is added to reduce silicomolybdic acid to the silicomolybdo blue complex. Phosphate interference is overcome by the addition of oxalic acid.

8.23.2 Atomic absorption spectrometry

Looyenga and Huber [115] used atomic absorption inhibition titration to determine silicate in waste water. The method is based on the strong inhibition by silicate of the absorption of magnesium ions which is measured continuously during titration. The sample solution (pH 3–4) is first passed through Amberlite IR-120 resin (H^+ form) to remove magnesium and other interfering cations and the percolate is then titrated with a standard solution ($100\text{--}200 \text{ mg L}^{-1}$); the titrated solution is simultaneously aspirated into the hydrogen air flame for measurement of the absorption at 285.2nm. The end point is detected by a sharp increase in the magnesium signal. The detection limit is 0.1 mg L^{-1} and there is no interference from phosphate or sulphate.

8.24 Thiocyanate**8.24.1 Spectrophotometric method**

The application of this technique is discussed under multianion analysis in section 14.2.3.2.

8.24.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.7.2.

8.24.3 Gas chromatography

The application of this technique is discussed under multianion analysis in section 8.8.7.

8.24.4 Miscellaneous

See section 14.12.5.1.

8.25 Thiosulphate

8.25.1 Anodic stripping voltammetry

The application of this technique is discussed under multianion analysis in section 14.8.1.1.

8.25.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.7.2.

8.26 Multianion analysis

8.26.1 Spectrophotometric method

8.26.1.1 Sulphite, sulphide and sulphate

Bhat *et al.* [116] have reported a Spectrophotometric method for the determination of low levels of sulphate (and sulphide and sulphate) in waste waters. The method involves the reduction of the bis-2,9 dimethyl 1–10-phenanthroline copper(II) ion by sulphite.

8.26.2 Ion chromatography, sulphite, chloride, fluoride, nitrate, nitrite, phosphate and sulphate

This technique has been applied to the determination of sulphite and chloride [117], also chloride, fluoride, nitrate, nitrite, phosphate and sulphate [118] in wastewaters.

3.26.3 Miscellaneous

8.26.3.1 Chlorite, nitrate, nitrite and ammonia

Canelli [119] has described an autoanalyser based procedure for the simultaneous determination of these ions in waste water.

Jenkins [120] has discussed the determination of nitrogen forms, including nitrite and nitrate in waste water.

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Chapter 9

Anions in sewage effluent

9.1 Borate

9.1.1 Spectrophotometric method

Borate has been determined [1] in amounts down to 0.02mg L^{-1} in sewage effluents spectrophotometrically by reaction with phenol and carminic acid in concentrated sulphuric acid to produce a coloured compound with an absorption maximum at 610nm.

9.2 Chloride

9.2.1 Ion selective electrodes

Hindin [2] has shown that chloride concentrations in sewage can be determined by the ion specific electrode method as an alternative to the standard mercuric nitrate method providing the following precautions are taken: the addition of an ionic strength adjusting solution to overcome any effect the ionic strength of the sample or standard may have, and the removal of sulphide ions by a cadmium ion precipitating solution.

9.2.2 Miscellaneous

Official methods issued by the Department of the Environment UK [3] describe various methods for the determination of chloride in sewage and trade effluents and waters. These methods are silver nitrate titration with chromate indicator (Mohr's method), mercuric nitrate titration with diphenyl-carbazone indicator, potentiometric titration with silver nitrate and an automated mercuric-ferric thiocyanate colorimetric method. With one or other of these methods concentrations from 1 to 1000mg L^{-1} chloride may be determined. Brief notes are given in respect of the chloride ion selective electrode, silver coulometry and ion chromatography, the latter being relevant at very low concentrations down to the $\mu\text{g L}^{-1}$ level.

Miscellaneous methods for the determination of chloride are also discussed in section 14.12.6.1.

9.3 Cyanide (free)

9.3.1 Spectrophotometric method

Kodura and Lada [4] determined cyanide in sewage spectrophotometrically using ferroin. Iron, copper sulphide, acrylonitrile, phenol, methanol, formaldehyde, urea, thiourea, caprolactam or hexamine did not interfere at concentrations up to 1 g L^{-1} .

9.3.2 Atomic absorption spectrometry

In an indirect atomic absorption procedure [5] for determining down to $20\mu\text{M}$ cyanide the sample is treated with sodium carbonate and a known excess of cupric sulphate to precipitate cupric cyanide. Excess copper in the filtrate is then determined by atomic absorption spectrometry and hence the cyanide content of the sample calculated. Iron(III) does not interfere except at low cyanide concentrations. Quantitative recovery of cyanide from sewage was obtained by this procedure.

9.3.3 Miscellaneous

See section 14.12.6.1.

9.4 Fluoride

9.4.1 Spectrophotometric method

Devine and Partington [6] have shown that errors in the determination of fluoride in sewage by the SPADNS colorimetric method are due to sulphate carried over during the preliminary distillation step. It is suggested that the colorimetric method should be replaced by the fluoride ion electrode method following distillation.

9.4.2 Ion selective electrodes

Rea [7] used an ion selective electrode to determine fluoride in sewage sludge—a trisodium nitrate buffer at pH 5.4 was used. Calibration was achieved by the standard addition procedure.

Standard deviations achieved range from $17\text{--}27\text{mg kg}^{-1}$ at the 244mg kg^{-1} fluoride level for low sludges to $830\text{--}2100\text{mg kg}^{-1}$ at the 32300mg kg^{-1} fluoride level for high sludges. Interference effects are negligible as indicated in Table 9.1.

Table 9.1 Interference effects in the determination of fluoride by ion selective electrode

<i>Interference</i>	<i>mg/kg⁻¹</i>	<i>Fluoride level (mg/kg⁻¹)</i>		
		50	200	5000
Aluminium sulphate (Al)	500	-2	-7	+200
	2000	-3	+233	-8
	5000	-3	-8	-400
Ferric nitrate (Fe)	2000	-1.3	-3	+210
	20000	-1.3	+11	+150
Potassium dihydrogen phosphate (P)	80000	+0.7	+9	+250
Calcium chloride (Ca)	100000	+1.7	+8	-
Magnesium sulphate (Mg)	20000	+1.7	+9	+250

Source: Reproduced with permission from the Bureau of National affairs Inc. US [7]

In this method approximately 10 ± 0.02 g of homogenised wet sludge is weighed into a polypropylene beaker, weight W_2 . 10.0 ± 0.1 ml of 2M perchloric acid is pipetted into a 50ml polypropylene beaker and both beakers treated on a water bath to between $85 \pm 5^\circ\text{C}$ 2M perchloric acid is added carefully to the sludge which is then removed from the water bath and allowed to cool to room temperature. The resulting mixture is transferred to a polypropylene volumetric flask (100ml) and diluted to volume with water.

Measurement of fluoride concentration

An appropriate volume V ml of the prepared extract is pipetted into a 100ml polypropylene graduated flask (see below) followed by 25ml of 0.2M perchloric acid.

<i>Expected F⁻ level (mg/kg⁻¹ dry sludge)</i>	<i>Volume V of extract (mL)</i>	<i>Standard fluoride solution (mg L⁻¹)</i>
20–800	25.0	10.0
200–2000	10.0	10.0
400–4000	5.0	10.0
800–8000	25.0	100
4000–40000	5.0	100

Add 50.0 ± 0.1 ml of pH 8.3 citrate buffer and make to the mark with deionised water and mix well. Ensure that the solution is blue to the bromocresol green end-point indicator at this stage ie pH 5.4 ± 0.2 . 50ml of this solution is pipetted into a 100ml polypropylene beaker containing a plastic covered stirring bar. Ensure the temperature of the solution is within $\pm 1^\circ\text{C}$ of other solutions within the batch and solutions used for calibration.

Whenever practicable the temperature should be as close as possible to 20°C Place the beaker on a heat shield on a magnetic stirrer and adjust the stirring speed to achieve rapid mixing but without vortexing. Immerse the fluoride selective ion electrode and reference electrode in the solution and record the millivolt potential P_0 to $\pm 0.2\text{mV}$. The time for the reading to reach equilibrium may extend to 5min for low fluoride levels. The Gran's Plot procedure is designed to overcome interferences in the determination of fluoride and should be used in all these cases.

To the above solution is added $1.0 \pm 0.01\text{ml}$ of standard fluoride solution ($100\mu\text{g F mL}^{-1}$ or $10\mu\text{g F mL}^{-1}$ depending on fluoride content of sample) and the equilibrium millivolt potential P_1 is recorded.

The above operation is repeated a further four times and the equilibrium millivolt potential recorded each time: P_2 , P_3 , P_4 and P_5 .

The potentials P_0 to P_5 are plotted versus the fluoride concentration added on 10% volume corrected Gran's Plot paper. The fluoride concentration is thus determined: $C_F \mu\text{g mL}^{-1}$.

Fluoride concentration, mg kg^{-1} dry solids:

$$\frac{C_F \times 10^6}{V \times S \times W_s}$$

9.5 Nitrate

9.5.1 Spectrophotometric method

Dodin *et al.* [8] observed that when a solution of nitrate at pH 2.0 is irradiated with ultraviolet light, the nitrate will oxidise methyl orange. They used this as the basis of a spectrophotometric method for determining nitrate in industrial effluents.

Slicko and Tawfik [9] have described an automated technicon on-line method for overcoming phosphate interference in the cadmium reduction method for the determination of nitrate. It involved removal of phosphate by precipitation with calcium chloride prior to the sample entering the reduction column.

9.5.2 Ion selective electrodes

Nitrate levels sewage in amounts down to 1mg L^{-1} have been determined by specific ion electrodes [10,11]. Petts [11] used a non-porous plastic membrane nitrate selective electrode and compared results obtained with this electrode and those obtained by a standard spectrophotometric method in a sewage works effluent. The results indicate that the selective ion electrode is suitable both for laboratory and plant monitoring

Table 9.2 Nitrate analysis of effluents of sewage treatment plants a

<i>Sample no.</i>	<i>Potentiometric NO₃⁻N, mg L⁻¹</i>	<i>Spectrophotometric^b NO₃⁻N, mg L⁻¹</i>
1	28	28
2	43	44
3	52	41
4	43	37
5	34	39

^aThe data represent a single analysis

^bAs measured independently

Source: Reproduced with permission from the Water Research Centre, UK [11]

purposes. Only chloride and, to a lesser extent, nitrite and bicarbonate interfere in these measurements of nitrate.

Table 9.2 gives a survey of results obtained by both methods on sewage effluents with a high nitrate content.

9.5.3 Miscellaneous

See section 14.12.6.1.

9.6 Nitrite

9.6.1 Miscellaneous

See section 14.12.6.1.

9.7 Nitrite and nitrate

9.7.1 Spectrophotometric method

Workers at the Water Research Centre UK [11] have described detailed procedures based on the use of the Technicon Autoanalyser AA11 for the determination of nitrate and nitrite in sewage and sewage effluents. Measurements of nitrate in sewage at the 10–50mg L⁻¹ level were made with a within batch standard deviation of 0.1mg L⁻¹ nitrate. Nitrate recoveries at the 12mg L⁻¹ level were in the range 100–100.7%. Standard deviations of nitrite determinations were in the range 0.003 (at 0.2mg L⁻¹ nitrite) to 0.010 (at 1mg L⁻¹ nitrite). Nitrite recoveries in the 0.4mg L⁻¹ region were between 98 and 102%. Nitrate recoveries in the 12mg L⁻¹ region were between 100 and 100.7%.

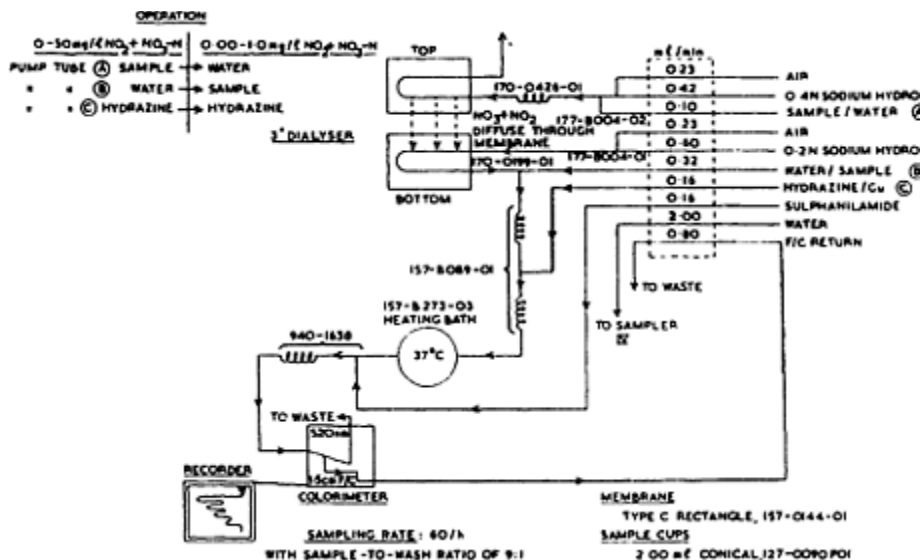


Fig 9.1 Flow diagram of analytical system for oxidised nitrogen (Technicon Industrial Method Sheet No 16-72E) Hydrogen-copper reagent. To 0.14g $\text{HN}_2\text{HN}_2\text{H}_2\text{SO}_4$ add 0.3ml copper sulphate ($3.9\text{g Cu SO}_4 \cdot 5\text{H}_2\text{O L}^{-1}$) and make up to 1L. Sulphanilamide reagent. 10g sulphanilamide plus 100ml conc.phosphoric acid plus 2g N (naphtylerylene) diamine dihydrochloride, diluted to 1L

Source: Reproduced with permission from the Water Research Center, UK[11]

The layout of the apparatus for determining 0.50mg L⁻¹ nitrate plus nitrite and 0.1–1mg L⁻¹ nitrite are shown respectively in Figs. 9.1 and 9.2.

9.8 Phosphate

9.8.1 Spectrophotometric method

The Department of the Environment UK [12] has issued details of the Spectrophotometric methods for the determination of orthophosphate in sewage effluents.

These methods are based on reaction with acid molybdate reagent to form a phosphomolybdenum blue complex which is determined at 882nm. The first method has a range of 0–0.40mg L⁻¹ (after dilution of sample if required) and the second is mainly designed for oligotrophic waters with phosphorus contents in the range 0–25µg L⁻¹. In addition, the report discusses various methods for converting other forms of phosphorus to orthophosphate, and the elimination of interference due to arsenic, based on the reduction of arsenate to arsenite.

Bretscher and Gas [13] discuss reduction reagents for the Spectrophotometric

determination of phosphate in sewage as the phosphomolybdenum blue complex. They point out that the disadvantage of aqueous stannous chloride reduction reagent is that it oxidises rapidly and a fresh solution must be prepared daily. Solutions of stannous chloride in glycerol were found to be stable for at least six months.

9.8.2 Flow injection analysis

Schulze and Thiele [14] compared results obtained by flow injection analysis and the standard DIN 38402 method for the determination of orthophosphate.

9.8.3 High performance liquid chromatography

Morgan and Danielson [15] have described the development of an enzymatic method of determining phosphate eluted from a reverse phase high performance liquid chromatographic column. The method is applicable to sewage effluents. It is based on the nucleoside phosphorylase catalysed conversion of inosine and orthophosphate to hypoxanthine. This method is claimed to give better results than standard molybdenum blue Spectrophotometric methods.

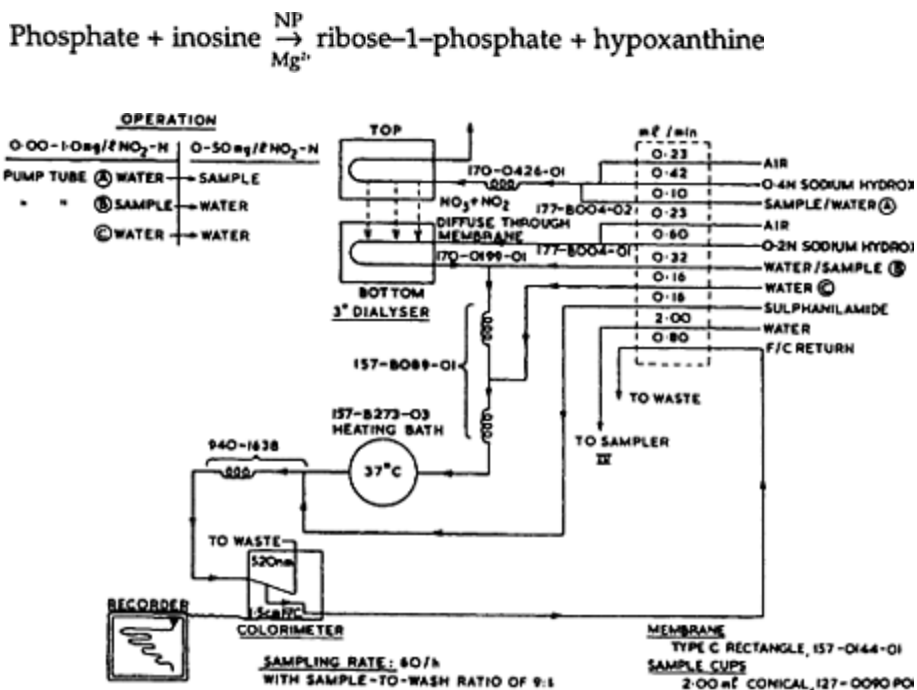


Fig. 9.2 Flow diagram of analytical system for nitrite nitrogen (Technicon Industrial Method Sheet No.162-72E) Sulphanilamide reagent 100ml conc phosphoric acid to 600ml water. Add 10g sulphanilamide then 2g N-(naphthylethylene) diamine diluted to 1L.

Source: Reproduced with permission from the Water Research Centre, UK [11]

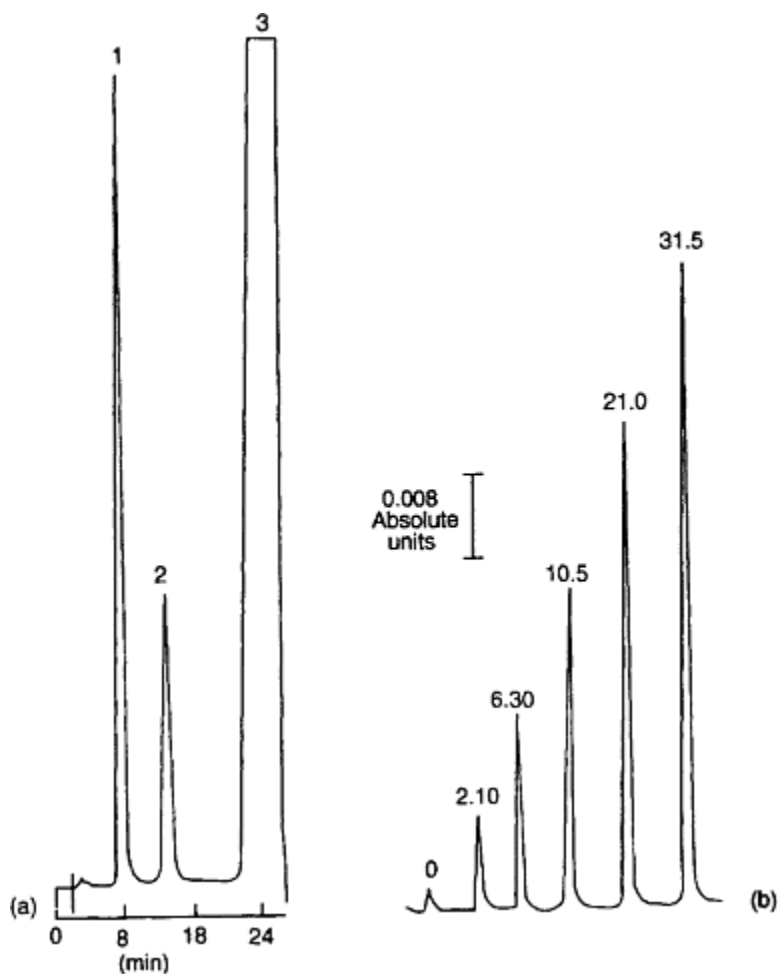


Fig. 9.3 Sample chromatogram of a 42 ppm phosphate sample. Absorbance units full scale, au.f.s.=0.08. Peaks: 1=hypoxanthine; 2=m-aminophenol; 3=inosine. (b) Hypoxanthine peak for various phosphate concentrations in mg L^{-1} (indicated above each peak)

Source: Reproduced with permission from Elsevier Science [15]

The inosine and hypoxanthine were separated by reversed phase high performance liquid chromatography and the amount of hypoxanthine produced was related to the phosphate concentration. Quantitation of the hypoxanthine peak was found to be linear with orthophosphate up to about 30mg L^{-1} . A detection limit of 0.75mg L^{-1} could be obtained after dialysis of the commercial enzyme. Interference studies showed that the enzymatic

assay, unlike the colorimetric molybdate blue technique, was essentially unaffected by complex matrices such as polyphosphates and phosphoesters.

Fig. 9.3 shows a typical chromatogram for a standard $42\mu\text{g L}^{-1}$ phosphate and hypoxanthine peaks resulting from various phosphate samples after reaction with the enzyme. The calibration curve had a slope of 0.043 ± 0.002 and an intercept of 0.124 ± 0.033 with a correlation coefficient of 0.9981. Linearity up to 30mg L^{-1} was observed. Relative standard deviation of triplicate runs was 10% or less. The detection limit, twice the signal of the blank, was determined to be 1.5mg L^{-1} . Dialysis of the commercial enzyme in 0.1mol L^{-1} Tris buffer, pH 7.4, for 24h was found to reduce the blank and therefore the detection limit by at least a factor of two.

A plot of phosphate concentration given by the enzymatic method vs that found by the molybdate blue method had a slope of 0.999 ± 0.046 and an intercept of 0.421 ± 1.222 with a correlation coefficient of 0.996.

To compare the selectivity of the enzymatic method with that of the molybdate blue method, interference studies were conducted for both methods. The first study was the effect of tripolyphosphate in the sample. The molybdate blue method showed a positive deviation with increasing amounts of tripolyphosphate. The reason for this positive deviation can be attributed to the acid hydrolysis of tripolyphosphate to orthophosphate. The enzymatic method also showed a slight positive deviation, probably due to orthophosphate impurity in the tripolyphosphate used.

9.8.4 Miscellaneous

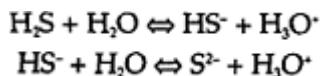
See section 14.12.6.1.

9.9 Sulphide

9.9.1 Draeger tube method

Ballinger and Lloyd [16] have described a detailed procedure for the rapid determination of down to 0.06mg L^{-1} sulphides in sewage samples. Hydrogen sulphide is brought to solution/vapour equilibrium in a closed flask under controlled conditions. The concentration of hydrogen sulphide vapour is determined by means of Draeger tubes, and related to the concentration in solution by means of a calibration graph.

In aqueous solution, hydrogen sulphide dissociates as a weak diprotic acid:



At a given pH, the degree of dissociation depends upon the temperature and activity of the sulphide species. At pH 5.0, dissolved sulphides are present almost entirely as undissociated hydrogen sulphide. It follows from Henry's law that the vapour pressure of hydrogen sulphide above its aqueous solution is a function of the mole fraction of dissolved hydrogen sulphide. In this method, hydrogen sulphide is brought to solution-

vapour equilibrium in a closed flask, and the concentration of hydrogen sulphide vapour in the air space is determined by conventional gas analyser. The pH of the solution is adjusted to 5.0 by means of a buffer solution and the ionic strengths of samples and standards are maintained at a constant level by the strong electrolytes incorporated into this solution. The above method determines undissociated hydrogen sulphides, hydrosulphide and sulphide ions. To determine total sulphide including above plus other compounds liberating hydrogen sulphide from a cold solution containing 0.5M hydrochloric acid, follow the above procedure using 50ml acid chloride solution instead of buffer solution.

The comparative freedom of interference from other sulphur-containing anions is of particular note. Sulphite, metabisulphite and thiosulphate do not interfere significantly at 100-fold excess, detergents depress the recovery of sulphide at 100-fold excess but do not interfere significantly at 10-fold excess.

9.9.2 Ion selective electrode

Glaister *et al.* [17] studied three sulphide ion selective electrodes in cascade flow and flow-through modes to investigate carrier stream, sample size and flow rate parameters in the analysis of sulphide in sewage effluents. Results were compared with those obtained by direct potentiometry. The electrodes were successfully used as detectors of sulphide during flow injection analysis and the presence of ascorbic acid in the standard antioxidant buffer minimised deleterious effects of hydrogen peroxide in the samples. Both the cascade flow and flow-through modes of electrodes yielded sulphide concentrations similar to those from colorimetric methods.

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Chapter 10

Anions in trade effluents

10.1 Borate

10.1.1 Spectrophotometric method

The standard curcumin method [1,2] has been found to be suitable for the determination of borate in industrial effluents.

10.1.2 Ion chromatography

Hill and Lash [3] have described an ion chromatographic method for the determination of down to 0.05mg L^{-1} of borate in environmental waters, nuclear fuel dissolvent solutions and effluents.

Borate is selectively concentrated on Amberlite XE-243 ion exchange resin and converted to tetrafluoroborate using 10% hydrofluoric acid. Tetrafluoroborate is strongly retained by the resin, thus allowing excess fluoride to be eluted without loss of boron. The tetrafluoroborate is eluted with 1M sodium hydroxide and is determined in the eluant by ion chromatography. Boron is quantified to a lower limit of 0.05mg L^{-1} .

None of the common ions interferes at a 100 to 1 mole ratio to boron. In addition, at least a 280 to 1 mole ratio of fluoride to boron, as well as a 100 to 1 mole ratio of chloride to boron, can be tolerated. Fig. 10.1 shows an ion chromatogram of a sample which initially contained sulphate, chloride, nitrate, fluoride and chromate at a 100 to 1 mole ratio and which was prepared according to the standard procedure. As shown, tetrafluoroborate peaks are well resolved from all the residual amounts of these anions not completely removed by the XE-243 column treatment.

10.2 Bromide

10.2.1 Ion chromatography

Applications of ion chromatography to the determination of bromide in treated waters are reviewed in Table 10.1 and discussed further under multianion analysis in sections 10.22.1, 12.8.1 and 12.8.2.

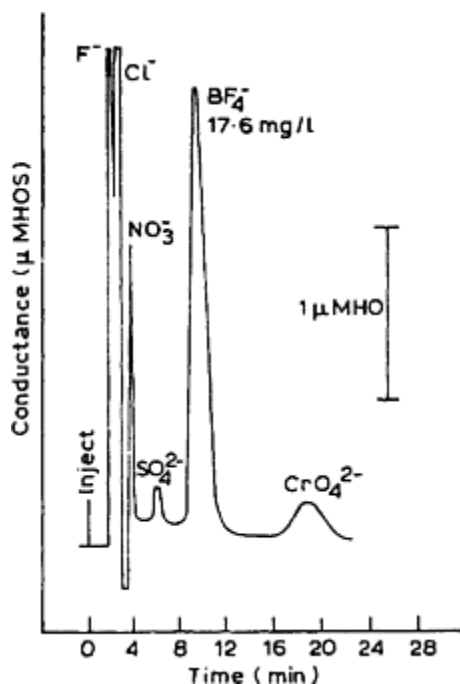


Fig. 10.1 Effects of diverse ions on 1C determination of tetrafluoroborate ion
Source: Reproduced with permission from the American Chemical Society [3]

Table 10.1 Determination of bromide in treated waters by ion chromatography

Type of sample	Codetermined anions	Ref.
Industrial effluents	S, CN, CNS, 1	[4]
Industrial effluents	Cl, SO_4 , NO_2 , NO_3 , PO_4	[5]

Source: Own files

10.3 Chloride

10.3.1 Titration method

Ilyukhina *et al.* [6] have described a volumetric method for the determination of chloride in aqueous effluents produced in the manufacture of the fungicides captan and phaltan (tolpet). This effluent contained tetrahydrophthalic acid, tetrahydrophthalimide, phthalic acid and phthalimide. The sample was treated with hydrogen peroxide, acidified with

nitric acid and then titrated with 0.1N mercurous nitrate in the presence of diphenylcarbozide indicator.

Official methods issued by the Department of the Environment UK [7] describe various methods for the determination of chloride in sewage, trade effluents and waters. These methods are silver nitrate titration with chromate indicator (Mohr's method), mercuric nitrate titration with diphenyl-carbazone indicator, potentiometric titration with silver nitrate, and an automated mercuric-ferric thiocyanate colorimetric method. With one or other of these methods, concentrations from 1 to 1000mg L⁻¹ chloride may be determined. Brief notes are given in respect of the chloride ion selective electrode, silver coulometry and ion chromatography, the latter being relevant at very low concentrations down to the µg L⁻¹ level.

10.3.2 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 10.22.1 and 12.8.1.

10.4 Cyanide (free)

10.4.1 Titration method

Kogan *et al.* [8] titrated down to 1mg L⁻¹ cyanide in coke works effluents, amperometrically in a basal electrolyte of 0.1N sodium hydroxide using silver nitrate as titrant. Titration was carried out at -0.2V (versus SCE) using a vibrating platinum electrode. Up to 500mg L⁻¹ thiocyanate, phenol and ammonia and 100mg L⁻¹ of chloride or sulphate do not interfere. Lead carbonate is added to avoid interference by sulphide.

Cadmium carbonate-magnesium chloride mixtures have also been used to prevent interference by sulphide [9] and more theoretical yields are claimed for this procedure.

In their method for the determination of cyanide in industrial effluents, Hewitt and Austin [10] distil the acidified sample in the presence of zinc and lead acetates (to prevent decomposition of complex cyanides and sulphides) and collect the liberated hydrogen cyanide in sodium hydroxide. Cyanide is then estimated by titration with standard silver nitrate solution using 4-dimethylaminobenzylidenerhodamine as indicator.

The application of this technique is discussed under multianion analysis in section 14.3.2.2.

10.4.2 Spectrophotometric method

Dimethylaminobenzylidenerhodamine [11] and pyrazolone [12] have been used as chromogenic reagents in the determination of cyanide in industrial effluents. In the latter method [12], free cyanide is separated from complex cyanides by distillation under reduced pressure in the presence of zinc and lead acetates. The hydrogen cyanide evolved is absorbed in sodium hydroxide solution, and Chloramine T is added, after slight acidification with acetic acid to produce cyanogen chloride. A pyridine/pyrazolone

reagent is added, and an optical absorbance measurement of the resultant blue dye is made at 620nm wavelength. Volatile aldehydes and ketones interfere in the final colour development. The detection limit is about $10\mu\text{g L}^{-1}$.

The micro diffusion chloramine-T spectrophotometric method [13] for the determination of free cyanide in non saline waters has been applied to industrial effluents.

10.4.3 Spectrofluorometry

McKinney *et al.* [14] have described a rapid fluorometric method for the determination of cyanide in mine waters. The method is based on the liberation of naphtho (2, 3-c) (1, 2, 5) selenadiazole from the reagent $\text{Pd}_2\text{I}_2\text{Cl}_4$ by cyanide at 25°C and pH 8. The naphthol (2, 3-c) (1, 2, 5) selenadiazole is then extracted into hexane and its fluorescence is measured at 520nm with excitation at 377nm. The calibration graph is approximately rectilinear for up to $100\mu\text{g}$ of cyanide per 3ml of hexane. Mercuric ions and sulphide interfered.

10.4.4 Continuous flow analyses

Pihlar *et al.* [15] developed the amperometric method of determining cyanides in industrial effluents to permit reliable and reproducible continuous flow measurements and flow injection analysis of discrete samples of galvanising plant effluents at the $\mu\text{g L}^{-1}$ level. The method is based on the measurement of the diffusion current arising from the oxidation of silver to dicyanoargenate(I). By use of the flow injection principle and a manifold arrangement, absolute amounts of less than one nanogram of cyanide can be determined precisely in volumes as small as $10\mu\text{L}$ and at a rate exceeding 100 samples per h.

Fig. 10.2 outlines a straight manifold arrangement and cylindrical flow through electrode. For operation in the injection mode, the sample is introduced into the carrier stream by means of a microsyringe through a septum in the injector and passes through 20cm of 0.5mm bore tubing before entering the detector. The amperometric flow through electrode consists of a 0.9mm diameter silver wire (99.9% Ag) mounted centrally by means of two Teflon stoppers in a stainless steel (or nickel) tube of 1.9mm bore which serves as a counter electrode. The cell hold-up volume is $130\mu\text{L}$. The mercurous sulphate reference electrode is bridged into the cell through capillary tubing as shown in Fig. 10.2. The potential of the silver electrode is controlled at -0.5V vs the MSE by means of a potentiostat.

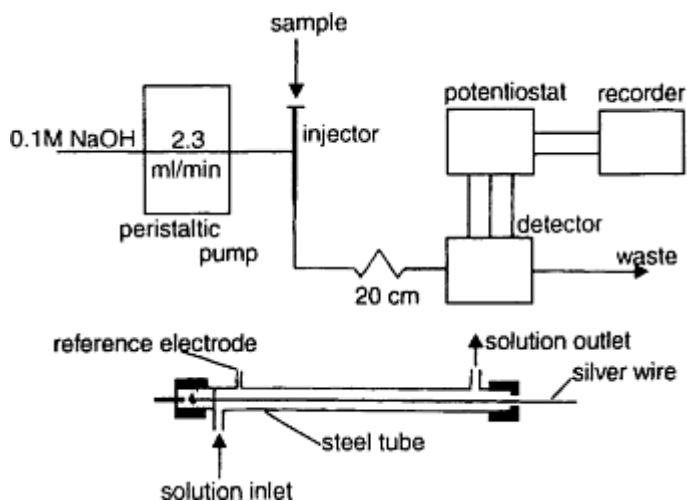


Fig. 10.2 Manifold arrangement and cylindrical flow through electrode used for the determination of cyanide. All tubes were 0.5mm bore

Source: Reproduced with permission from Elsevier Science [15]

The current was continuously monitored by measuring the voltage drop across a $10\text{k}\Omega$ precision resistor connected in series with the counter electrode, with an electronic voltmeter (Radiometer GVM 30) coupled to a Varian A-25 strip chart recorder.

Current voltage curves were recorded with a PAR 174 polarographic analyser under hydrodynamic conditions and at a scan rate of 1mV sec^{-1} . The relationship between limiting current and velocity of the fluid was measured with the aid of a waters M-5000 A pump at volume flow rates of between 0.1 and 10ml min^{-1} .

Free cyanide was separated by micro diffusion in Conway cells. The volume of 0.1mol L^{-1} sodium hydroxide used as absorbing solution was between 0.1 and 1.0ml according to the amount of free cyanide present in the sample. The free cyanide released upon acidifying the samples (up to 5ml) with 0.5ml of 3mol L^{-1} sulphuric acid was quantitatively recovered after 3h of distillation at room temperature ($20\text{--}25^\circ\text{C}$). The absorption solution was subsequently injected directly into the analyser. A 0.1mol L^{-1} solution of sodium hydroxide was used as the carrier stream.

Of the numerous substances tested, only sulphide, iodide and thiocyanate interfere seriously in this method and they can be eliminated by distillation or precipitation. Oxidants such as hypochlorite or hydrogen peroxide, which are common agents for detoxification of cyanide effluents, must be fixed by addition of arsenite or sulphite since they are reduced at the silver electrode and this results in a cathodic current. This is a disadvantage of the method compared with potentiometric techniques in which oxidants and reductants usually do not interfere. However, such compounds can be eliminated by simple chemical treatment ordinarily performed at the sampling stage.

10.4.5 Atomic absorption spectrometry

Jones [16] devised a procedure for determining cyanides whereby the cyanide is collected on silver powder and cyanide determined on the silver by atomic absorption spectrometry.

10.4.6 Polarography

Cyanide has been determined in industrial effluents by methods based on measurement of the potential at -0.45V (vs SCE) in 0.01mol L^{-1} sodium hydroxide medium [17]. There is no interference from phenol, acrylonitrile, urea or cyanide but sulphide and thiocyanate interfere.

Square wave polarography has also been used to determine $1\text{--}100\mu\text{g L}^{-1}$ cyanide in industrial effluents [18].

10.4.7 Ion selective electrodes

The application of cyanide selective electrodes has been discussed [19,20], Cuthbert [19] used the technique to analyse steel works effluents. For cyanide concentrations above 1mg L^{-1} the electrode method and the standard argentimetric method gave similar results; for lower cyanide concentrations, the colorimetric pyridine-pyrazolone method gave higher results than either the potentiometric method or the colorimetric pyridine-barbituric acid method. Cuthbert [19] discusses the problems associated with the determination of cyanide in waste waters containing complex iron cyanides and sulphides.

Hafton [21] used a silver ion selective electrode for the continuous determination of free cyanide in effluents in concentrations of $0.01\text{--}1.0\mu\text{g L}^{-1}$.

10.4.8 Microdiffusion

Rubio *et al.* [22] give details of a simple rapid procedure for the determination of cyanide involving separation by microdiffusion followed by potentiometric determination in the inner chamber of the microdiffusion cell. The limit of detection was $0.02\mu\text{g L}^{-1}$ cyanide.

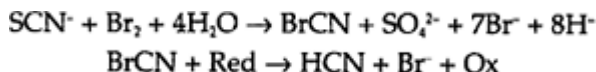
10.4.9 Gas chromatography

Nota and Improta [23] determined cyanide in coke oven waste water by gas chromatography. The method is based on treatment of the sample with bromine and direct selective determination of the cyanogen bromide by gas-solid chromatography using a BrCN selective detection as an electron capture detector. No preliminary treatment of the sample to remove interferences is necessary in this method, and in this sense, it has distinct advantages over many of the earlier procedures. Bromine also oxidises thiocyanate to cyanogen bromide. Previous treatment of the sample with aqueous formaldehyde destroys thiocyanate and prevents its interference in the method.

Nota *et al.* [24] have made the cyanogen bromide technique for determining cyanides

and thiocyanate more sensitive and reproducible by adopting the head space technique. This technique lends itself to automation.

Nota *et al.* [25] have also described a gas chromatographic head space method based on different principles for the determination of 0.01–1 00mg L⁻¹ of cyanide and thiocyanate in coke oven waters and waste effluents. This method involves firstly transforming the cyanides, or the thiocyanates, into hydrogen cyanide by acidification, then removing hydrogen cyanide from the aqueous sample by the head space technique and finally separation of hydrogen cyanide by gas solid chromatography and selective detection with a nitrogen phosphorus detector. This procedure for the determination of cyanide is based on three stages: first, transformation into hydrogen cyanide by acidification; second, removal of hydrogen cyanide by the head space technique, and third, gas chromatographic separation of hydrogen cyanide and selective detection with a nitrogen phosphorus detector. A similar procedure is adopted for the determination of thiocyanate, the only difference being the quantitative transformation of thiocyanate into hydrogen cyanide according to the reactions:



(where **Red** = SO₂ or I⁻ and **Ox** = SO₄²⁻ or I₂⁻). If cyanide is present prior to the oxidation step, it must be transformed into unreactive cyanohydrin by an excess of formaldehyde or removed by boiling the solution previously acidified to pH 2.

The presence of iron(II), iron(III) and copper(II) in the sample decreases the response for hydrogen cyanide. The greatest effect is caused by copper (II). Reducing agents do not interfere in the analysis of cyanide but oxidising substances have to be reduced prior to heating of the sample. Oxidants and reducing agents do not interfere in the determination of thiocyanate.

10.4.10 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.8.2.

10.4.11 Miscellaneous

Gregorowicz and Gorka [26] have reviewed methods for the determination of cyanide in industrial effluents.

Cyanide and cyanate in waste water have also been separated by paper chromatography [27]. Separation is achieved by use of isopropyl alcohol:ethanol:water (9:4.3) as solvent with Filtrak FN 8 paper. After drying, the paper is sprayed with bromocresol green solution. On a green background the ions appear as clear blue spots (RF values-cyanide 0.04, cyanate 0.29). The spots may also be located by treating the paper with silver nitrate solution and exposing it to hydrogen sulphide.

10.5 Complex cyanides

10.5.1 Spectrophotometric method

In a method described by Drikas and Routley [28] a stoichiometric amount of lead acetate is added to the sample to remove sulphide interferences. Addition of excess lead caused a low recovery of cyanide. The stoichiometric amount of lead to be added was determined by titration with lead acetate using a redox electrode for endpoint detection; cyanide recoveries averaged 91%.

In a continuous Technican Autoanalyser method [29] for determining total cyanide ion cyanide was reacted with pyridine-barbituric acid and the colour produced was evaluated spectrophotometrically. Percentage recoveries from industrial waste samples spiked with potassium ferricyanide and cyanide, respectively, were 98.9% and 100%.

10.5.2 Ion pair chromatography

Grigороva *et al.* [30] separated and determined stable metallo-cyanide complexes of copper(II), silver(I), iron(II), cobalt(III), nickel(II), iron(III) and gold(I) in metallurgical plant solutions by reversed phase ion-pair partition chromatography and ultraviolet detection. The mobile phase contained 2.5mm tetrabutyl ammonium hydrogen sulphate and methanol and the stationary phase consisted of carbon-18 Novapak cartridges with 4µm packing. Precision was good with relative standard deviation ranging from 1.1 to 2.8%.

10.6 Dithionate

10.6.1 Ion chromatography

Petrie *et al.* [31] applied this technique to the determination of dithionates in mineral leachates. The application of this technique is also discussed under multianion analysis in section 12.8.4.

10.7 Ferrocyanide

10.7.1 Spectrophotometric method

Ferrocyanides in coke plant effluents have been determined spectrophotometrically using 2,2'-bipyridyl or 1,10-phenanthroline [32]. The ferrocyanide is first broken down by digestion with formaldehyde prior to the determination of uncomplexed iron.

10.8 Fluoride

10.8.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 10.22.1 and 12.8.1.

10.8.2 High performance liquid chromatography

Hannah [33] has described a high performance liquid chromatographic anion exclusion method for the determination of fluorides in complex trade effluents. Pharmaceutical industrial effluents were examined for fluoride using an Ion-100 anion-exchange column coupled with a GA-100 guard column. Organics were removed from the samples at pH 8.2–8.3 by passing through disposable G18 extraction columns. Conductivity detection allowed determination of fluoride at low mg L^{-1} levels in the presence of high concentrations of chloride and sulphate through an ion exclusion mechanism in the polymeric liquid chromatographic column. The limit of detection was 0.2mg L^{-1} fluoride L^{-1} with a working linear dynamic range of $0.2\text{--}100\text{mg L}^{-1}$.

10.9 Iodide

10.9.1 Ion sensing optrodes

As the field of fibre optic sensors grows, interest in the development of indirect optrodes is increasing. The ability to detect chemical species whose spectroscopic properties cannot be directly probed (eg metal and halide ions) in a remote, continuous manner is highly desirable. Several industrial processes, from plating baths to bromine-producing process streams, would benefit greatly from the implementation of halide-ion optrodes. In these applications, the ability to monitor halide-ion concentrations would result in tighter control and increased productivity.

Because the spectroscopic properties of iodide ion cannot be directly probed with wavelengths compatible with optical fibres, indirect approaches must be adopted.

Wyatt *et al.* [34] carried out a characterisation and comparison of three fibre optic sensors for the determination of iodide based on dynamic fluorescence quenching of rhodamine eg their results indicate that the local environment of the rhodamine 6G molecules dictates strongly the sensitivity of a given optrode system. For example, the new sensor's sensitivity clearly parallels the fluorophore's accessibility by iodide ion.

10.9.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 10.22.1.

10.10 Nitrate

10.10.1 Spectrophotometric method

Dodin *et al.* [35] observed when a solution of nitrate at pH 2.0 is irradiated with ultraviolet light nitrate will oxidise methyl orange. They used this as the basis of a Spectrophotometric method for determining nitrate in industrial effluents.

10.10.2 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 10.22.1 and 12.8.1.

10.11 Nitrite

10.11.1 Spectrophotometric method

Maly and Kosikova [36] have described two Spectrophotometric methods for the determination of nitrites in industrial effluents. These workers compared their methods with the standard method using sulphanilic acid and N-(1-naphthyl)ethylenediamine and a new modification of the process with sulphanilic acid and 1-naphthol. The advantage of the latter is the possibility of diluting coloured solutions where, owing to high nitrite concentrations, the absorbance exceeds the range of the calibration curve. Urea and glycine (up to 100mg L^{-1}) do not interfere with these methods. Iron at levels about 5mg L^{-1} can be eliminated by clarifying the sample with an aluminium salt.

10.11.2 Amperometry

Oxidation flow injection amperometry using an electrochemically pretreated glassy carbon electrode has been used to determine nitrite in water [37].

Table 10.2 Interference effects in the determination of phosphate by the molybdenum blue method

Arsenate	serious interference
Silicon	will tolerate 10mg L^{-1} silicon
Chromium	1mg L^{-1} interferes
Oxidising agents	may interfere
Nitrite	1mg L^{-1} tolerated
Nitrate	20g L^{-1} tolerated

Sulphide

complete removal recommended

Source: Reproduced with permission from the Water Research Centre, UK [39]

10.11.3 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 10.22.1 and 12.8.1.

10.11.4 Miscellaneous

Paper chromatography has been used to identify nitrites in industrial effluents [38].

10.12 Phosphate

10.12.1 Spectrophotometric method

Official methods have been described for the determination of phosphates in trade effluents and sewage [39].

In these methods phosphate is reacted with an acidic molybdate reagent to form a reduced phosphomolybdenum blue complex whose absorption is measured spectrophotometrically at 882nm. The method is applicable in the range 0–40mg L⁻⁵ phosphate with a detection limit of 0.003–0.006mg L⁻¹. Standard deviations range from 0.002mg L⁻¹ at the 0.04mg L⁻¹ phosphate level to 0.11–0.17mg L⁻¹ at the 11mg L⁻¹ phosphate level.

Interference effects are reviewed in Table 10.2.

10.12.2 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 10.22.1 and 12.8.1.

10.13 Polysulphide

10.13.1 Gas chromatography

Borchardt and Easty [40] developed a gas chromatographic method for determining polysulphide in kraft pulping liquors. The polysulphide is decomposed to elemental sulphur in buffer solution. The elemental sulphur is derivatised with triphenyl phosphine. The resulting triphenylphosphine sulphur is determined by flame ionisation-gas chromatography.

10.14 Polythionate

10.14.1 Titration method

The application of this technique is discussed under multianion analysis in section 14.3.2.1.

10.14.2 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.4.1.

10.15 Selenate and selenite

10.15.1 Spectrofluorometry

A fluorometric procedure based on the use of 2,3-diaminonaphthalene has been used to determine μg amounts of total selenate and selenite in industrial wastes then desorbed using an acetonitrile gradient [41]. The eluate was monitored with an ultraviolet variable wavelength detector.

10.15.2 Polarography

AC polarography and differential pulse polarography [42] and anodic stripping voltammetry [43] have been used to determine selenium.

Batley [44] has given details of a procedure for determination of tetravalent selenium in effluents, in the concentration range $2\text{--}100\mu\text{g L}^{-1}$ by using the sensitive adsorption controlled peak obtained by differential pulse polarography in dilute acid solution. Heavy metals which could interfere were removed on Chelex 100 resin. Hexavalent selenium could be determined by the same method after photolytic reduction in the absence of oxygen. For selenium concentrations below $2\mu\text{g L}^{-1}$ preconcentration by anion exchange was necessary.

10.15.3 X-ray fluorescence spectrometry

Robberecht and Agemian [45] determined $\mu\text{g L}^{-1}$ levels of total dissolved selenium and selenite in natural waters by X-ray fluorescence spectrometry. Detection limits for tetravalent selenium and total selenium are 50ng L^{-1} and 60ng L^{-1} .

10.16 Silicate

10.16.1 Spectrophotometric method

A modification of the standard molybdenum blue Spectrophotometric method has been used to determine silicate in industrial effluents [46].

10.16.2 Atomic absorption spectrometry

Flameless atomic absorption spectrometry has been shown to be capable of determining down to $25\mu\text{g L}^{-1}$ silica in industrial process waters [47].

10.17 Sulphate

10.17.1 Titration method

Methods have been described for determining sulphate in electroplating works effluents [48], chromium plating bath effluents [49] and industrial effluents [50]. For electroplating works effluents [48], the sample was first passed down a column of ion exchange resin in the H^+ form to remove interfering cations. Sulphate in the eluate is then determined by titration at pH 5.5 to 6.5 with 0.01N barium chloride to the carboxyarsenazo endpoint. 3-(2-Carboxylphenylazo), chromotropic acid and 3,6-bis (4-chloro2-phosphorophenylazo) chromotropic acid, and, in the presence of phosphate or arsenate, nitroorthoanilic S (3,6-bis-(4-nitro-2-sulphophenylazo) chromotropic acid have also been used as indicators in the direct titration of sulphate with barium chloride. An alternate method is to precipitate sulphate as barium sulphate, dissolve the precipitate in excess 0.02mol L^{-1} ammoniacal EDTA and titrate unconsumed EDTA with standard magnesium chloride solution to the Eriochrome Black T end-point.

Standard UK official titration methods for the determination of sulphate have been published [51,52]. In one method [52] interfering ions are first removed by cation exchange in Amberlite IR 120H in the hydrogen form. Sulphate ions are then precipitated by excess barium chloride and the residual excess of barium ions determined by titration with standard 0.01M sodium ethylene diamine tetraacetic acid solution. The method is capable of determining up to 1400mg L^{-1} sulphate and has a detection limit of 1.5mg L^{-1} sulphate. Standard deviations range from 0.36mg L^{-1} at the 19.6mg L^{-1} sulphate level to 0.68mg L^{-1} at the 98.4mg L^{-1} sulphate level. Phosphate and chromate are known to interfere in this procedure but compensation procedures are available. Coloured substances may interfere with end-point detection.

In a second method [52] following treatment with amberlite IR 120H resin as above sulphate ions are titrated directly with 0.005M barium chloride titrant to the carboxyarsenazo-bromocresol purple end point. The range of application is up to 20mg L^{-1} sulphate using 0.005M barium chloride titrant. Down to 0.2mg L^{-1} sulphate can be determined. Standard deviations range from 0.15mg L^{-1} sulphate at the 5mg L^{-1} sulphate

level to 0.45mg L^{-1} sulphate at the 50mg L^{-1} sulphate level.

Several common anions interfere including phosphate, fluoride, chromate, sulphide, sulphite, and various oxy-acids of sulphur. Strongly coloured waters may interfere. Compensations can be carried out for interference by phosphate chromate, sulphite and oxy-acids of sulphur.

10.17.2 Spectrophotometric method

Pilipenko *et al.* [53] compared various methods for the determination of sulphate in mine waters. These include a direct photometric method using octamine-u-amino-ol-dicobaltisol, which gave reproducible results in the concentration range $0.05\text{--}10\text{g L}^{-1}$. Chelatometric methods using barium rhodizonate or acidic chrome blue indicators were both rapid and convenient, although chloride concentrations of greater than 1g L^{-1} interfered with barium rhodizonate determinations. For desalinated water, turbidimetric methods proved satisfactory.

In a standard UK method [54] for determining sulphate, the sulphate ions are precipitated with 2-aminoperimidine and excess reagent is determined by Spectrophotometric evaluation at 525nm or by ultraviolet spectroscopy at 305nm . This method is capable of determining $10\text{--}120\text{mg L}^{-1}$ sulphate in amounts down to 4mg L^{-1} . Standard deviations range from 1.99mg L^{-1} at the 50mg L^{-1} sulphate level to 2.28mg L^{-1} at the 100mg L^{-1} sulphate level for the Spectrophotometric method and 17.3mg L^{-1} at the 50mg L^{-1} sulphate level to 1.33mg L^{-1} at the 100mg L^{-1} sulphate level for the ultraviolet spectroscopic method. There are no interferences from commonly occurring constituents of trade effluents. An automated version of this procedure is described [54].

10.17.3 Atomic absorption spectrometry

Stock [55] applied atomic absorption spectrometry to an indirect method for determining sulphate in pulp mill effluents. Sulphate was precipitated in barium sulphate and barium subsequently determined by atomic absorption spectrometry in amounts down to $0.12\mu\text{g L}^{-1}$. Potassium chloride was added for optimal suppression of barium ionisation.

A standard UK method has been described [56] in which excess $1.666 \times 10^{-2}\text{M}$ barium chloride is added to the sample. After the precipitation of barium sulphate excess barium is determined by atomic absorption spectrometry using an air-acetylene flame. The range of application is up to 175mg L^{-1} sulphate and the limit of detection approximately 5mg L^{-1} .

Standard deviations range from 1.2mg L^{-1} sulphate at the 20mg L^{-1} sulphate level to 1.6mg L^{-1} sulphate at the 175mg L^{-1} sulphate level.

Calcium exerts a complex effect on this determination and levels above 200mg L^{-1} will cause marked interference. The levels of other anions cause no significant interference.

10.17.4 Solid state membrane electrode

Srivastava and Jain [57] estimated sulphate in paper and tannery industry effluents using

a solid state membrane electrode. The solid membrane electrode was prepared from hydrous thorium oxide gel with polystyrene as binder. Although the electrode is non-Nernstian in nature it can be utilised to estimate sulphate ions in the concentration range 10^{-1} – 10^{-4} M. The useful pH range for this assembly is 6–10. The membrane electrode shows good selectivity to sulphate ions and there is practically no interference of a large number of anions and cations.

10.17.5 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.8.1.

10.18 Sulphide

10.18.1 Titration method

A sulphide ion selective electrode has been used [58] as an indicator electrode in the potentiometric titration of sulphide in paper mill effluents with standard mercuric chloride. In 0.1N sodium hydroxide medium, sulphide and polysulphide are titrated. As the electrode responds to mercuric ions, thiosulphate and sulphite can also be titrated at pH 7.0 to 7.5. The polysulphide plus sulphite can be converted to thiosulphate and can be titrated. Sulphite can be decomposed with formaldehyde and, consequently, thiosulphate can be titrated alone.

A standard UK method [59] describes an idiometric titration procedure for the determination of sulphide.

In this method the sample is acidified and liberated hydrogen sulphide swept by a stream of carbon dioxide into a solution of zinc acetate. Zinc sulphide formed is oxidised by the addition of excess 0.00417M potassium iodate-iodine and unused iodine back titrated with standard 0.0126M sodium thiosulphate. Up to 40mg L⁻¹ sulphide can be determined with a detection limit of 0.20mg L⁻¹. The standard deviation is 0.22mg L⁻¹ sulphide at the 10.3mg L⁻¹ sulphide level. Anions such as sulphite, thiosulphate and dithionate can produce sulphur dioxide on acidification which if carried over into the zinc acetate will react with iodine causing a positive bias in results. Formaldehyde forms an addition compound with sulphur dioxide which is unreactive towards iodine under the test conditions and its use in this procedure is effective for at least 1000mg L⁻¹ sulphite (as SO₃). Levels of sulphite below 50mg L⁻¹ do not interfere.

Sulphides of silver, mercury and copper are insoluble under the test conditions so their presence will not be detected. Caution is also needed in the case of samples containing sulphides of cadmium, lead, nickel, cobalt, antimony and tin. Any volatile compounds which react with iodine will interfere.

10.18.2 Spectrophotometric method

In this method [60] the sulphide in the sample is reacted with N,N diethyl-p-phenylene diamine and potassium dichromate to form a blue colour with an absorption maximum at

670nm whose intensity is proportional to the sulphide content of the sample. This method is applicable to sulphide levels up to 0.5mg L^{-1} . Down to 0.0027mg L^{-1} sulphide can be determined. Standard deviations range from 0.0023mg L^{-1} sulphide at the 0.048mg L^{-1} sulphide level to 0.0042mg L^{-1} sulphide at the 0.4mg L^{-1} sulphide level. Noteworthy is the fact that heavy metal sulphides may be only partly recovered, also thiosulphates above 10mg L^{-1} cause temporary loss of colour.

Sulphites cause a permanent loss of colour as do zinc and iodides. Cyanides do not retard colour formation unless present in concentrations exceeding 500mg L^{-1} .

10.18.3 Spectrofluorometric methods

Fluorometric methods are based on substitution reactions in spite of the redox character of the sulphide ion. The sensitivity of these methods is extremely high; for example, the method with di(acetoxymercuri)-fluorescein [61–65] is sensitive to $1\mu\text{g L}^{-1}$, and with the mercury(II)-2,2'-pyridylbenzimidazole system [66] $0.03\mu\text{g L}^{-1}$ can be detected.

None of the fluorometric methods for determining sulphide is selective and often they are subject to interference from cyanide and thiocyanate ions.

10.18.4 Polarography

Kakiyama and Komatsu [67] evaluated sulphide in industrial effluents by measurement of the peak at -0.61V vs the mercury pool anode in a sodium hydroxide base electrolyte containing EDTA as lead masking agent. Sulphite, thiosulphate, sulphate, thiocyanate, iodide, bromide or chloride do not interfere.

10.18.5 Ion selective electrodes

An ion selective electrode can be used for the selective analysis of sulphide especially in rivers and other relatively clean waters. It can be used as a direct measure of the sulphide ion activity or as an end point detector for potentiometric titration of sulphide with silver nitrate solutions.

There is only one type of sulphide ion selective electrode, based on a compressed disc of silver sulphide. It should be noted that under the correctly buffered operating conditions, the ion selective electrode will detect only the S^{2-} ion and does not respond to other sulphur ions or molecules, eg HS^- , H_2S .

The electrode has a linear Nernstian response between $0.1\text{--}300\text{ppm S}^{2-}$ and can be used down to about 0.01mg L^{-1} with additional calibration standards at closely spaced concentration intervals.

In common with most ion selective electrodes the sulphide ion selective electrode is very dependent on pH and exhibits a linear dependence on pH over the range 9–12. To be operated successfully the electrode should be used only in samples buffered to pH 13.

The electrode is calibrated against standard solutions. Full calibration is only required if the electrode is used below the limit of Nernstian response.

Since the response of the sulphide ion selective electrode is dependent of the $\text{H}_2\text{S}/\text{HS}^-/\text{S}^{2-}$ equilibrium and in common with all ion selective electrodes is dependent on

temperature, ionic strength and pH, standards used for calibration should have a similar temperature, ionic strength and pH. The usual way of achieving these conditions and preventing air oxidation at the same time is to use a sulphide anti-oxidant buffer.

A sulphide ion selective electrode has been used [68] as an indicator electrode in the potentiometric titration of sulphide in paper mill effluents with standard mercuric chloride. In 0.1N sodium hydroxide medium, sulphide and polysulphides are titrated. As the electrode responds to mercuric ions, thiosulphate and sulphite can also be titrated at pH 7.0–7–5. The poly sulphide plus sulphite can be converted to thiosulphate and can be titrated. Sulphite can be decomposed with formaldehyde and, consequently, thiosulphate can be titrated alone.

The construction, characteristics and application of a custom-built coated tubular solid-state sulphide-selective electrode are described by Van Staden [69]. The tubular flow-through sensor is made from silver foil that is treated with a sodium sulphide solution. The electrode was used in association with flow-injection analysis and gave a working range up to 1000mg L^{-1} with a detection limit of 0.4mg L^{-1} when $30\mu\text{L L}^{-1}$ samples were injected. The system was suitable for determining soluble sulphide in effluent water samples in the range $0.4\text{--}24\text{mg L}^{-1}$ with a relative standard deviation better than 1.8% at a sampling rate of 60 samples L^{-1} .

Jovanovic and Jovanovic [70] determined low sulphide and cyanide levels using a deposited on wire silver-silver sulphide electrode.

10.18.6 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.8.2.

10.18.7 Gas chromatography

Hawke *et al.* [71] described a method for the determination of sulphides in effluents using gas chromatography with a flame photometric detector. Samples were acidified and the hydrogen sulphide brought to solution vapour equilibrium. Following analysis by gas chromatography the concentration of hydrogen sulphide was determined by interpolation on a calibration graph. The precision, accuracy, bias and effect of potentially interfering substances were determined. The samples could be processed in 1h by this method.

Knoery and Cutter [72] have described a method for the determination of sulphide and carbonyl sulphide in non saline waters using specialised collection procedures followed by gas chromatography using flame photometric detector. The following species were determined: $\text{H}_2\text{S}_{\text{aq}}$, HS^- , S^{2-} and particulate metal sulphides. The sample was stripped with helium and the evolved gases analysed by gas chromatography. Down to 0.2pmol L^{-1} of total dissolved sulphide could be determined.

10.19 Sulphite

10.19.1 Ion chromatography

Ion chromatography has been applied to the determination of sulphite in photographic processing effluents [73].

Petrie *et al.* [31] applied ion chromatography to the determination of sulphite and dithionite in mineral leachates.

The application of this technique is also discussed under multianion analysis in section 12.8.4.

10.20 Thiocyanate

10.20.1 Titration method

The application of this technique is discussed under multianion analysis in section 14.3.2.2.

10.20.2 Spectrophotometric method

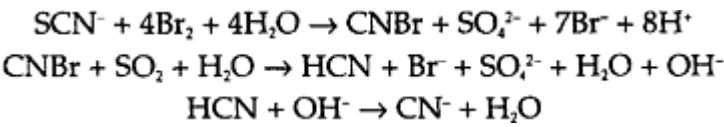
In a method [74] for the determination of thiocyanate in the effluent from a film processing unit, ferro and ferricyanides are first precipitated by the addition of zinc sulphate. Zinc is then precipitated from the filtrate by adding sodium carbonate and thiocyanate is determined in the final filtrate absorbtometrically using ferric chloride. Down to 1mg L^{-1} thiocyanate can be determined.

Luthy *et al.* [75] have described a spectrophotometric method for the determination of thiocyanate and cyanide in coal gasification waste waters. They showed that the copper pyridine method with pre-extraction was applicable but that high concentrations of carbonate and sulphide must first be removed from the sample.

Botto *et al.* [76] used p-phenylenediamine as the chromogenic reagent in the spectrophotometric determination of thiocyanate and uncomplexed cyanide in waste water.

10.20.3 Ion selective electrodes

Thiocyanate has been determined in waste water using a cyanide-selective electrode [77]. In this method thiocyanate is first converted to cyanogen bromide using bromine water. Excess bromine is removed by the addition of phenol. The cyanogen bromide is then converted to cyanide by the addition of sulphurous acid and then sodium hydroxide added. Cyanide is then estimated using the cyanide selective electrode:



10.21 Thiosulphate

10.21.1 Titration

The application of this technique is discussed under multianion analysis in section 14.3.2.1.

10.21.2 Atomic absorption spectrometry

Chakraborty and Das [78] have described a method for preconcentrating and determining thiosulphate in photographic waste effluents in which a stable ion associated complex is formed between lead, thiourea, and thiosulphate in alkaline medium. This complex was extracted into *n*-butyl acetate:butanol (2:1) solvent mixture prior to determination in amounts down to 19µg L⁻¹ by atomic absorption spectrometry.

10.21.3 High performance liquid chromatography

The application of this technique is discussed under multianion analysis in section 13.1.4.1.

10.22 Multianion analysis

10.22.1 Ion chromatography

See Table 10.3.

Table 10.3 Determination of sulphate in treated waters by ion chromatography

Type of water sample	Co-determined anions	Ref.
Industrial effluents	NO ₂ , NO ₃ , PO ₄ , F, Br	[79]
Industrial effluents	Cl, F	[80]
Industrial effluents	Cl, F, Br	[82]
Industrial effluents	Br, I	[83]

Source: Own files

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Chapter 11

Anions in high purity, boiler feed and nuclear reactor cooling waters

11.1 High purity waters

11.1.1 Carbonate

11.1.1.1 Ion chromatography

Carbonate has been determined in high purity water in amounts down to $0.02\mu\text{g L}^{-1}$ by ion chromatography on Zipax SAX phthalic acid or muconic acid at pH 6.5 and 7.2 as eluting agent and an indirect ultraviolet detector set at $321\mu\text{m}$ [1].

11.1.2 Chloride

11.1.2.1 Spectrofluorometry

Fluorescence spectroscopy has been used to determine down to $1\mu\text{g L}^{-1}$ chloride in high purity water. The method is based on the quenching effect of silver chloride on the fluorescence of sodium fluorescein. The coefficient of variation is within 15% at the $10\mu\text{g L}^{-1}$ chloride level [2].

11.1.2.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.9.1.

11.1.3 Nitrite

11.1.3.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.9.1.

11.1.4 Sulphate

11.1.4.1 Molecular emission cavity analysis

Sulphate has been determined in high purity water by molecular emission cavity analysis

[3].

11.1.4.2 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.9.1.

11.1.5 Silicate

11.1.5.1 Spectrophotometric method

Spectrophotometric methods have been described for the determination of traces of silicate in high pressure boiler feed water [4,5], and deionised water [6]. Silicomolybdate procedures employing 4-amino-3-hydroxynaphthalene-1-sulphonic acid have been employed [7,8]. Spectrophotometric evaluation of the reduced complex is carried out at 805–810nm in these methods.

It is essential in order to avoid silica contamination, to use precleaned polyethylene sample bottles and apparatus. Ramachandran and Gupta [6] performed studies on the effects of different reducing agents on silicate determination by the molybdenum blue method. Best results were obtained using ascorbic acid and antimony. The antimony did not participate in the complex but enhanced its absorbance. The recommended procedure is described. It was relatively rapid and sensitive. Beer's Law was obeyed for silicate concentrations of 20–1000 $\mu\text{g L}^{-1}$.

Pilipenko *et al.* [9] compared Spectrophotometric and chemiluminescent methods of determining silicate in deionised water. They studied different reducing agents in the molybdenum blue Spectrophotometric method, viz. tungstosilicic acid, stannous chloride, 1-amino-2-naphthol-sulphonic acid and mixtures of metol and sodium sulphite. They also studied the extraction of the blue tungstosilicic acid with crystal violet and methylene blue. The chemiluminescent method was based on the oxidation of luminol by molybdosilicic acid in alkaline medium. These workers concluded that the best method, from the points of view of detection limit, reproducibility, simplicity and rapidity, was one based on the reduction of molybdosilicic acid by 1-amino-2-naphthol-4-sulphonic acid.

11.2 Boiler feed waters

11.2.1 Chloride

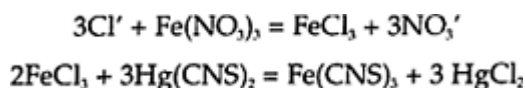
It is generally accepted that the presence of chloride in the steam-water circuit of power stations can be associated with corrosive conditions within the boiler, consequently chloride levels have to be controlled. The concentration of chloride treated in boiler waters varies with the design of the boiler and the chemical treatment accorded to the boiler water, but in every instance it is essential that any ingress of chloride is detected so that remedial action can be taken. In order to identify the source of the chloride, it is necessary to monitor plant streams, eg feed water or the effluent from a water treatment

plant, where chloride levels may be as low as a few micrograms per litre.

11.2.1.1 Titration method

A titrimetric method for the determination of milligram per litre quantities of chloride (and bromide) in boiler feed water involves titration of the sample at pH 1 to 4 with 0.1N mercuric nitrate to the tetra(ethyl di-(1-sodiotetrazol-5-ylazo)acetate yellow to red end point [7]. A 300-fold excess of sulphate, nitrate, carbonate or acetate can be tolerated, but cobalt, fluoride, iodide or nickel interfere.

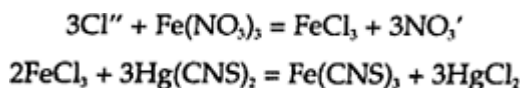
Samples can be acidified with perchloric acid and ferric nitrate solution added followed by ethanolic [8] or methanolic [10] thiocyanate.



The extinction of the mercuric thiocyanate complex is measured at 460nm [8] or 463nm [10]. Chloride can be determined down to $1\mu\text{g L}^{-1}$ by these procedures. Hydrogen peroxide or hydrazine used as boiler water treatment chemicals do not interfere. Interference arises from the presence of comparatively large amounts of cupric sulphate, potassium dichromate, lithium hydroxide or ammonium fluoride. The coefficient of variation at the $50\mu\text{g L}^{-1}$ level was 12%.

11.2.1.2 Spectrophotometric method

Two Spectrophotometric procedures involving the formation of the red coloured ferric thiocyanate complex formed between chloride ion and ethanolic mercuric thiocyanate in the presence of ferric ions have been described for the determination of chloride in boiler feed water.



In these methods the sample is acidified with perchloric acid or nitric acid and ferric nitrate solution is added followed by ethanolic [8] or methanolic [11] thiocyanate. The extinction of the mercuric thiocyanate complex is measured at 460nm or 463nm [11]. Down to $1\mu\text{g L}^{-1}$ chloride can be determined by these procedures. Hydrogen peroxide and hydrazine used as boiler water treatment chemicals did not interfere. Interference arises from the presence of comparatively large amounts of cupric sulphate, potassium dichromate, lithium hydroxide or ammonium fluoride. The coefficient of variation at the $50\mu\text{g L}^{-1}$ level was 12%.

11.2.1.3 Ion selective electrodes

Silver-silver chloride electrodes [11–14] and solid state mercurous chloride electrodes

[15,16] have been used to determine traces of chloride in high purity power station waters. Detection limits claimed are $6\text{--}100\mu\text{g L}^{-1}$ [14] for silver-silver chloride electrodes and $1\text{--}10\mu\text{g L}^{-1}$ solid-state mercurous chloride electrodes.

Silver-silver chloride electrodes

Measurements have been made in two ways. In one method [14] two solid-state Orion 94-17A silver chloride membrane electrodes are used. The reference electrode is contained in a compartment connected to the sample compartment by a ground glass sleeve. The reference compartment contains a $100\mu\text{g L}^{-1}$ solution of chloride in 0.1mol L^{-1} nitric acid. A graph is constructed from cell potential readings after adding increments of standard chloride solution to the sample solution (made 0.1mol L^{-1} in nitric acid) in the sample compartment. A similar graph is obtained by adding increments of the chloride solution to a blank solution containing 0.1mol L^{-1} nitric acid. The chloride content of the sample is given by the distance along the concentration axis between the two lines.

Concentrations of copper(II), iron(II), nickel(II) and aluminium interfere when present at concentrations exceeding 10mg L^{-1} and ammonia and hydrazine also interfere. It is claimed that better precision is obtained using these electrodes than by using the conventional silver-silver chloride electrodes discussed below.

In the alternative method, measurements are made using silver-silver chloride electrodes vs a mercurous sulphate reference electrode [11,13].

A manual version of this procedure has been described having a detection limit of $100\mu\text{g L}^{-1}$. The continuous analyser version (discussed below) has been described with a detection limit nearer to $1\mu\text{g L}^{-1}$ [11].

In this apparatus the electrodes are immersed in a buffered sample stream. The temperature of the electrode flow cell is controlled at $10 (\pm 0.1)^\circ\text{C}$ at which level the sensitivity of 3.54mV per $100\mu\text{g L}^{-1}$ is approximately 50% greater than that at $25 (\pm 0.1)^\circ\text{C}$, and a linear response of cell potential to changes in chloride concentration is observed up to $0.150\mu\text{g L}^{-1}$. The standard deviations at 10°C for nominal chloride

Table 11.1 Recovery of chloride from samples of power station waters

Sample	Initial chloride concentration $\mu\text{g L}^{-1}$	Chloride spike added $\mu\text{g L}^{-1}$	Final chloride concentration $\mu\text{g L}^{-1}$	Recovery %
Condensed steam (A)	<1	5.0	$5.3^{\text{a}}(0.23)^{\text{b}}$	106.0
Condensed steam (B)	<1	19.7	$19.5(0.40)$	98.9
Boiler water	108.0	47.2	$156.9(0.40)$	103.6

^aEach result is the mean of six determinations

^bThe figures in parenthesis are the standard deviations for single determinations with five degrees

of freedom

Source: Reproduced with permission from the Electrochemical Society Inc., USA [14]

concentrations of 50, 100 and 250 $\mu\text{g L}^{-1}$ are ± 1.7 , ± 2.8 and $\pm 2.7 \mu\text{g L}^{-1}$ respectively. Substances normally present in these waters do not interfere appreciably.

Table 11.1 shows the satisfactory recoveries obtained in some spiking experiments carried out using this system. In most instances there was no significant interference in the procedure by substances likely to occur in boiler feed water and in every instance except one, where an interference was detected, the effect was positive (Table 11.2). The small effects noted for sodium hydroxide, trisodium orthophosphate and sodium carbonate could be explained by a change in the pH of the system. The unexpected interference from sodium sulphate and sodium sulphite could arise from trace amounts of chloride in the reagent chemicals. However, the effects were so small, even at the excess levels of these substances added, that for most practical purposes they could be ignored.

Solid state mercurous chloride electrodes

This is the more recent development in the determination of chloride in high purity water. Marshall and Midgley [15,16] have described a procedure for the determination of 0–20 $\mu\text{g L}^{-1}$ chloride in high purity water, using two types of ion selective membrane electrode incorporating mercurous chloride. At these low concentrations, more chloride will dissolve from the mercury (1) chloride in the electrode than is present in the sample itself. The extent of the dissolution is controlled, however, by the chloride in the sample. In these circumstances, the electrode potential is linearly related to the concentration of chloride in the sample. With the electrode housed in a flow cell with a thermostatically controlled water

Table 11.2 Effect of other substances at 10°C

Substance	Concentration of substance mg L^{-1}	Interference effects ($\mu\text{g L}^{-1}$) of chloride at chloride concentrations of	
		0 $\mu\text{g L}^{-1\text{a}}$	50 $\mu\text{g L}^{-1\text{a}}$
Na_2SO_4	75	1.7	3.1
Na_2HPO_4	50	1.4	2.7
NaOH	4	<1	<1
NaOH	40	4.1	3.8
Na_3PO_4	50	2.7	<1
Na_2CO_3	50	2.7	<1
NH_3	10	<1	<1
Morpholine	10	<1	<1

Cyclohexylamine	10	<1	<1
Hydrazine	1	<1	<1
H ₂ SO ₄	10	<1	<1
Na ₂ ¹⁺ SO ₃	5	4.4	4.5
Fe ²⁺ , Cu ²⁺ , Zn ²⁺	1+1+1	-2.9	<1
Ca ²⁺ , Mg ²⁺ , K ⁺	2+2+20	1.5	<1
O ₂	-4	<1	-

^aIf the other substances had no effect the results would have been expected to fall within the limits of 0 ± 1.2 and $50 \pm 3.4 \mu\text{g L}^{-1}$ at the 95% confidence level

Source: Reproduced with permission from the Electrochemical Society Inc., USA [14]

jacket, the correlation coefficient between EMF and concentration was always greater than 0.99. The sensitivity ($0.18\text{mV } \mu\text{g L}^{-1}$ of chloride at 25°C and $0.4\text{--}0.5\text{mV } \mu\text{g L}^{-1}$ of chloride at 4°C) was about 10 times greater than that of the silver-silver chloride electrode. Total standard deviations at 10, 5 and $2 \mu\text{g L}^{-1}$ of chloride were 0.4, 0.5 and $0.3 \mu\text{g L}^{-1}$ of chloride respectively.

Potentials were measured with a digital pH meter reading to 0.1mV and displayed on a chart recorder. Two types of ion selective electrodes were used, those made from Radiometer F3012 Universal electrodes, and the Ionel Model SL-01 (Ionel electrodes, Mount Hope, Ontario, Canada). Both have membranes made of a mixture of mercury(II) sulphide and mercury(II) chloride. In the electrode developed at CERL, the mixture is used to impregnate a graphite PTFE electrode, while in the Ionel electrode the mixture is hot pressed into a disc. The reference electrode was a mercury-mercury(I) sulphate electrode with a 0.5mol L^{-1} sodium sulphate filling solution (instead of the usual 1mol L^{-1} solution, which would have precipitated at the lowest operating temperature of 4°C). The reservoir containing the filling solution and the reference element could be raised to 0.5m above the remote liquid junction, which was of the ground glass sleeve type.

The chloride electrode and the remote junction were housed in a flow cell fitted with a water jacket through which thermostatically controlled water was circulated by means of a Techne C-100 thermocirculator operated in conjunction with a Techne Model 1000 chiller unit. The remote junction was in a separate compartment downstream of the chloride electrode compartment, which contained a magnetic stirrer bar. The flow cell was painted black to exclude light.

A Technicon Model 1 proportioning pump delivered the solutions to the flow cell, pumping the sample or standard solutions at 3.9ml min^{-1} and the acid reagent solution at 0.8ml min^{-1} . Air was injected at 1ml min^{-1} to improve mixing. The air-segmented mixture of sample and reagent solutions passed through a glass mixing coil to a T-piece, from which the air and a portion of the solution were extracted at 1.6ml min^{-1} . The rate of delivery of solution to the flow cell was, therefore, 4.1ml min^{-1} . The pump tubes were made of PVC, but the transmission lines were made of PTFE.

Before entering the cell, the solution passed through a short length of stainless steel tubing, which was connected to the chassis ground terminal on the pH meter. A stainless

steel wire was immersed in the solution downstream of the electrode pair and also connected to the chassis ground point. Without these connections the signal was noisy.

The use of mercury(I) chloride electrodes for determining chloride concentrations can be extended from the levels attainable by manual analysis to very low levels (less than $20\mu\text{g L}^{-1}$) by housing the electrode in a flow cell at a controlled temperature. At a given temperature, the electrode is about 10 times more sensitive than the silver chloride electrode.

One advantage of this greater sensitivity is that the mercury(I) chloride electrode does not need to be operated at sub-ambient temperatures in order to obtain adequate precision in the concentration range $1\text{--}20\mu\text{g L}^{-1}$. Two kinds of electrode can be used, that developed at CERL and the Ionel SL01. The two electrodes are almost equally sensitive and precise, but the Ionel has a faster response time and requires no preparation.

11.2.1.4 Ion chromatography

Roberts *et al.* [17] have described a method for the determination of chloride in boiler feed water. The application of this technique is also discussed under multianion analysis in section 12.10.1.

11.2.2 Nitrite

11.2.2.1 Ion chromatography

The application of this technique is discussed under multianion analysis in section 12.10.1.

11.2.3 Phosphate

11.2.3.1 Ion chromatography

Stevens and Turkelson [18] have described a procedure for the determination of down to 1mg L^{-1} of phosphate in boiler blow down water. The application of this technique is also discussed under multianion analysis in section 12.10.2.

11.2.4 Silicate

11.2.4.1 Spectrophotometric method

Spectrophotometric methods have been described for the determination of traces of silicate in high pressure boiler feed water [4,18] and deionised water [6]. Silicomolybdate procedures employing 4-amino-3-hydroxynaphthalene-1-sulphonic acid have been employed [4,18]. Spectrophotometric evaluation of the reduced complex is carried out at 805–810nm in these methods.

It is essential, in order to avoid silica contamination, to use precleaned polyethylene

sample bottles and apparatus. Ramachandran and Gupta [6] performed studies on the effects of different reducing agents on silicate determination by the molybdenum blue method. Best results were obtained using ascorbic acid and antimony. The antimony did not participate in the complex but enhanced its absorbance. The recommended procedure is described. It was relatively rapid and sensitive. Beer's law was obeyed for silicate concentrations of 20–1000 $\mu\text{g L}^{-1}$.

Pilipenko *et al.* [9] compared Spectrophotometric and chemiluminescent methods of determining silicate in deionised water. They studied different reducing agents in the molybdenum blue Spectrophotometric method, namely tungstosilicic acid, stannous chloride, 1-amino-2-naphtholsulphonic acid and mixtures of metal and sodium sulphite. They also studied the extraction of the blue tungstosilicic acid complex by isobutanol and the formation of complexes of tungstosilicic acid with crystal violet and methylene blue. The chemiluminescent method was based on the oxidation of luminol by molybdosilicic acid in alkaline medium. These workers concluded that the best method, from the points of view of detection limit, reproducibility simplicity and rapidity, was one based on the reduction of molybdosilicic acid by 1-amino-2-naphthol-4-sulphonic acid.

11.2.5 Sulphate

11.2.5.1 Ion chromatography

The application of this technique is discussed under multianion analysis in sections 12.10.1 and 12.10.2.

11.2.6 Sulphite

11.2.6.1 Ion chromatography

Stevens and Turkelson [18] have described a procedure for the determination of down to 1mg L^{-1} of sulphite in boiler blow down water.

11.3 Nuclear reactor cooling waters

11.3.1 Iodide

11.3.1.1 Titration method

Erdey and Kozmutza [19] used xenon difluoride as a reagent for the determination of mg L^{-1} quantities of iodide and iodine in nuclear reactor cooling waters. The test solution is made IN in sulphuric acid and excess solid xenon difluoride added to convert iodide to periodate which is then determined by standard iodometric procedures.

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Chapter 12

Multianion analysis, applications of ion chromatography

Ion chromatography as originally developed by Small and co-workers in 1975 provided a method for the separation and determination of inorganic anions and cations [1]. This original method used two columns attached in series packed with ion exchange resins to separate the ions of interest and suppress the conductance of the eluant, leaving only the species of interest as the major conducting species in the solution. Once the ions were separated and the eluant suppressed, the solution entered a conductivity cell where the species of interest were detected. Since its introduction, ion chromatography has advanced considerably and the technique is now routinely used for the analysis of organic and inorganic anions and cations and substances, including organic acids and amines, carbohydrates and alcohols. Ion chromatography is not restricted to the separate analysis of only anions or cations. With the proper selection of eluant and separation columns, the technique can be used for the simultaneous analysis of both anions and cations.

The simultaneous determinations of anions and cations using single injection ion chromatography was introduced by Yamamoto and co-workers in 1984 [2]. This technique determined cations and anions simultaneously using a complexing agent, ethylenedinitrilotetraacetic acid, to complex the divalent metals. These divalent metals were later separated and detected as anions along with the uncomplexed inorganic anions.

The technique has progressed rapidly since 1975 and in 1978 a book was published on ion chromatographic analysis of environmental pollutants [3]. Other early papers on the application of ion chromatography cover the determination of selected ions in geothermal well water [4], the determination of anions in potable water [5,6], and the separation of metal ions and anions and anions and cations [7].

12.1 Ultraviolet versus conductivity detectors

Cochrane and Miller [8] state the sensitivity of an ultraviolet detector is about 10 times greater than that of an electrical conductivity detector. Ultraviolet detection of anions is not generally applicable except at very low wavelengths such as 215nm. An alternative method of detection of non-ultraviolet absorbing species is to add a low level of ultraviolet absorbing substances to the eluant. The emergence of a component is then shown by a negative detector response.

The effect is easily achieved in the ion chromatography system where the preferred buffer solution (potassium hydrogen phthalate ($5 \times 10^{-3} \text{M}$ at pH 4.6) has a strong ultraviolet response with λ_{max} at 280nm. At this wavelength the excessively strong absorbance will not allow adequate zero suppression and the wavelength was therefore

increased to a much less absorbing region (308nm) where the background response could be backed off sufficiently for the detector to be used at maximum sensitivity. A comparison of the conductivity and ultraviolet detectors showed that:

- (1) The response is greater for ultraviolet detection by a factor of 5–30. A relatively stronger, negative ultraviolet response occurs for weakly acidic anions because there is no dependence on their ionisation.
- (2) Linearity ranges using ultraviolet detection are greater than those for conductance.
- (3) Conductance detection may give positive or negative peaks depending on eluant concentration and pH. Ultraviolet detection of non-ultraviolet absorbing ions give a response in one direction only.

An ultraviolet detector used in series with a conductivity detector is the basis for a method [9] for the determination of anions in non saline waters. This combination of detectors greatly increases the amount of information that can be collected on a given sample. The application of ultraviolet detection has the following advantages:

- (1) aid in the identification of unknown peaks;
- (2) use in resolving overlapping peaks;
- (3) help in eliminating problems associated with the carbonate dip;
- (4) reduction of problems associated with ion exclusion in the suppressor column;
- (5) ability to detect anions not normally detected by the conductivity detector, eg sulphide and arsenite.

For maximum sensitivity, the preferred position of the ultraviolet detector is after the suppressor column. The suppressor column also decreases the background absorbance of the other common ion chromatographic eluents such as 0.0002M Na_2CO_3 /0.002M NaOH, 0.006M Na_2CO_3 and 0.005M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Fig. 12.1 shows a separation of seven common anions monitored using the conductivity detector. Fig. 12.1 (b) was obtained with the ultraviolet detector after the suppressor column. As is illustrated in Fig. 12.1, nitrite, bromide, and nitrate absorb strongly in the ultraviolet, while fluoride,

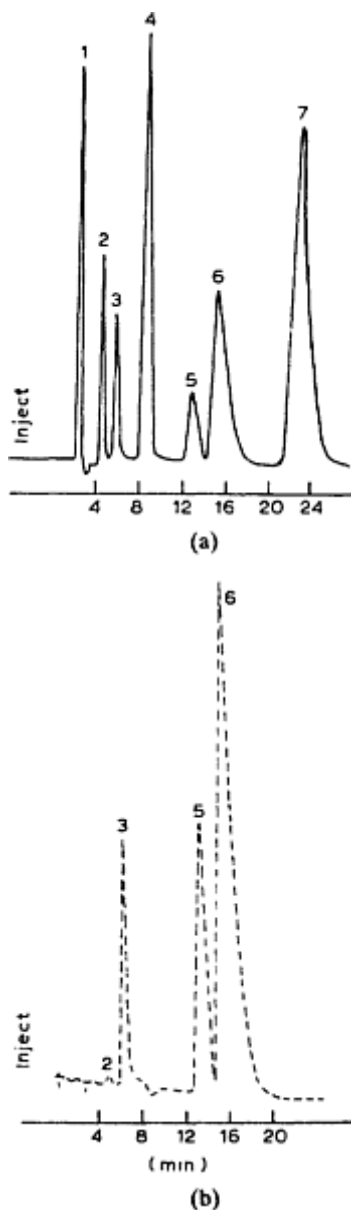


Fig. 12.1 Ion chromatogram of seven common anions (a) conductivity detectors (—) peak 1, $3\text{mg L}^{-1}\text{F}^{-}$; peak 2, $4\text{mg L}^{-1}\text{Cl}^{-}$ peak 3, $10\text{mg L}^{-1}\text{NO}_2^{-}$; peak 4, $50\text{mg L}^{-1}\text{PO}_4^{3-}$; peak 5, $10\text{mg L}^{-1}\text{Br}^{-}$; peak 6, $30\text{mg L}^{-1}\text{NO}_3^{-}$; peak 7, $50\text{mg L}^{-1}\text{SO}_4^{2-}$; (b) ultraviolet detector (- - -) at 192nm , position 2; peak 2, $4\text{mg L}^{-1}\text{Cl}^{-}$ peak 3, $10\text{mg L}^{-1}\text{NO}_2^{-}$; peak 5, $10\text{mg L}^{-1}\text{Br}^{-}$; peak 6, $30\text{mg L}^{-1}\text{NO}_3^{-}$ Dip at

approx. 8min=PO₄

Source: Reproduced with permission from the American Chemical Society [9]

Table 12.1 List of ultraviolet absorbing and non-absorbing inorganic anions

Anion	Retention time (min)	UV active	UV detection limite (mg L ⁻¹)	UV detector position	Wavelength (nm)	Chromotographic condition
F ⁻	2.4	N ^a		2 ^c	195	A
S ²⁻	2.4	Y ^b		M	205	A
IO ₃ ⁻	2.6	Y	0.08	2	195	A
ClO ₂ 1 ⁻	3.0	Y	0.2	2	195	A
H ₂ PO ₂ ⁻	3.0	N		2	195	A
NH ₂ SO ₃ ⁻	3.8	N		2	195	A
BrO ₃ ⁻	4.3	Y	0.16	2	195	A
Cl ⁻	4.6	Y	2	2	192	A
S ²⁻	5.4	Y		1	195	C
NO ₂ ⁻	5.9	Y	0.1	2	195	A
BF ₄ ⁻	6.6	N		2	195	B
HPO ₃ ²⁻	6.7	N		2	195	A
SeO ₃ ²⁻	6.9	Y	0.5	2	195	A
I ⁻	7.8	Y	0.15	2	195	B
PO ₄ ⁻	8.4	N		2	195	A
SCN ⁻	10.8	Y	0.2	2	195	B
AsO ₄ ³⁻	10.9	Y	1.5	1	200	D
AsO ₄ ³⁻	12.2	Y	2	2	195	A
S ₂ O ₃ ⁻	12.6	Y		2	195	B
Br ⁻	13.0	Y	0.1	2	195	A
AsO ₃ ³⁻	13.3	Y	1.2	1	200	D
SO ₃ ²⁻	13.4	Y		2	195	A
N ₃ ⁻	14.1	Y	0.3	2	195	A
NO ₃ ⁻	15.2	Y	0.1	2	195	A
ClO ₃ ⁻	15.2	Y	4	2	195	A
SeCN ⁻	18.8	Y	0.4	2	195	B

ClO_4^-	19.6	N		2	195	B
S^2	21.2	Y	0.4	1	200	D
SO_4^{2-}	22.8	N		2	195	A
SeO_4^{2-}	27.2	Y	15	2	195	A

^aN, not UV active. ^bY., UV active. ^c2, after suppressor. ^d1, before suppressor. ^e100 μL injection, peak height 2 $\times$ noise level

Source: Reproduced with permission from the American Chemical Society [9]

phosphate and sulphate do not show appreciable absorption above 190nm. Chloride absorbs weakly in the ultraviolet region below 200nm. Note that non-absorbing anions are sometimes observed by the ultraviolet detector as negative peaks, as is shown in Fig. 12.1(b) for phosphate. Table 12.1 contains a more extensive list of ultraviolet active anions and also lists the detection limits for many of the anions. Detection

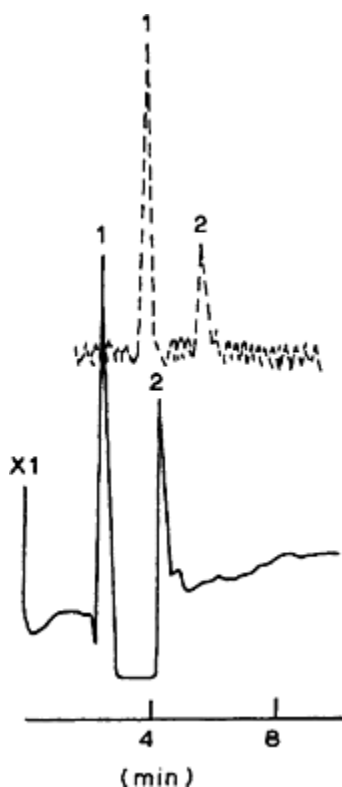


Fig. 12.2 Separation of iodate and bromate by ion chromatography ultraviolet detector (---) at 195nm, position 2; conductivity detector (—); peak 1, 0.5mg L⁻¹ IO₃⁻; peak 2, 0.8mg L⁻¹ BrO₃⁻

Source: Reproduced with permission from the American Chemical

Society [9]

limits are generally in the sub parts per million range. No attempt was made to optimise the chromatographic conditions for a particular anion.

Out of the 27 anions listed in Table 12.1 all but eight absorb in the ultraviolet above 190nm. This demonstrates that the commonly held assumption regarding the lack of suitable chromophores by inorganic ions for ultraviolet detection is incorrect. This misconception has probably come about from the fact that although many anions absorb in the 190–220nm region, few of them show an absorption maximum above 190nm. This has limited the analytical usefulness of direct ultraviolet absorbance measurement for the determination of inorganic anions. However, the lack of an absorption maximum does not severely limit the analytical usefulness when the ultraviolet spectrometer is combined with a separation technique such as ion chromatography.

The ultraviolet detector, in combination with the conductivity detector, offers a number of advantages in ion chromatography. Fig. 12.2 shows the separation of sub-part-per million iodate and bromate monitored using

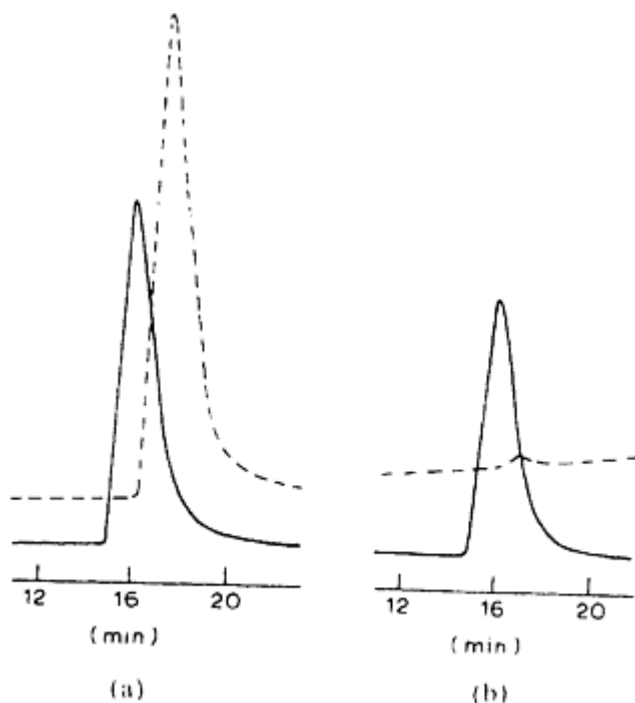


Fig. 12.3 Separation of nitrate and chlorate by ion chromatography: (a) conductivity detector (—) $30\text{mg L}^{-1} \text{NO}_3^-$ UV detector (---) at 195nm, position 2; (b) conductivity detector (—) $30\text{mg L}^{-1} \text{ClO}_3^-$ UV detector (---) at 195nm respectively

Source: Reproduced with permission from the American Chemical Society [9]

both detectors. The iodate and bromate peaks monitored with the conductivity detector (solid line chromatogram) were distorted by the so called carbonate dip. The size of the carbonate dip is controlled by the eluant (both its concentration and composition), the size of the injection loop and the size of the suppressor column. The peak distortion caused by the carbonate dip makes both qualitative and quantitative analysis more difficult. Little or no carbonate dip is observed in Fig. 12.2 (broken line chromatogram) with the ultraviolet detector after the suppressor column.

Fig. 12.3(a) shows the ultraviolet and conductivity peaks from a 30mg L^{-1} nitrate injection while Fig. 12.3(b) shows the ultraviolet and conductivity peaks from a 30mg L^{-1} chlorate injection. Both species have the same retention time and peak shape (tailing) and with just the information from the conductivity detector it would be impossible to identify which species is present. With both detectors, it is possible to obtain a ultraviolet/conductivity peak height ratio and this information can be used as an aid in identifying unknown peaks. Additional ultraviolet/conductivity peak height ratios can be obtained by varying

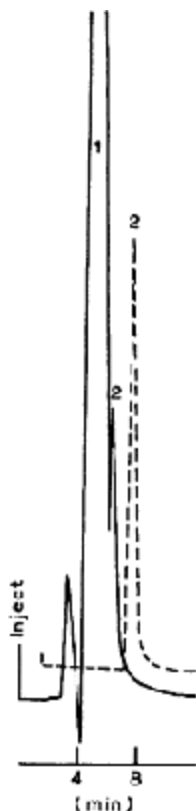


Fig. 12.4 Nitrite determination in the presence of $100\text{--}2000\text{mg L}^{-1} \text{Cl}^{-}$ ultraviolet detector (---) at 210nm position 1; conductivity detector (—); peak 1, $1000\text{--}2000\text{mg L}^{-1}$

Source: Reproduced with permission from the American Chemical Society [9]

the wavelength. Identification is then made by running a standard solution of the suspected species (same retention time) and comparing the peak height ratios at the same wavelengths as the unknown species.

The ion chromatographic determination of weak acid anions is complicated by ion exclusion in the suppressor column, resulting in faster elution and sharper peaks, directly proportional to the degree of exhaustion of the suppressor column. A 10mg L^{-1} nitrite standard showed a 37% increase in peak height over an 8h period when monitored with the conductivity detector while only a minor 2% increase in peak height was observed over the same time period by using the ultraviolet detector after the separator column.

The ultraviolet detector can also be used in some cases to resolve overlapping peaks. Fig. 12.4 shows the ion chromatogram of 10mg L^{-1} nitrite in the presence of $1000\text{--}2000\text{mg L}^{-1}$ chloride. Determination of the nitrite peak by using the conductivity detector is complicated by both the ion exclusion effect and incomplete resolution between the large chloride peak and the much smaller nitrite peak. The ion exclusion interference can be eliminated for ultraviolet active anions by placing the ultraviolet detector between the separator and suppressor columns (position 1). In addition, the problem of overlapping peaks can sometimes be resolved spectrophotometrically by proper choice of wavelength as shown in Fig. 12.4 (broken line chromatogram).

Sulphide cannot be detected under normal ion chromatographic conditions. It is converted into hydrogen sulphide in the suppressor column. Hydrogen sulphide acid is a very weak acid that does not ionise sufficiently to be detected with the conductivity detector. The ultraviolet detector, however, is able to detect sulphide at low levels. Since sulphide is a weak acid anion, the ultraviolet detector was placed between the separator and suppressor columns.

Arsenous acid is a very weak acid and cannot be detected at low levels by the conductivity detector. However, like sulphide, it is easily detected with the ultraviolet detector. The simultaneous determination of arsenite and arsenate is possible.

Arsenite also can be separated by ion chromatography using standard conditions. It elutes early, near the carbonate dip. For this application the ultraviolet detector should be placed between the separator and suppressor columns.

12.2 Non saline waters

12.2.1 Chloride, bromide, fluoride, iodide, nitrite, nitrate, sulphate, phosphate, bicarbonate, cyanide and sulphide

Ion chromatography has been used for the measurement of background concentrations of fluoride, chloride, nitrate and sulphate in non saline waters [10].

Shown in Fig. 12.5 is a schematic diagram of the Dionex ion exchange liquid chromatograph used by Smee *et al.* [10]. The instrumentation consists essentially of a low capacity anion exchange column, the 'separator', a high capacity cation exchange column, the 'suppressor' and the detection system, a high sensitivity conductivity meter

and recorder. Following the injection of a small volume (100 μ L) of sample, rapid exchange and separation of the anions is accomplished with a specially prepared low capacity resin (containing quaternary ammonium exchange sites existing as a thin film on the surface to facilitate fast equilibrium).

The otherwise highly conducting background of the eluant (0.003mol L⁻¹ sodium bicarbonate/0.0024mol L⁻¹ sodium carbonate) is virtually

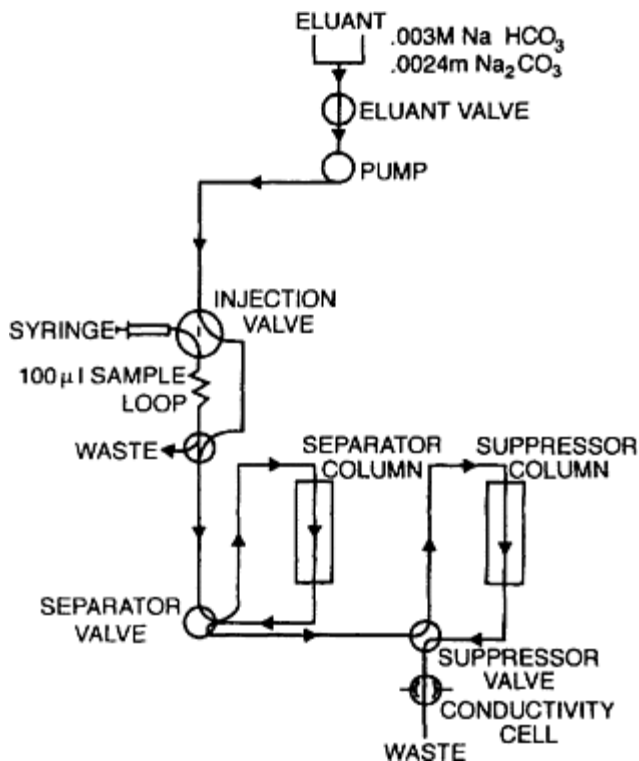


Fig. 12.5 Ion chromatographic flow diagram. Eluant conditions used for anion analysis

Source: Reproduced with permission from Elsevier Science [10]

eliminated by passage through the high capacity suppressor column whereupon carbonic acid is formed together with the acid forms of the anions of interest. The conductivity meter used as a detector then only sees a small residual background due to the weakly dissociated carbonic acid and the conductivity of the acids of interest separated in time. Additional to this basic instrumentation, there are four reservoirs (2 eluant, 1 regenerant, 1 water), a sample injection valve with a 100 μ L loop, two Milton Roy fluid pumps with adjustable flow rates and an automatic timer for controlling the regeneration cycle of the cation exchange resin.

Approximately 1ml of untreated sample was injected into the entrance port by means of a hypodermic syringe; 100 μ L of sample was used to fill the sample loop, the

remainder passing to waste. The determination began with a freshly regenerated separator column and proceeded sequentially through the sample series. Retention times of peaks from the resulting chromatograms were compared with known synthetic standards analysed under the same eluant strength and flow conditions. Measurements of anion concentrations in each sample were obtained by

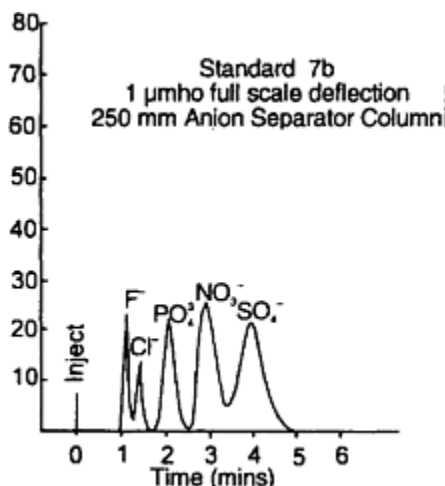


Fig. 12.6 Calibration chromatogram for a 250mm anion separator column using standard 7b containing $0.1\mu\text{g mL}^{-1}$ F, $0.1\mu\text{g mL}^{-1}$ Cl, $0.1\mu\text{g mL}^{-1}$ PO₄³⁻, $1.0\mu\text{g mL}^{-1}$ NO₃⁻ and $1.0\mu\text{g mL}^{-1}$ SO₄²⁻

Source: Reproduced with permission from Elsevier Science [10]

comparing peak heights with a standard curve generated from peak heights of mixed synthetic standard.

Two separator columns were studied by Smee *et al.* [10]—one 250mm and one 500mm in length. Examples of chromatograms obtained from standards injected into a 250mm column are shown in Fig. 12.6. Standard 7b used in the 250mm long column (Fig. 12.6) does not contain nitrite and bromide but concentrations of fluoride, chloride, phosphate, nitrate and sulphate are the same as for the 500mm column. Both columns exhibit advantages and disadvantages. Better resolution of chromatographic peaks, particularly those involving nitrate, nitrite, phosphate and bromide is obtained with the 500mm column. A depression of the baseline created by elution of the water portion of the sample, thus lowering the background conductivity, occurs between the fluoride and chloride peaks and can result in a depression of the chloride response. This depression is negligible with the 500mm column. Disadvantages in using the 500mm column include a longer elution time for each sample, a decrease in precision at moderate to high concentrations created by broadening of chromatographic peaks (this may be compensated for by integrating peak areas rather than measuring peak heights), and a progressive deterioration of efficiency of the suppressor column caused by an increased volume of eluant required for the longer elution time. This latter problem may be solved

by regenerating the column more frequently or by an increased use of standards with samples.

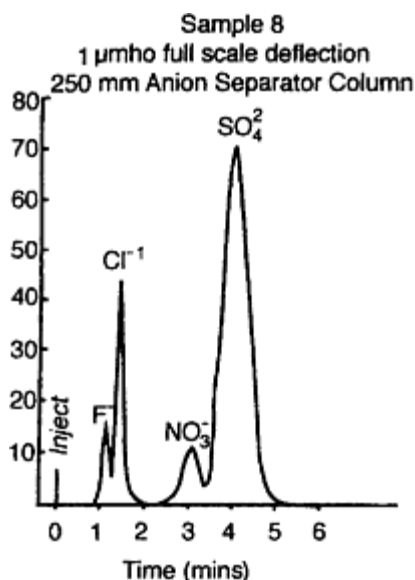


Fig. 12.7 Chromatogram of sample 8 using the same conditions as for the calibration in Fig. 12.6

Source: Reproduced with permission from Elsevier Science [10]

Typical chromatograms obtained from a sample of northern Ontario stream water are shown in Fig. 12.7 (250mm column). No advantage is gained by using the 500mm column rather than the 250mm column. The time for analysis is more than doubled and peak heights have decreased. The increased separation of anion chromatographic peaks is not required for this sample type.

The relationship between fluoride determination by ion selective electrode and ion chromatography is good but a larger spread of values is evident with the 500mm column, especially with samples containing above average amounts of fluoride. Values reported by ion chromatography are usually higher than those obtained by the selective ion technique. The minimum reported concentration for fluoride by ion chromatography is $3\mu\text{g L}^{-1}$ and for selective ion electrodes $20\mu\text{g L}^{-1}$.

The detection limit of the 2-aminoperimidine method for sulphate is $5\text{--}10\text{mg L}^{-1}$. Sulphate contents reported by both columns usually correlate well with one another. The lower limit of detection for sulphate reported for the 250mm column is 0.05mg L^{-1} and for the 500ml column 0.05mg L^{-1} two orders of magnitude below the limit reported for the 2-aminoperimidine method.

A comparison between nitrate determination by ion chromatography and by the colorimetric technique shows that there is a correlation between the two sets of results but nitrate values obtained by the chromatographic method are consistently higher than those

obtained by colorimetry. Furthermore, the 500mm column yields higher values than the 250mm column. Values above 0.2mg L^{-1} generally agree well. The limit of detection (0.02mg L^{-1}) reported for the 250mm column is below that reported for the 500mm column (0.05mg L^{-1}) because of the sharper peaks obtained with the shorter column.

Chloride contents of the non saline waters varied from 0.5 to 312mg L^{-1} by the spectrophotometric method. A comparison of the chloride determinations reveal an excellent correlation between the chloride values obtained from the 500mm column and the expected values. The 250mm column exhibits a gradational increase in the difference between the ion chromatograph and the expected results with increasing chloride concentration. This difference is probably caused by a progressive overlap of the chloride peak with the fluoride peak. Minimum reported concentrations for chloride using the 250mm column is 0.02mg L^{-1} and for the 500mm column, 0.01mg L^{-1} against 0.5mg L^{-1} for spectrophotometric methods.

Estimates of precision based on five analyses of the replicate non saline water samples are presented in Table 12.2. The 250mm column is more precise than the 500mm column for all anions analysed, mainly because the peak height of a response was measured rather than peak area, the shorter column producing the more narrow peaks. Fluoride determinations using the 500mm column exhibit a progressive upward increase in fluoride content caused by the aging of the column during the analytical run. This apparent increase in fluoride content may occur at the expense of the chloride ion, the next anion through the column, as there appears to be a gradual decrease in chloride content with time. No data on nitrate was obtained from the replicate sample. Precision for sulphate through both columns is excellent, although the 250mm column consistently produces the higher analytical values.

Van Os *et al.* [11] achieved complete separations in 6min of $1\text{--}30\text{mg L}^{-1}$ concentrations of bromide, chloride, nitrite, nitrate and sulphate using a Zipax. SAX separation column, with eluent suppression and electrical conductivity detection. The necessary high pressure packing techniques for packing the separation column is described in detail. With sample preconcentration, detection limits were reduced to about $5\mu\text{g L}^{-1}$ but calibration graphs for chloride and nitrate were not linear.

Reagents

Adipate and succinate solutions were prepared by adjusting the corresponding acid solutions to the desired pH with sodium hydroxide.

Apparatus

Separator column Zipax SAX beads (particle diameter $25\text{--}37\mu\text{m}$, Du Pont de Nemours, Den Bosch, The Netherlands). (Zipax SAX is a strong

Table 12.2 Dionex replicate samples, non saline waters

Sample no.	F (250mm) ($\mu\text{g L}^{-1}$)	F (500mm) ($\mu\text{g L}^{-1}$)	Cl (250mm) (mg L^{-1})	Cl (500mm) (mg L^{-1})
7	852	860	20.0	14.5

18	852	860	20.0	14.7
22	870	880	19.7	14.5
26	852	920	20.0	13.5
30	852	960	20.0	13.5
Mean	855.6	896.0	19.9	14.1
S.D.	8.05	43.4	0.14	0.59
R.S.D.	0.9%	4.8%	0.7%	4.2%
NO ₃ (250mm) (mg L ⁻¹)	NO ₃ (500mm) (mg L ⁻¹)	SO ₄ (250mm) (mg L ⁻¹)	SO ₄ (500mm) (mg L ⁻¹)	
<0.02	<0.05	27.3	25.0	
<0.02	<0.05	27.5	25.0	
<0.02	<0.05	27.3	24.2	
<0.02	<0.05	27.3	24.6	
<0.02	<0.05	27.5	24.2	
0.02	0.05	27.4	24.6	
—	—	0.11	0.4	
—	—	0.5%	1.6%	

Source: Reproduced with permission from Elsevier Science [10]

pellicular anion exchanger with a capacity of about 12µeq of quaternary ammonium groups per gram of dry material). Suppressor column resin Ag-5OW-X12 (>400 mesh: Bio-Rad Laboratories). This is a strong cation exchanger prepared from a styrene-divinylbenzene copolymer with 12% cross links. It has a capacity of 5meq of SO₃H groups per gram of dry resin.

Ion chromatographic apparatus, Fig. 12.8, is equipped with a reciprocating piston pump (Kipp Analytica, Emmen, The Netherlands). The pulse dampener system consists of an Orlita (Giessen/Lahn, West Germany) pulse dampener and a stainless steel resistance capillary (length 3m, id 0.25mm). The stainless steel eluent filter (Chrompack, Middelburg, The Netherlands) has a pore diameter of 2µm. The six port sample injection valve and the eight port valve were supplied by Valco (Houston, Texas). The former is equipped with a 60µL sample loop. Both are actuated pneumatically. The home made conductivity cell consists of two platinum electrodes in a perspex housing and has a cell volume of 6µL. The digital conductivity detector has been described elsewhere [12].

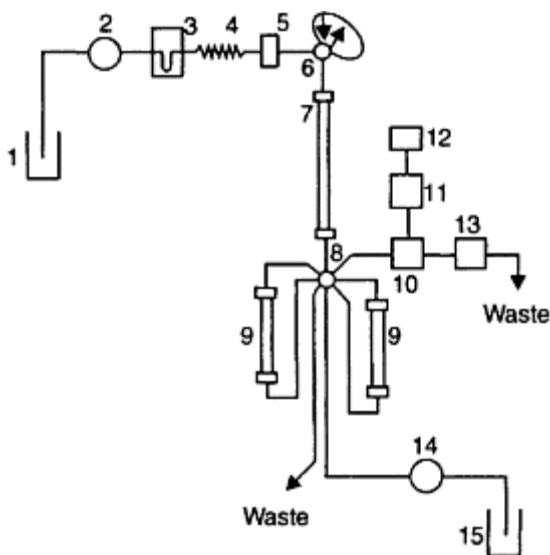


Fig. 12.8 Schematic diagram of the ion chromatograph: 1, eluent reservoir; 2, pump; 3, pulse dampener; 4, capillary; 5, filter; 6, 6-port injection valve; 7, analytical column; 8, 8-port valve; 9, suppressor columns; 10, conductivity cell; 11, conductivity detector; 12, recorder; 13, syphon counter; 14, regeneration pump; 15, regeneration liquid (nitric acid or water)

Source: Reproduced with permission from Elsevier Science [11]

The columns (precision bore polished stainless steel, id 4.5mm) and the detector cell are surrounded by water jackets and thermostated by a thermostat to within 0.01°C. The connecting tubing (id 0.25mm) is kept as short as possible. Low dead volume connectors are used to minimise extracolumn peak broadening. The eluent flow rate is monitored continuously with a calibrated syphon counter.

The column packing apparatus is outlined in Fig. 12.9. The pump is of the reciprocating type and should attain a pressure of at least 400bar when columns have to be packed with 10µm particles. A Milton Roy pump (Chicago, Illinois) was used. Pulse dampening is achieved with a flow through Bourdon gauge, a resistance capillary, an Orlita pulse dampener and another capillary in series. The stainless steel capillaries (length 3m, id 0.25mm) ensure a nearly pulse free flow. The slurry reservoir is a thick-walled stainless steel tube equipped with teflon sealed stainless steel nuts. The lower nut is part of the polished precolumn (length 10cm). The internal diameter of the precolumn, connector and column should be equal. The packed bed in the column is kept in place by means of a thin plug of wool in a low dead volume connector.

The columns are packed according to the viscous slurry method [13]. The Zipax SAX (5g) is suspended in 25ml of ethyleneglycol and 2.5g of AG-50W-X12 in 25ml of isopropanol. The slurries are degassed and

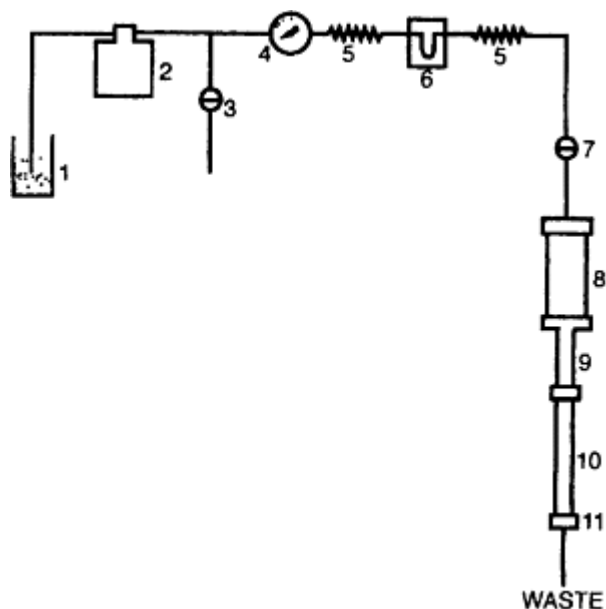


Fig. 12.9 Scheme of the column packing apparatus. 1, reservoir (methanol or water); 2, pump; 3, valve; 4, manometer; 5, capillary; 6, pulse dampener; 7, valve; 8, slurry reservoir; 9, precolumn; 10, column; 11, plug of wool in low dead volume connector

Source: Reproduced with permission from Elsevier Science [11]

homogenised by sonication. The column and precolumn are filled with tetrachloromethane in order to prevent inclusion of air bubbles in the packed bed. The slurry reservoir is filled with the slurry and thereafter methanol is added to remove all air up to the shut off valve. When the pump and dampers have been filled with methanol, the slurry reservoir is connected to the pump (with valve 7 closed). The apparatus is pressurised with methanol up to 400bar. Thereafter, valve 7 is opened and the slurry is forced into the column. The packed bed is settled by flushing 200ml of methanol and 200ml of water through the column at maximum pressure.

Glass columns can also be slurry packed by this method when the pressure across the column is kept below 60bar. A short glass column (100 × 4.0mm) packed with Zipax SAX was used as a concentrator column.

The void volume of the separator column (V_m) is estimated from the retention volume of water. The capacity ratio k is calculated from the equation $k = (V_R - V_M)/V_m$, where V_R and V_M are the retention volumes of the solute and water respectively in the separator-suppressor column combination. The k values are independent of sample size (50–200 μL of solutions of 10mg L^{-1} nitrate and 10mg L^{-1} sulphate), only slightly dependent on the eluent flow rate (1.5–4.5ml min^{-1}), and reproducible within 3%.

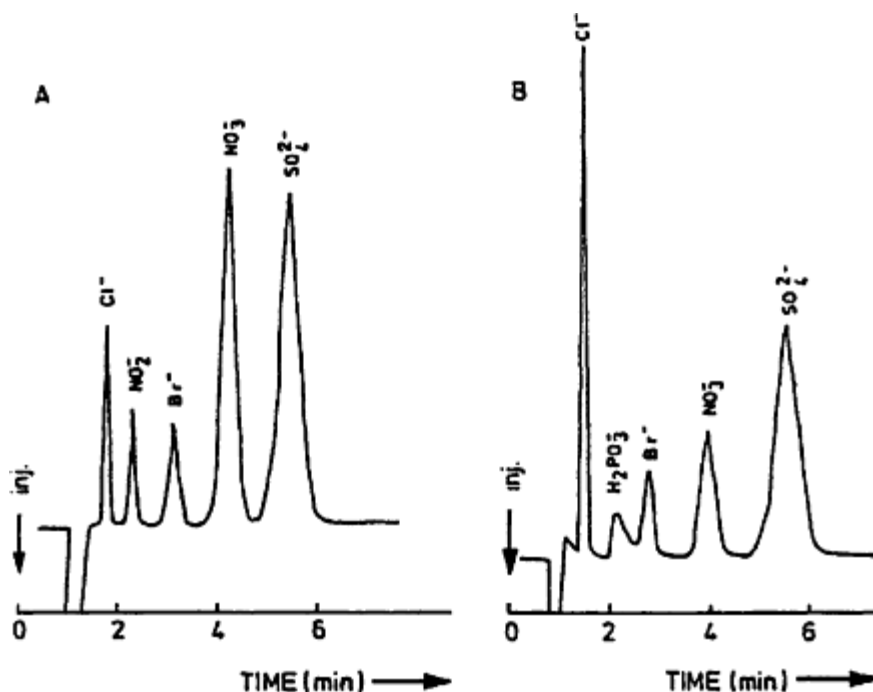


Fig. 12.10 Separation of trace anions on a 200×4.5mm Zipax SAXC column: A separation of 2mg L⁻¹ Cl⁻, 5mg L⁻¹ NO₂⁻, 5mg L⁻¹ Br⁻, 20mg L⁻¹ NO₃⁻ and 20mg L⁻¹ SO₄²⁻ with 2×10⁻³mol L⁻¹ Na₂ adipate as eluent; B separation of 5mg L⁻¹ Cl⁻, 5mg L⁻¹ H₂ PO₄⁻, 5mg L⁻¹ Br⁻, 7.5mg L⁻¹ NO₃⁻ and 1.5mg L⁻¹ SO₄²⁻ with 1.4×10⁻³mol L⁻¹ Na₂ succinate as eluent. Other conditions: 50μL loop, eluent flow rate 2.5ml min⁻¹, 25°C

Source: Reproduced with permission from Elsevier Science [11]

In Fig. 12.10 are shown the separations achieved on this system when (A) 2×10⁻³mol L⁻¹ disodium adipate and (B) 1.4×10⁻³mol L⁻¹ disodium succinate used as eluants, both at pH 7.

On Zipax SAX the ions are eluted in the order $F^- < Cl^- < NO_2^- = H_2PO_4^- < Br^- < NO_3^- < SO_4^{2-}$. Fluoride is eluted together with the negative water peak. On Zipax SAX the optimal eluent temperature for obtaining good resolution in the minimal time is about 25°C.

Detection limits (three times the background noise) for chloride, nitrate and sulphate were determined for a 200μL loop and for a concentrator column. These are given in Table 12.3.

The lifetime of a Zipax SAX slurry packed separator column was at least 400h. Deterioration of the packing resulting in peak broadening did not appear and almost no reduction of capacity was observed during that period. The lifetime of the suppressor

column is at least 3 months.

Determination of anions in non saline water is disturbed by the inevitable presence of humic substances which are strongly adsorbed on the ion chromatographic column.

Table 12.3 Detection limits of chloride, nitrate and sulphate on the Zipax-SAX column with $1.4 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{-succinate}$ as eluent

Ion	Detection limit ($\mu\text{g L}^{-1}$)	
	200 μL loop	Concentrator column
Chloride	10	2
Nitrate	30	4
Sulphate	30	10

Source: Reproduced with permission from Elsevier Science [11]

Marko Varga *et al.* [14] found that a cleanup column prior to the separation column, packed with a chemically bonded amine material (Nucleosil 5 HN_2) was found to be effective in removing interfering humic substances. No influence was found from humic substances in concentrations up to $45 \mu\text{g L}^{-1}$ on ion chromatographic analysis of nitrate and sulphate ($10\text{--}100 \text{ mg L}^{-1}$) after passage through the cleanup column.

A short column packed with an amine bonded polymer (weak anion exchange material) connected prior to the anion separation column was found to be very effective for the selective removal of humic substances prior to anion separation by ion chromatography. About 500 sample injections could be performed before breakthrough of humic substances occurred as indicated by ultraviolet measurements made on the eluate at 225nm.

Apparatus

Chromatographic system consisting of a pump (constametric III, LDC, Riviera Beach, Florida) a loop (200 or, 500 μL an injector) Model 7000 Rheodyne, Cotati, California) a column (see below), two detectors in series (a conductometric detector 'Conductomonitor', LDC and a variable wavelength ultraviolet detector, 'Spectromonitor III' 1.08), and a dual channel recorder (Model 2066, LKB, Bromma, Sweden).

For the adsorption of humic substances a stainless steel column (50mm $\times$ 4.9mm id) was used, filled with 0.8g of Sum amine bonded polymer (Nucleosil 5 NH_2). Anions were separated by an anion exchange resin (Dionex, Sunnyvale, California) packed into a glass column (5mm id bed length 50mm) (Pharmacia Fine Chemicals: Uppsala Sweden) which permits the length of the resin bed to be easily adjusted.

Potassium hydrogen phthalate, $5 \times 10^{-4} \text{ mol L}^{-1}$, pH 5.5 was used as mobile phase. The flow rate was 2 ml min^{-1} and the conductometric detector was used in the 'absolute' mode (10 μS) full scale deflection. The conductance of the eluent was electronically offset.

Under the chosen conditions, nitrate and sulphate were well resolved from other anions

expected to be found in non saline waters. Typical k' values were as follows: bicarbonate, H_2PO_4 , chloride and nitrite <0.5 , sulphate 7.2, nitrate 1.4.

Procedure

A 500 μL water sample is injected onto the adsorption column and the eluate collected in a fraction collector. The fraction (around 2.5ml) which contained the anions, as seen by the conductometric detector, is evaporated to dryness (80°C overnight) and redissolved in 250 μL of water. 100 μL aliquots are analysed on the ion chromatographic system using the ion exchange separation column and conductance detection as described above.

Marko Varga *et al.* [14] prepared a series of model solutions with 10, 30, 50, 70 and 100mg L^{-1} of both nitrate and sulphate additionally containing 0.00, 0.09, 0.90, 4.5, 27 or 45mg L^{-1} of reference humic acid. By use of the procedure described above, nitrate and sulphate were determined in the solutions. The calibration curve was constructed from the solutions without added humic acid.

A separate analysis of 45mg L^{-1} reference humic acid (without anions added) gave the result: nitrate 3.7mg and sulphate 5.2mg L^{-1} . This is considered as the background level of these ions in the reference humic acid. Thus, significant amounts of nitrate and sulphate are added to the model solutions together with the humic acid.

Considering these background levels, the percent recovery (concentration found/expected concentration) was calculated for all model solutions analysed and is presented in Table 12.4. The relative standard deviation within each set of six values was typically 2–3% both for nitrate and sulphate.

Most of the recoveries in Table 12.4 are not significantly different from 100%. For sulphate, recoveries tend to be about 10% low at high concentrations of humic acid while an opposite tendency can be noted for nitrate. One reason for this behaviour might be the competition between sulphate and nitrate and other ions present in the humic acid for the binding sites of the humic substances.

In all chromatograms an unknown peak appears. This is probably due to a disturbance in the phthalate protonation equilibrium created by the injection of aqueous samples. The retention time of the peak is independent of pH and the concentration of the eluent, but the intensity is affected by these factors. It is possible to adjust the eluent composition so the peaks of interest are separated from the 'ghost peak'.

Ion chromatography has been used for the measurement of background concentrations of fluoride, chloride, nitrate and sulphate in non saline waters [10].

Table 12.4 Percent recovery of nitrate and sulphate from solutions containing humic acid

Ion concn. mg L^{-1}	% recovery for concn. of humic add added (mg L^{-1})					
	0.09	0.9	4.5	9	27	45
NO_3^-						
10	102	98	105	94	103	94
30	101	109	99	108	103	105

50	107	104	103	105	99	106
70	101	106	106	108	106	102
100	106	101	108	104	102	108
SO ₄ ²⁻						
10	96	94	94	90	106	110
30	95	112	101	93	93	103
50	109	102	100	94	90	93
70	101	98	99	91	90	93
100	101	97	97	94	90	93

Source: Reproduced with permission from the American Chemical Society [14]

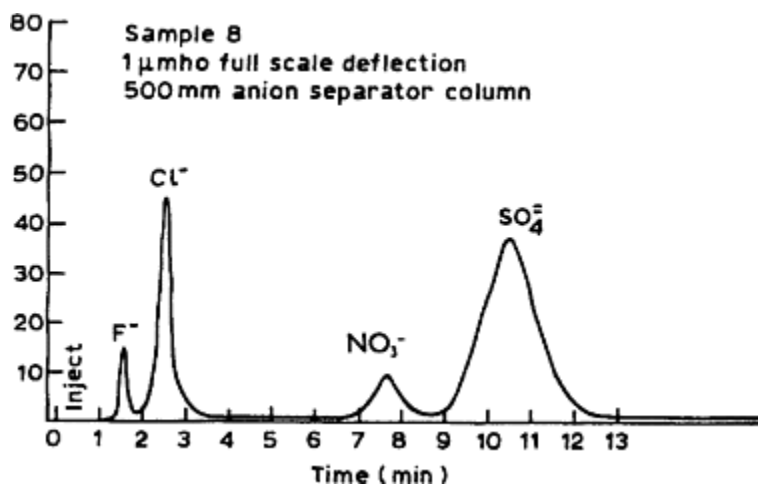


Fig. 12.11 Calibration chromatogram for a 250nm anion separator column using standard 8 containing 0.1 $\mu\text{g mL}^{-1}$ F⁻; 0.1 $\mu\text{g mL}^{-1}$ Cl⁻ 0.1 $\mu\text{g mL}^{-1}$ PO₄³⁻; 1.0 $\mu\text{g mL}^{-1}$ NO₃⁻ and 1.0 $\mu\text{g mL}^{-1}$ SO₄²⁻

Source: Reproduced with permission from Elsevier Science [10]

Typical chromatograms obtained from a sample of northern Ontario stream water are shown in Fig. 12.11 (500mm column). It is evident from these illustrations that no advantage is gained by using the 500mm column rather than the 250mm column. The time for analysis is more than doubled and peak heights have decreased. The increased separation of anion chromatographic peaks is not required for this sample type.

Van Os *et al.* [11] achieved complete separations in 6min of 1–30mg L⁻¹ concentrations of bromide, chloride, nitrite, nitrate and sulphate using a Zipax SAX separation column, with eluant suppression and electrical conductivity detection. The necessary high pressure packing techniques for packing the separation column is

described in detail. With sample preconcentration detection limits were reduced to about $5\mu\text{g L}^{-1}$ but calibration graphs for chloride and nitrate were not linear. Sodium adipate and $1.4 \times 10^{-3}\text{M}$ disodium succinate are used as eluants, both at pH 7.

On Zipax SAX the ions are eluted in the order $\text{F}^- < \text{Cl}^- < \text{NO}_2^- \approx \text{H}_2\text{PO}_4^- < \text{Br}^- < \text{NO}_3^- < \text{SO}_4^{2-}$. Fluoride is eluted together with the negative water peak. On Zipax SAX the optimal eluent temperature for obtaining good resolution in the minimal time is about 25°C .

Tong and Shi [15] used ion chromatography with an electrical conductivity detector to determine fluoride, chloride, nitrate, sulphate and hydrogen phosphate (HPO_4^{2-}) in non saline water with detection limits of 0.8, 1.0, 8.0, 10.0 and $12.5\mu\text{g L}^{-1}$ respectively.

The Environmental Protection Agency has issued a standard ion chromatographic method for the determination of chloride, fluoride, nitrate, nitrite, orthophosphate and sulphate in non saline waters [16,56]. This is an approved method for the determination of chloride, nitrate and sulphate. In this method a 2–3ml sample is introduced into the ion chromatograph. The anions are separated and measured using a system comprised of a guard column, separator column, suppressor column and conductivity detector.

Ground column 4×50mm Dionex P/N 030825

Separator column 4×250mm Dionex P/N 030827

Suppressor coulumn, fibre Dionex P/N 35350

Detector, conductivity cell approx 6 μL

Volume, an eluent comprising sodium bicarbonate (0.003M), sodium carbonate (0.0024M) is used.

Samples are collected in clean glass or polyethylene bottles and must be analysed within 28d (chloride and fluoride, 48h (nitrate, nitrite and phosphate) and 28d (sulphate).

Table 12.5 lists the analysis conditions required and detection limits achieved in this method. Recovery and accuracy are listed in Table 12.6.

Wilken and Kock [17] have described a method for the determination of chloride, nitrate and sulphate in sediment pore waters. Depth versus concentration profiles are reproduced for each of these ions and differences between those for the inner estuary, the mixing zone and the *outer estuary are commented on*. The method was particularly useful as it permitted the simultaneous determination of the three ions in samples of only 100 μL , unaffected by the natural colour of the sample.

Table 12.5 Chromatographic conditions and method detection limits in reagent water

Analyte	Retention ¹ time (min)	Relative retention time	Method ² detection limit mg L^{-1}
Fluoride	1.2	1.0	0.005
Chloride	3.4	2.8	0.015
Nitrite-N	4.5	3.8	0.004

o-Phosphate-P	9.0	7.5	0.061
Nitrate-N	11.3	9.4	0.013
Sulphate	21.4	17.8	0.206

Standard conditions:

Columns—as specified [29]; Detector—as specified [29]; Eluent—as specified [29]

Sample loop 100µL; Pump volume 2.30ml min⁻¹

¹Concentrations of mixed standard (mg L⁻¹)

Fluoride 3.0; Chloride 4.0; Nitrite-N 10.0; O-Phosphate-P 9.0; Nitrate-N 30.0; Sulphate 50.0

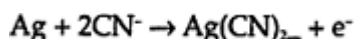
²MDL calculated from data obtained using an attenuator setting of 1 µMHO full scale. Other settings would produce an MDL proportional to their value

Source: Reproduced with permission from the Environmental Protection Agency, US [16]

Cyanide, sulphide, iodide and bromide

Rocklin and Johnson [18] used an electrochemical detector in the ion chromatographic determination of cyanide and sulphide. They showed that by placing an ion exchange column in front of an electrochemical detector, using a silver working electrode, they were able to separate cyanide, sulphide, iodide and bromide and detect them in water samples at concentrations of 2, 30, 10 and 10µg L⁻¹ respectively. Cyanide and sulphide could be determined simultaneously. The method has been applied to the analysis of complexed cyanides and it is shown that cadmium and zinc cyanides can be determined as total free cyanide while nickel and copper complexes can only partially be determined in this way. The strongly bound cyanide in gold, iron or cobalt complexes cannot be determined by this method.

This method is based on the work of Pihlar and Kosta [19,20] who showed that a silver working electrode has the ability to produce a current that is linearly proportional to the concentration of cyanide in an amperometric electrochemical flow through cell. The reaction for cyanide is:



Under these conditions sulphides and halides produce insoluble precipitates rather than soluble complexes:

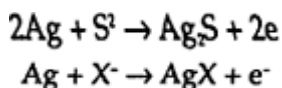


Table 12.6 Single-operator accuracy and precision

Analyte	Sample type	Spike (mg L ⁻¹)	No. of replicates %	Mean recovery (mg L ⁻¹)	Standard deviation

Chloride	RW	0.050	7	97.7	0.0047
	DW	10.0	7	98.2	0.289
	SW	1.0	7	105.0	0.139
	WW	7.5	7	82.7	0.445
Fluoride	RW	0.24	7	103.1	0.0009
	DW	9.3	7	87.7	0.075
	SW	0.50	7	74.0	0.0038
	WW	1.0	7	92.0	0.011
Nitrate-N	RW	0.10	7	100.9	0.0041
	DW	31.0	7	100.7	0.356
	SW	0.50	7	100.0	0.0058
	WW	4.0	7	94.3	0.058
Nitrite-N	RW	0.10	7	97.7	0.0014
	DW	19.6	7	103.3	0.150
	SW	0.51	7	88.2	0.0053
	WW	0.52	7	100.0	0.018
o-Phosphate-P	RW	0.50	7	100.4	0.019
	DW	45.7	7	102.5	0.386
	SW	0.51	7	94.1	0.020
	WW	4.0	7	97.3	0.04
Sulphate	RW	1.02	7	104.3	0.066
	DW	98.5	7	111.6	1.475
	SW	10.0	7	134.9	0.709
	WW	12.5	7	102.1	0.466

RW=Reagent water; DW=drinking water; SW=surface water; WW=wastewater

Source: Reproduced with permission from the Environmental Protection Agency, US [16]

Rocklin and Johnson [18] overcame the latter problem by placing an ion exchange column in front of the electrochemical detector. Cyanide and sulphide are separated and thus are determined simultaneously. Although bromide and iodide can be determined by ion chromatography with conductivity detection, the use of electrochemical detection results in greater selectivity as well as increased sensitivity.

Sulphide and cyanide

Bond *et al.* [21] have described a method for the simultaneous determination of down to 1mg L^{-1} free sulphide and cyanide by ion chromatography with electrochemical

detection. These workers carried out considerable exploratory work on the development of ion chromatographic conditions for separating sulphide and cyanide in a basic medium (to avoid losses of toxic hydrogen cyanide and hydrogen sulphide) and on the development of a suitable amperometric detector.

12.2.2 Arsenate, arsenite, selenate and selenite

Hoover and Jager [22] have described a procedure for the determination of traces of arsenite, selenite and selenate in the presence of major interferences (chloride, nitrate, and sulphate) in potable waters, surface waters and ground waters. By collecting a selected portion of the ion chromatogram, after suppression, on a concentrator column and reinjecting it under the original chromatographic conditions, it was possible to separate selenate, selenite and arsenite from chloride, nitrate and sulphate. Statistical detection limits varied from 0.02 to 1.2 µg of trace element depending on the minor components to be separated and on the water matrix. The maximal reliably separated molar ratio was 2300 for sulphate/selenate.

Ion chromatography can readily determine arsenate, selenite, and selenate species in water in the absence of interferences. However, they will usually be completely obscured by the major anions. Arsenic and selenium are ordinarily at their highest oxidation state in surface waters but that is not necessarily the case in ground waters.

Apparatus

Dionex Model 10 ion chromatograph equipped with AG-1 guard column, AS-3 'fast run' separator column and ASC-1 suppressor. AG-3 concentration columns were used for introduction of the sample and for collection of and recycling of selected portions of the chromatogram. For recycle chromatography, modify the plumbing as shown in Fig. 12.12. The original injection valve was connected to two additional dual four-port slider valves. Solid lines in the figure correspond to the 'Down' position of the toggle switches. The dummy concentrator in the waste line of the recycle valve was added to maintain approximately constant back pressure on the conductivity detector because the base line conductance of the suppressed eluent is highly pressure sensitive.

Concentrator columns were loaded in place with a Harvard Apparatus infusion pump at 1.5 mL min^{-1} using a Hamilton 5ml glass syringe with a gas tight Teflon tipped plunger and Luer fitting to 0.5ml id. Teflon tubing. The volume of solution loaded was measured by collecting the effluent in a volumetric flask, shown in Fig. 12.12. All recycle runs were made at 15% pump rate (1.51 mL min^{-1}) and at room temperature $25 \pm 1^\circ\text{C}$.

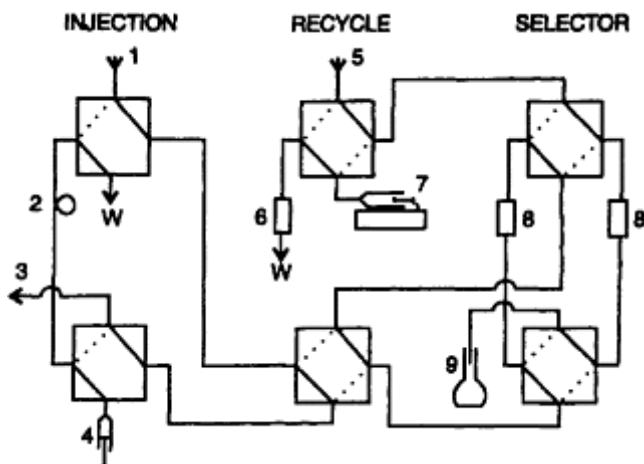


Fig. 12.12 Valving: (1) eluent supply; (2) sample loop; (3) to separator; (4) injection port; (5) from detector; (6) dummy concentrator column; (7) syringe pump; (8) concentrator columns; (9) volumetric flask 2.5 or 10ml

Source: Reproduced with permission from the American Chemical Society [22]

Reagents

Stock solution of 1000mg L^{-1} of the test ions. Prepared from reagent grade sodium salts in water that had been purified by reverse osmosis and mixed bed ion exchange. The stock solutions were adjusted to the composition of the Dionex standard eluent ($3.0\text{m mol L}^{-1} \text{NaHCO}_3$, $2.4\text{m mol L}^{-1} \text{Na}_2\text{CO}_3$) and membrane filtered through $0.45\mu\text{m}$ pore size Metrical GA-6. Solutions of 1 or 10mg L^{-1} were prepared by dilution of the stock with the water under test and further dilutions were made from these shortly before injection. Potable water had to be boiled briefly to remove available chlorine before stable dilute solutions of selenite in it could be obtained.

Results

An eluent composition of 2.0m mol L^{-1} sodium bicarbonate and 1.5m mol L^{-1} sodium carbonate was found to elute arsenate about midway between nitrate and sulphate. Selenite eluted between chloride and nitrate in an eluent that was 3.0m mol L^{-1} in sodium bicarbonate and 2.0m mol L^{-1} in sodium carbonate.

Suppressed eluent retained in the concentrator columns produced a large carbonate peak on direct reinjection. This peak obscured or interfered with everything eluting before nitrate. In the determination of selenite, the concentrator was washed with deionised water for 5min after collection and before injection. The wash step was omitted in the determinations of arsenate and selenate where the carbonate did not interfere.

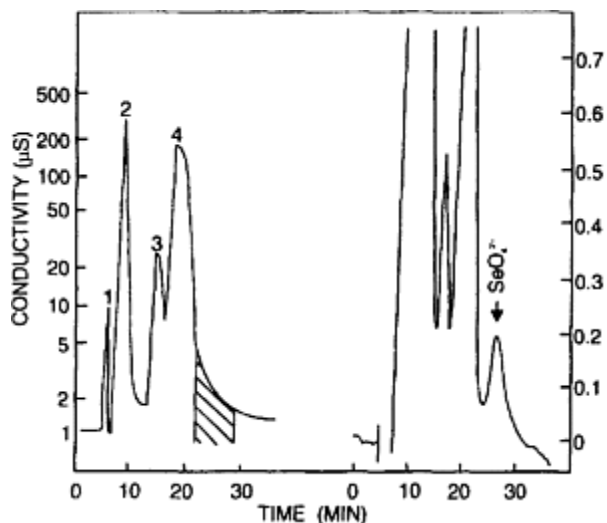


Fig. 12.13 Selenate in drinking water: sample size 5ml, 10ng of Se(V) added—major peaks: (1) fluoride; (2) chloride; (3) nitrate; (4) sulphate. Shaded area was collected for recycle

Source: Reproduced with permission from the American Chemical Society [22]

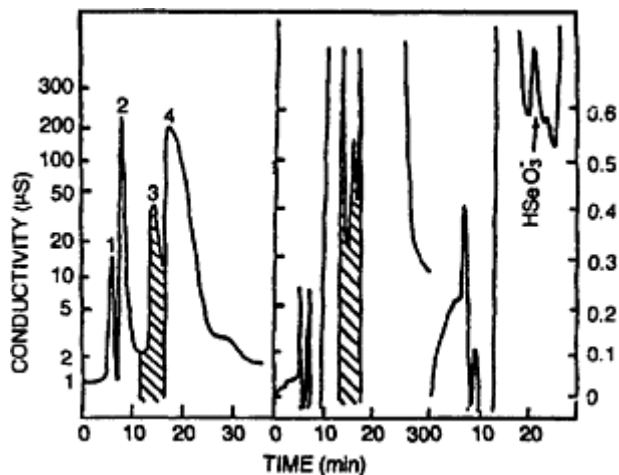


Fig. 12.14 Selenite in potable water, recycled twice; sample size 10ml, 100ng of Se(IV) added—major peaks: (1) fluoride; (2) chloride; (3) nitrate; (4) sulphate. Shaded areas were collected for recycle

Source: Reproduced with permission from the American Chemical Society [22]

Figs. 12.13–12.15 show representative chromatograms for each of the trace anions at close to the statistical detection limit. The initial injection is shown on a logarithmic scale of conductance to include complete peaks of the major constituents. The recycle portion of the chromatogram was obtained at the linear scale, usually $1\mu\text{S cm}^{-1}$ full scale sensitivity. Fig. 12.14 shows a second collection and recycling of selenite. The process can be repeated indefinitely but there is evidence (below) of 10–15% loss of material each time.

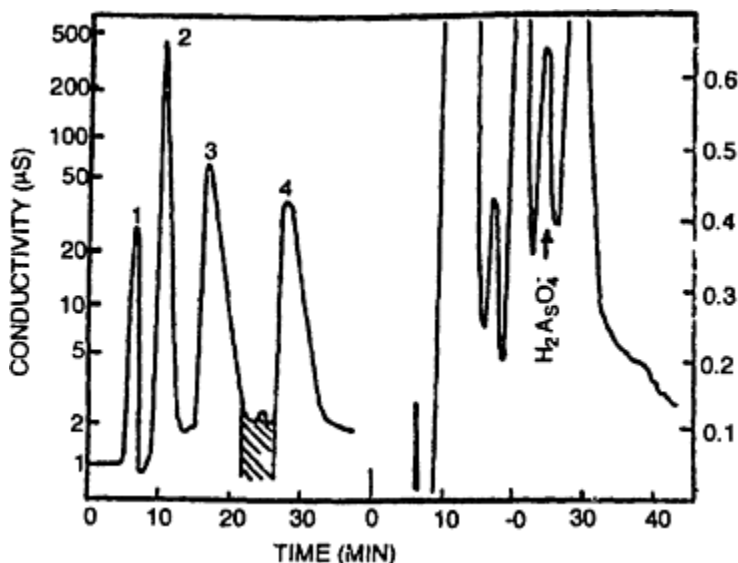


Fig. 12.15 Arsenate in river water: sample size 5ml, 50ng of As(V) added—major peaks: (1) fluoride; (2) chloride; (3) nitrate; (4) sulphate. Shaded area was collected for recycle

Source: Reproduced with permission from the American Chemical Society [22]

Calibration curves for each trace ion in each matrix are summarised in Table 12.7. Amounts of trace anion injected were run in a randomised order and most calibrations included both 2ml and 5ml initial injections. Increasing the sample size allows lower concentrations of the minor constituent to be collected but does not affect the relative proportions that must be separated. Variation of sample sizes between 0.1 and 5ml did not affect mass detection limits.

The detection limits shown in Table 12.7 are all 3σ (ie $3\times$ standard deviation) limits based on the standard deviation of the ordinates from the least squares linear fit. In all cases this limit is appreciably greater than the detectability of trace amounts in individual runs, as shown in Figs. 12.13–12.15.

One effect of the matrix water on trace determination is the concentration of major ion interference. In the case of selenite, the major interferent is nitrate and the exceptional results in river water may be related to the high nitrate level in that medium. If that were

the controlling factor, however, one would expect a greater difference between well and potable water than was observed. Similarly, for selenate the critical separation is from sulphate, which is greatest in drinking water, but river and well water differ more in sulphate content than well and potable water, in contrast to the calibration curves.

Table 12.7 Calibrate data for recycle determination of trace anions in water

Water	Intercept, $S \text{ cm}^{-1}$	Slope, $S \text{ cm}^{-1} \text{ g}^{-1}$	Detection limit, μg	<i>N</i>
Selenate ($3.0\text{mmol L}^{-1} \text{NaHCO}_3$, $2.4\text{mmol L}^{-1} \text{Na}_2\text{CO}_3$, pH 9.72)				
Drinking (1)	0.26 ± 0.15^a	3.49 ± 0.30^a	0.21	6
Drinking (2)	0.20 ± 0.06	2.37 ± 0.26	0.18	10
Well	0.011 ± 0.03	1.166 ± 0.016	0.020	8
River	0.012 ± 0.004	1.226 ± 0.016	0.018	6
Selenite ($3.0\text{mmol L}^{-1} \text{NaHCO}_3$, $2.0\text{mmol L}^{-1} \text{Na}_2\text{CO}_3$, pH 9.24)				
Drinking	-0.034 ± 0.052	2.23 ± 0.10	0.20	19
Well	-0.089 ± 0.056	2.33 ± 0.16	0.18	11
River	0.77 ± 0.25	1.63 ± 0.25	1.2	13
Arsenate ($2.5\text{mmol L}^{-1} \text{NaHCO}_3$, $1.5\text{mmol L}^{-1} \text{Na}_2\text{CO}_3$, pH 9.56)				
Drinking	0.024 ± 0.10	0.83 ± 0.20	0.47	6
Well	-0.017 ± 0.10	0.781 ± 0.038	0.68	8
River	-0.03 ± 0.09	0.902 ± 0.045	0.83	12

^aStandard deviation

Source: Reproduced with permission from the American Chemical Society [22]

12.2.3 Metal cyanide complexes

The cyanide ion in inorganic cyanides can be present as both complexed and free cyanide. In order to study the chromatography of metal cyanides, Rocklin and Johnson [23] prepared and assayed solutions of cadmium, zinc, copper, nickel, gold, iron and cobalt cyanides. Table 12.8 lists the percentage of total cyanide detected.

The results suggest that the complex cyanides can be grouped into three categories depending on the cumulative formation constant and stability of the complex. Category 1 includes the weakly complexed and labile cyanides $\text{Cd}(\text{CNO})_4^{2-}$ ($\log \beta_4=18.8$) and $\text{Zn}(\text{CN})_4^{2-}$ ($\log \beta_4=16.7$). These complexes completely dissociate under the chromatographic conditions used; the cyanide being indistinguishable from free cyanide. Category 2 includes the moderately strong cyanide complexes $\text{Ni}(\text{CN})_4^{2-}$ ($\log \beta_4=31.3$) and $\text{Cu}(\text{CN})_4^{3-}$ ($\log \beta_4=30.0$). Although the complexes are labile, they are retained on the column and slowly dissociate during the chromatography. This slow dissociation produces tailing which lasts for several minutes as the free cyanide elutes and is detected.

As the results presented in Table 12.8 demonstrate, the tailing and the non-quantitative recovery of cyanide preclude the use of direct injection to determine total cyanide in samples containing copper and nickel.

Table 12.8 Percentage of total cyanide in metal complexes determined as 'free' cyanide

Metal complex	$\log \beta_1$	%
$\text{Cd}(\text{CNO})_4^{2-}$	18.8	102
$\text{Zn}(\text{CN})_4^{2-}$	16.7	102
$\text{Ni}(\text{CN})_4^{2-}$	31.3	81
$\text{Cu}(\text{CN})_4^{3-}$	30.3	52
$\text{Cu}(\text{CN})_3^{2-}$	28.6	42
$\text{Cu}(\text{CN})_2^-$	24.0	38
$\text{Au}(\text{CN})_2^-$	38.3	0
$\text{Fe}(\text{CN})_6^{3-}$	42	0
$\text{Co}(\text{CN})_6^{3-}$	64	0

Source: Reproduced with permission from the American Chemical Society [23]

These samples may be analysed after acid distillation and caustic trapping. The cyanide in the caustic solution can then be determined by ion chromatography with electrochemical detection.

Category 3 includes those cyanides which are inert and therefore totally undissociated, such as $\text{Au}(\text{CN})_2^-$ ($\log \beta_2=38.3$), $\text{Fe}(\text{CN})_6^{3-}$ ($\log \beta_6=42$) and $\text{Co}(\text{CN})_6^{3-}$ ($\log \beta_6=64$). No free cyanide was detected for these complexes. Although these complexes do not elute under the chromatographic conditions used, they can be eluted and determined by using different chromatographic conditions and conductivity detection.

Samples containing both free cyanide (or weakly complexed cyanide) and strongly complexed cyanide can be analysed for free cyanide by direct injection. The determination of total cyanide (both free and strongly complexed) requires distillation of the sample with caustic trapping.

Determinations of anions in non saline water are disturbed by the inevitable presence of humic substances which are strongly adsorbed on the ion chromatographic column.

Marko Varga *et al.* [14] found that a cleanup column prior to the separation column, packed with a chemically bonded amine material (Nucleosil 5 NH₂) was effective in removing interfering humic substances. No influence was found from humic substances in concentrations up to 45 $\mu\text{g L}^{-1}$ on ion chromatographic analysis of nitrate and sulphate (10–100 mg L^{-1}) after passage through the clean up column.

A short column packed with an amine bonded polymer (weak anion exchange material) connected prior to the anion separation column was found to be very effective for the selective removal of humic substances prior to anion separation by ion

chromatography. About 500 sample injections could be performed before breakthrough of humic substances occurred as indicated by ultraviolet measurements made on the eluate at 225nm.

Most of the recoveries are not significantly different from 100%. For sulphate, recoveries tend to be about 10% low at high concentrations of humic acid while an opposite tendency can be noted for nitrate. One reason for this behaviour might be the competition between sulphate and nitrate and other ions present in the humic acid for the binding sites of the humic substances.

12.2.4 Mixtures of organic and inorganic anions (bromate, chloride, bromide, nitrite, nitrate, hypophosphite (HPO_2^{2-}), selenite, selenate, sulphate, phosphate, pyrophosphate, arsenate, chromate, α -hydroxybutyrate, butyrate, formate, acetate, glycolate, gluconate, valerate, α -hydroxy valerate, pyruvate, monochloroacetate, dichloroacetate, trifluoroacetate, galactonurate, gluconurate, α keto glutarate, oxalate, fumarate, phthalate, oxalacetate, citrate, isocitrate, cis aconitate, trans aconitate, succinate, maleate, malonate, quinate, tartrate, hexane sulphonate, octane sulphonate, octane sulphate, decane sulphonate, dodecane sulphonate and dodecane sulphate)

Dionex Corporation [24] have issued a technical note covering the application of anion exchange chromatography to the determination of the very wide range of anions, quoted above, in non saline waters.

Mobile phase ion chromatography is a form of reversed phase ion pair chromatography in which chemically suppressed conductivity detection is used. As in reversed phase high performance liquid chromatography, gradient elution is accomplished by varying the percentage of organic solvent in the eluant during the run.

Although the ionic strength of the eluant may remain the same throughout the run, the background conductivity can decrease due to the changing dielectric constant. These baseline changes can be compensated either by chemical means or by computer baseline subtraction. Often, mobile phase ion chromatography is used to elute ions which are very strongly retained. When this is the case, the baseline conductivity change can be minimised without affecting the separation by adding very weakly retained ions directly to the stronger eluant (higher percentage of organic solvent). Using gradient mobile phase ion chromatography, the separation of five alkyl sulphonates and sulphates is shown in Fig. 12.16. The AMMS-mobile phase ion chromatography suppressor (P/N 37106 Dionex Inc) should be used.

The analytical conditions recommended by Dionex for analysing mixtures of anions listed under the heading to this section are given below.

Although many columns and eluants can be used for gradient elution, the conditions used in Figs. 12.17 and 12.18 are recommended as a good starting point. The HPIC-ASSA (5 μ) separator with sodium hydroxide

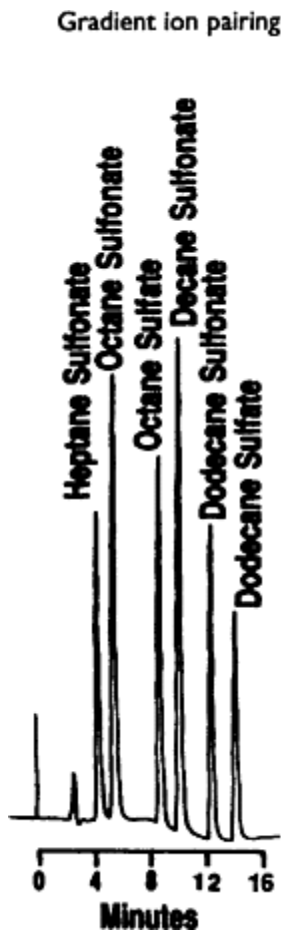


Fig. 12.16 Ion chromatogram of organic sulphates and sulphonates

Conditions:

- Columns: MPIC-NSI Flow rate: 1.0mL min⁻¹
Eluant 1: water
Eluant 2: CH₃CN
Eluant 3: 0.5M H₃BO₃, 10mM TMAOH, 40mM mannitol
Eluant 4: 0.5M H₃BO₃, 10mM TMAOH, 50% CH₃CN

Time (min)	1%	2%	3%	4%
0	74	8	4	14
7.5	17	47	24	12

10	7	47	20	16
15	9	5	16	14
15.1	74	8	4	14

Suppressor AMMS-MPIC

Regenerant: 25mN H₂SO₄

Source: Reproduced with permission from Dionex Corporation [24]

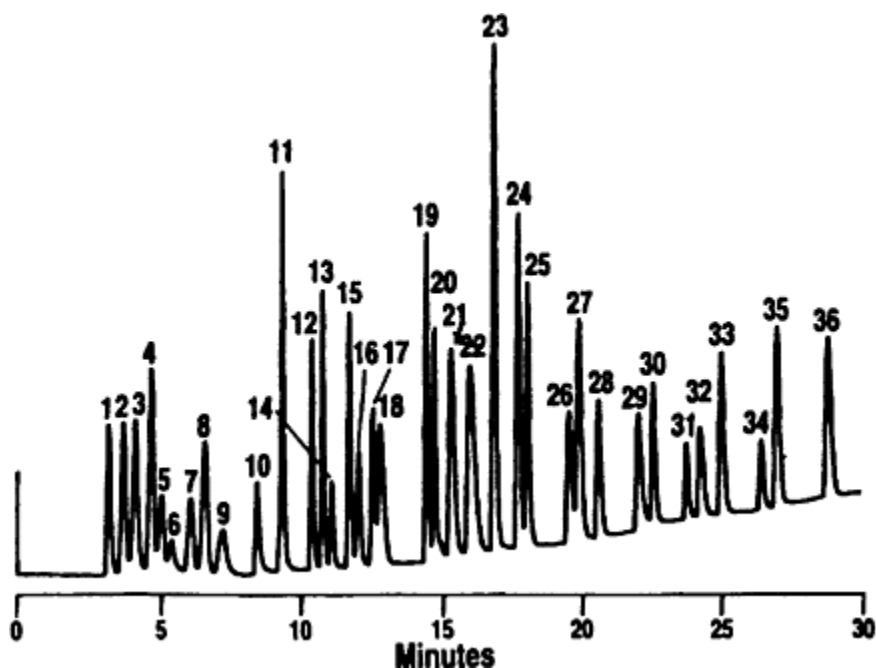


Fig. 12.17 Ion chromatography of inorganic and organic anions

All anions 10ppm unless noted

1 F ⁻ (1.5ppm)	19 HPO ₃ ²⁻
2 α -Hydroxybutyrate	20 SeO ₃ ²⁻
3 Acetate	21 Br ⁻
4 Glycolate	22 NO ₃ ⁻
5 Butyrate	23 SO ₄ ²⁻
6 Gluconate	24 Oxalate
7 α -Hydroxyvalerate	25 SeO ₄ ²⁻
8 Formate (5ppm)	26 α -Ketoglutarate

9 Valerate	27 Fumarate
10 Pyruvate	28 Phthalate
11 Monochloroacetate	29 Oxalacetate
12 BrO_3^-	30 PO_4^{3-}
13 Cl^- (3ppm)	31 AsOV
14 Galacturonate	32 CrO_4^{2-}
15 NO_2^- (5ppm)	33 Citrate
16 Glucuronate	34 Isocitrate
17 Dichloroacetate	35 cis-Aconitate
18 Trifluoroacetate	36 trans-Aconitate

Source: Reproduced with permission from Dionex Corporation [24]

eluant provides the optimum combination of efficiency, selectivity, and speed without an unacceptable baseline slope. If fewer ions than the 36 shown in Fig. 12.17 need to be separated, the gradient steepness can be increased to reduce the run time. Changing the gradient will affect the

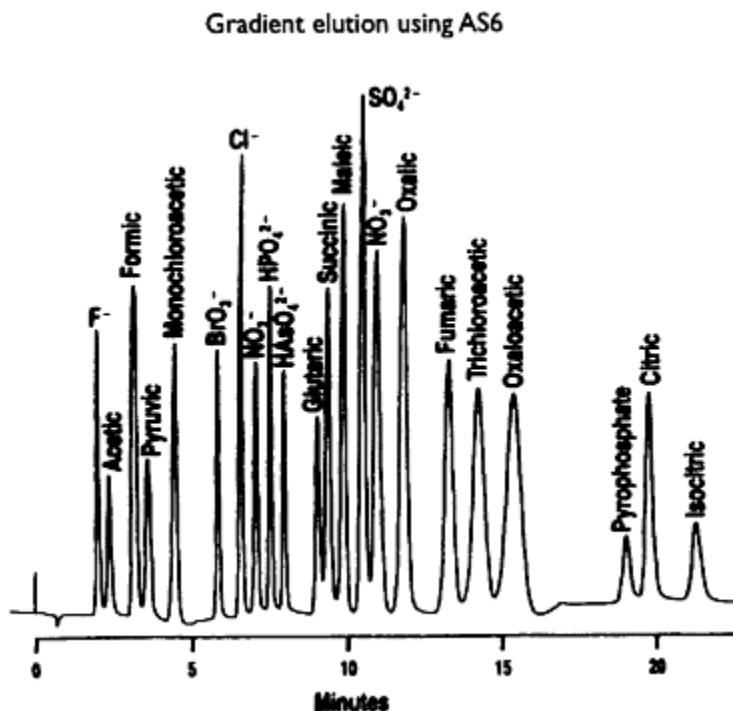


Fig. 12.18 on chromatography of inorganic and organic anions

Conditions:

Eluant 1:	50mM Mannitol, 2% CH ₃ CN
Eluant 2:	35mM p-cyanophenol, 50mM NH ₃ , 2% CH ₃ CN
Eluant 3:	% CH ₃ CN
Flow rate:	20mL min ⁻¹
Columns:	ATC, AS6, AMMS
Regenerant	10mM H ₂ SO ₄ , 200mM H ₃ BO ₃
Range	30μS

Gradient program

Time	0	3	3.1	7	13	15
%1:	45	40	40	30	25	0
%2:	7	15	30	53	53	100
%3:	48	45	30	17	22	0

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elution order of ions of different charge. In particular, increasing the gradient ramp slope will cause sulphate and other divalent ions to elute earlier than nitrate. When the considerations discussed in this technical note are followed, gradient elution can be used to solve many chemical analysis problems that are difficult to solve using isocratic elution.

Ion chromatograph:	Dionex series 400i or 1C with GPM
Trap column:	ATC (P/N 37151) or HPIC-AG8 (P/N37023)
Guard column:	HPIC-AG5A (P/N 37134)
Separator column:	HPIC-AS5A (P/N 3731)
Eluant 1:	0.75mM sodium hydroxide
Eluant 2:	200mM sodium hydroxide
Eluant flow rate:	1.0mL min ⁻¹
Suppressor:	Anion MicroMembrane, AMMS (P/N 38019)
Regenerant:	25mN H ₂ SO ₄
Regenerant flow rate:	10mL min ⁻¹

These workers made the following interesting observations.

Eluants used in anion exchange contain an anionic compound in high concentration which competes with the analyte ions for sites on the resin. Gradient elution is best accomplished by increasing the concentration of the eluant anion during the run, ie by performing a concentration gradient. In addition, a pH gradient can be used, in which a

fixed concentration of a weak acid is mixed with an increasing concentration of a strong base such as sodium hydroxide. pH gradients are essentially concentration gradients, as the purpose of increasing the pH during an anion exchange run is to increase the concentration of the dissociated form of the weak acid eluant.

Other types of gradients are more difficult to use. For example, a composition gradient can be performed by changing from a weakly retained eluant ion to a much more strongly retained ion. There is a wide difference in affinity for the resin between weakly and strongly retained analytes, such as monovalent acetate and trivalent citrate. To elute the more strongly retained citrate, ions from the stronger eluant must completely displace the weakly retained eluant ions from the resin. Depending on the ratio of column ion exchange capacity to eluant concentration, it may take a long time for the resin to be converted from the weak eluant to the strong eluant form. (This effect is similar to solvent demixing in reversed phase high performance liquid chromatography.) Also, to repeat the run, the resin form must be converted back to the weak eluant. This can only be done by pumping a high concentration of the weak eluant, thus increasing the equilibration time between runs. Concentration gradients avoid these problems by always keeping the form of the resin the same.

With gradient elution, changing the concentration of the eluant results in changes in background conductivity. By using chemical eluant suppression to reduce the highest background conductivity to less than $10\mu\text{S}$, baseline changes during a run can be limited to only a few μS . This is accomplished using an appropriate eluant and an Anion Micro-Membrane Suppressor. In addition, baseline changes of up to $20\mu\text{S}$ can be compensated by a technique described later.

There are two types of eluants which can be suppressed to produce background conductivities of only a few μS . One type is the salt of a weak acid. The weakest acid in aqueous solution capable of forming a salt is water itself, with the salt being a strong base such as sodium hydroxide. It is an excellent choice as an eluant for gradient elution as it is converted in the suppressor to water regardless of its concentration. There are other salts of weak acids which can be suppressed to produce low background conductivities. These include borate and many phenates such as *p*-cyanophenate. In general, the salts of weak acids with pK_a 's greater than 7 are acceptable. As pK_a decreases, the extent of dissociation following suppression increases, resulting in increased background conductivity and increased baseline shift during gradient elution. The other type of eluant which can be used includes those anions which are anionic at high pH but are converted to zwitterions or cations following suppression. Amino acids such as glycine are good choices because they are primarily converted to their cationic form and removed by the suppressor.

Because sodium hydroxide is converted to water in the suppressor, it is the best choice for an eluant. As long as the capacity of the suppressor is not exceeded, the eluant hydroxide concentration has little effect on background conductivity. The suppression capacity of the AMMS-MPIC Suppressor (P/N 37106) usually exceeds 100mM sodium hydroxide at a flow rate of 1.0mL min^{-1} . A gradient run could begin with a few mM sodium hydroxide and end at 100mM. Examples of gradient elution using sodium hydroxide are shown in Figs. 12.17 and 12.19. In Fig. 12.19, the HPIC-AS5 column is used. This column can elute anions with charges ranging from monovalent for chloride to

hexavalent for tetrapolyphosphate. In Fig. 12.17, the HPIC-AS5A (5 μ) column is used to elute a large number of anions in one run. The initial eluant is weak enough to retain fluoride well out of the void volume and separate several weakly retained monoprotic organic acids, while the final eluant concentration is capable of eluting triprotic phosphate and citrate. As shown in Fig. 12.17, 36 ions eluted in 30min illustrates the power of gradient elution.

Carbon dioxide readily dissolves in basic solutions, producing carbonate. Carbonate contamination in sodium hydroxide eluants can greatly increase the baseline shift during a gradient run. Eluants should be prepared from 50% solutions of sodium hydroxide, as they contain lower concentrations of carbonate than the solid. 18 meg- Ω deionised water should be used and degassed prior to addition of sodium hydroxide. Eluants should be maintained under an inert atmosphere during use. The Dionex Eluant Degas Module (P/N 37124) and Eluant Container Set (P/N 38752) provide a convenient method for ensuring that the eluants are properly degassed and free from carbonate contamination. *p*-Cyanophenate is a more powerful eluant than sodium hydroxide and should be used with higher capacity separators. The HPIC-AS6 provides

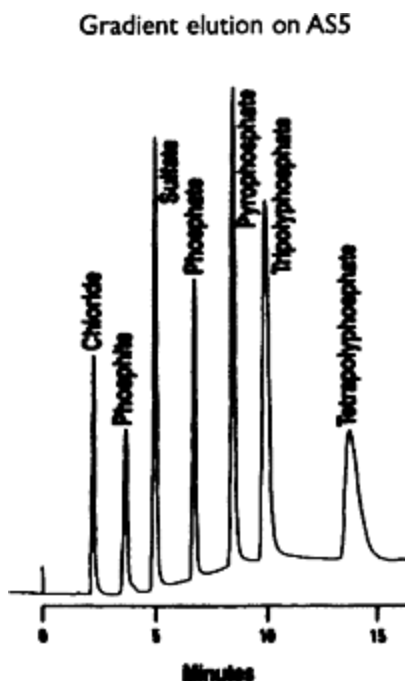


Fig. 12.19 Ion chromatography of phosphorous containing anions [24]

Eluant 1:	Water
Eluant 2:	100mM NaOH
Flow rate:	1ml min ⁻¹

Gradient program:

Time	%1	%2
0	75	25
5	0	100

Source: Reproduced with permission from Dionex Corporation [24]

excellent selectivity of diprotic organic acids. Due to its higher capacity (approximately 10 times that of the AS5A), the stronger eluant ion *p*-cyanophenate is necessary to elute di- and trivalent ions. An example of gradient elution on the HPIC-AS6 using *p*-cyanophenate is shown in Fig. 12.18. In this run, the concentration of *p*-cyanophenate in the eluant is increased from 2.4mM at the beginning of the run to 35mM at the end.

Carbonate containing eluants are generally not acceptable for gradient elution. Following suppression, carbonic acid is formed. With a relatively low pK_a of 6.2, the baseline drift is too severe. Although salts of weak acids with pK_a s as low as 5 can be used for isocratic elution, due to their higher background conductivity following suppression, they are generally not acceptable for gradient elution.

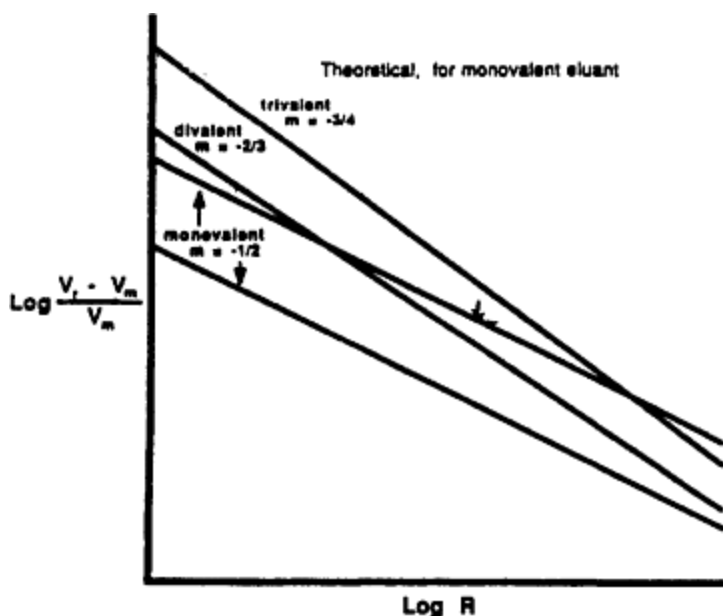


Fig. 12.20 Retention versus ramp slope

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The relationship between elution volume and gradient steepness (ie how rapidly the eluant concentration is being increased) is described by equation (1) and shown

graphically in Fig. 12.20. In this equation, elution volume is used instead of retention time; the two are related by the eluant flow rate.

$$\log \frac{V_r - V_m}{V_m} = \frac{A}{A + E} \log R + \log \text{Const.} \quad (1)$$

V_r is the retention volume, V_m is the mobile phase volume (column void volume), A is the analyte ion's charge, E is the eluant ion's charge, R is the gradient ramp steepness in mM of eluant concentration per mL of eluant pumped, and $\log \text{Const.}$ is the Y intercept of the log/log plot. This equation predicts that an increase in gradient steepness will decrease the retention time of divalent ions more than monovalent ions. An advantage monovalent eluants have over divalent (or other polyvalent) eluants is that a given change in eluant concentration produces a greater change in analyte retention time. Compared to a monovalent eluant during a gradient run, the concentration of a divalent eluant must be changed by a much larger amount to elute ions of widely differing retention.

For ions of different charge, the elution order, and therefore the selectivity, can be changed by adjusting the gradient. For example, if two ions with different charge co-elute, an increase in gradient steepness will

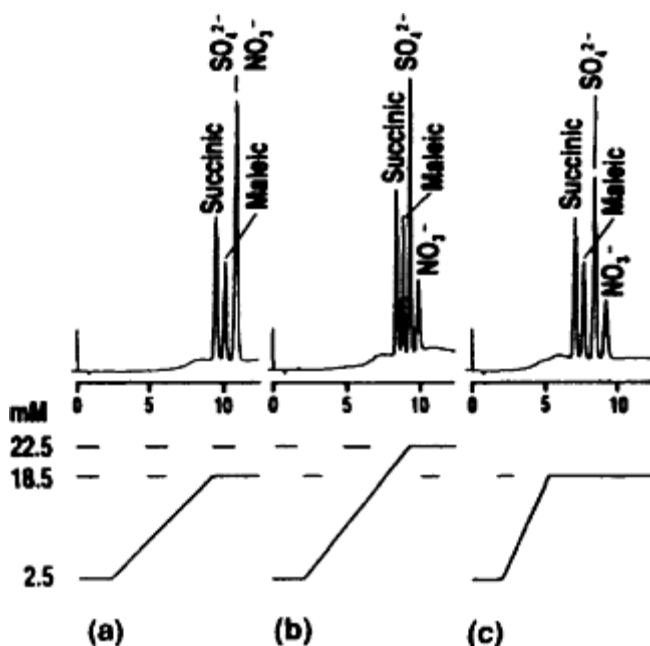


Fig. 12.21 Effect of gradient ramp on elution AS6 *p*-cyanophenolate eluant
Source: Reproduced with permission from Dionex Corporation [24]

separate the two, causing the ion of higher charge to elute first. In theory, one could obtain the optimum conditions for a gradient elution from a plot such as that shown in

Fig. 12.20. In practice, this is not straight-forward because equation (1) assumes that a single linear gradient is used with the initial eluant concentration equal to zero. Faster gradient runs can be obtained by starting the eluant concentration at a higher value. Also, the best combination of speed and selectivity is often the result of combining several different gradients, often with isocratic sections and step changes. With more complicated gradient programs, the retention equation becomes unwieldy.

Equation (1) can be easily used to predict trends. This is demonstrated in Fig. 12.21. In all three chromatograms, the initial eluant concentration is 2.5mM *p*-cyanophenate. This concentration is increased between 2 and 7min to 18.5mM in (a) (where sulphate and nitrate co-elute) to 22.5mM in (b), resulting in baseline separation. In (c), the eluant concentration is increased as in (a) to 18.5mM, but in 5min. instead of 9min. The effect is similar in that the divalent anions elute earlier, but because of the long period holding at 18.5mM, the separation between the divalent anions is not compressed as in (b), but is instead similar to (a). The chromatogram in Fig. 12.18 of anions on the HPIC-AS6 was developed with this method and uses a combination of step changes, linear gradients and isocratic sections.

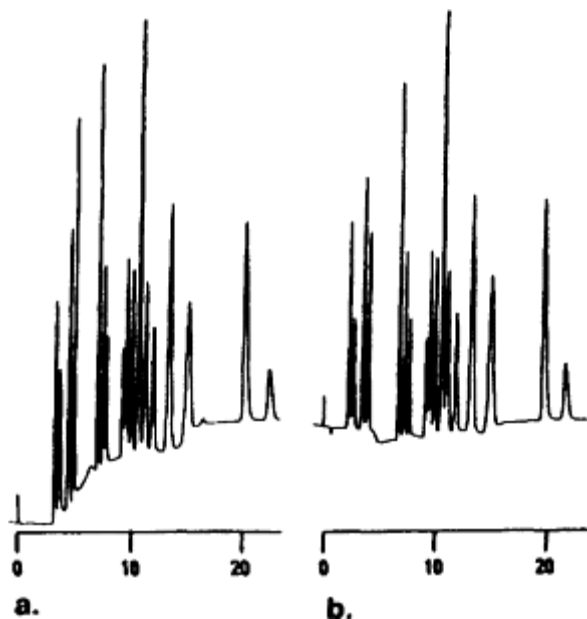


Fig. 12.22 Balancing the gradient baseline with (a) mannitol and (b) boric acid AS6, *p*-cyanophenate eluant

Source: Reproduced with permission from Dionex Corporation [24]

When eluants other than sodium hydroxide are used, it is often necessary to minimise the baseline slope which results as the eluant concentration is increased. In anion exchange, this can be accomplished chemically by adding mannitol to the weak eluant and boric acid to the regenerant. Although the reaction between boric acid and mannitol is not well

understood, they do combine to produce an acid considerably stronger than either of the two by themselves. As a neutral polyalcohol, mannitol has little effect on either separation or detection. Boric acid in the dilute sulphuric acid regenerant is neutral, and can diffuse through the cation exchange membranes of the MPIC suppressor. The two then combine in the suppressor, producing a conductive species. By decreasing mannitol concentration in approximately inverse proportion to the increase in eluant concentration, the baseline changes can be counteracted. This method is demonstrated in Fig. 12.22, in which the mannitol was used to balance the baseline in (b), but not in (a).

Another method of baseline compensation is computer baseline subtraction. For this method, a blank run with no injection is stored in the computer's memory and subtracted point by point from succeeding runs. This method works well as long as the baseline profile is reproducible.

A problem encountered in gradient elution is the presence of extraneous peaks in the chromatogram caused by trace impurities in the eluant. In anion exchange, the most common impurities are chloride, sulphate and carbonate. In the early part of a gradient run, while the eluant is weak, these ions are concentrated at the front of the separator. As the eluant strength increases, they are eventually eluted, and appear as interfering peaks at the expected retention times. Carbonate can be minimised by using properly deionised water and low carbonate sodium hydroxide. The effect of contaminants can be minimised by placing a small column, called the anion trap column, in front of the injection valve. The anion trap column is filled with high capacity, low efficiency anion exchange resin. It successfully prevents trace anionic contaminants from reaching the separator column during the early part of the run. Later in the run, the eluant strength may be high enough to elute the contaminants. The low efficiency of the resin spreads out the contaminant peaks so that they do not interfere with the chromatography. A consequence of the use of an anion trap column is that if a composition gradient is used, the time needed to convert the form of the resin in the anion trap column must be considered.

An alternate approach is to use a higher efficiency trap column which is regenerated at the end of each gradient run with a high concentration eluant, removing any accumulated ionic contaminants. The HPIC-AG8 guard column can perform as a trap column because of its high affinity for carbonate, the primary contaminant in sodium hydroxide eluants. An example of the use of an AG8 as a trap column is the separation of anions shown in Fig. 12.23. For this chromatogram, carbonate and other contaminants on the trap column were removed with a strong borate eluant. The sample is then injected before the sodium hydroxide eluant has removed all of the borate from the trap column. The small amount of borate left forms a complex with quinate, increasing its retention from co-elution with acetate to elution between glycolate and formate.

12.2.5 Miscellaneous

Motomizu *et al.* [25] compared the efficiencies of derivatives of various benzenecarboxylic acids as eluting agents in the ion chromatographic determination of anions and cations.

Various workers have discussed the applications of ion chromatography to the analysis of mixtures of anions and cations in peatland waters [26] and non saline waters [27–34].

Singh *et al.* [35] used suppressed ion chromatography to analyse low concentrations of anions in non saline waters in the presence of high concentrations of matrix ions.

Table 12.9 gives a summary of various other methods described in the literature for the determination of anions in non saline waters.

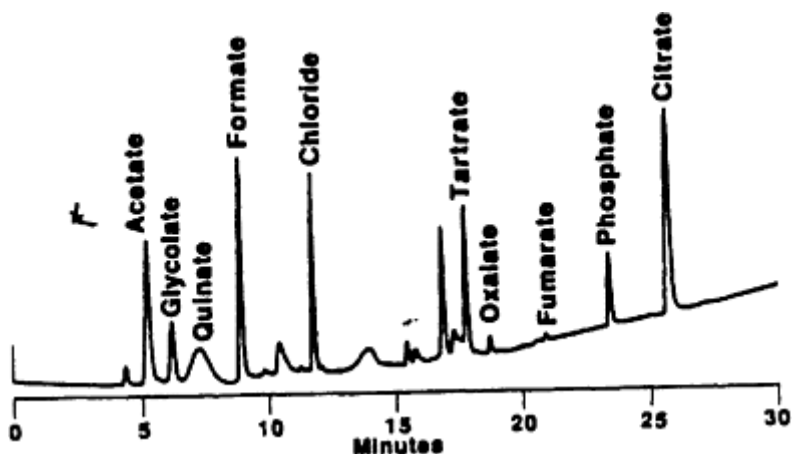


Fig. 12.23 Determination of anions in an aqueous sample

Conditions:

Eluant 1: 0.75mM NaOH

Eluant 2: 200mM MaOH

Eluant 3: 200mM H₃BO₃

Flow rate: 1.0mL min⁻¹

Gradient program

%1:	100	100	85	55	0	0	0	0	100
%2:	0	0	15	45	40	40	100	100	0
%3:	0	0	0	0	60	60	0	0	0

The next injection was always made 42min after the beginning of the previous run

Source: Reproduced with permission from Dionex Corporation [24]

12.2.6 Mixtures of plant and soil extracts

12.2.6.1 Chloride, nitrate, sulphate and phosphate

Bradfield and Cooke [55] described an ion chromatographic method using an ultraviolet detector for the determination of chloride, nitrate, sulphate and phosphate in water extracts of plants and soils. Plant materials are heated for 30min at 70°C with water to

extract anions. Soils are leached with water and Dowex 50-X4 resin added to the aqueous extract which is then passed through a Sep-Pak C₁₈ cartridge and the eluate then passed through the ion chromatographic column. The best separation of these ions was obtained using a $5 \times 10^{-4} \text{ mol L}^{-1}$ potassium hydrogen phthalate solution in 2% methanol at pH 4.9. A reverse phase system was employed. Retention times were 5.5, 7.9, 12.6 and 18min for

Table 12.9 Ion chromatography of anions

Anions	Eluent	Column	Type of sample	Detector	Ref.
$\text{AsO}_4^{3-}/\text{SO}_3^{2-}$	—	—	Environmental waters	—	[36]
PO_4^{3-}	—	—	Sea	—	[37]
CN^{1-} , S^{1-} , OCl^{1-}	—	—	Ground waters	—	[38]
$\text{SO}_3^{2-}/\text{S}_2\text{O}_3^{2-}$	4.8mmol L ⁻¹ NaHCO ₃ then 6.9mmol L ⁻¹ elution NaHCO ₃ /0.86mmol L ⁻¹ Na ₂ CO ₃	Gradient	Not stated	—	[14]
$\text{NO}_3^{1-}/\text{SO}_4^{2-}$	—	—	Non saline	—	[39]
$\text{F}^{1-}/\text{o}^{1-}\text{PO}_4^{3-}/\text{Br}^{1-}$	—	—	River	—	[17]
$\text{Cl}^{1-}/\text{NO}_3^{1-}/\text{SO}_4^{2-}$	—	—	Pure waters	—	[40]
$\text{CO}_3^{2-}/\text{HCO}_3^{1-}$	—	Zipax Sax and Westcan	—	Electrical conductivity and uv	[41]
SiO_3^{2-} (22µg L ⁻¹)	—	—	Non saline	—	[42]
SO_4^{2-} (50p mole)	5-sulpho-isophthalic acid	Nucleosil SB anion exchange	Freshwater sediment Pure water	Radio ion chromatography	[43]
Misc, anions	—	resin	Non saline	conductiometric	[3]
$\text{NO}_2^{1-}/\text{NO}_3^{1-}$	—	Polystyrene	Non saline divinyl benzene copolymer	—	[44]
NO_2^{1-} , Br^{1-} , NO_3^{1-} , SO_4^{2-} , I^{1-} , SCN^{1-}	—	Na naphthalene trisulphonate	Non saline	Spectrophotometric	[45]

<i>Anions</i>	<i>Eluent</i>	<i>Column</i>	<i>Type of sample</i>	<i>Detector</i>	<i>Ref.</i>
F^{1-} , ClO_4^{1-} , Cl^{1-} , NO_2^{1-} , HPO_4^{2-} , AsO_4^{3-} , NO_3^{1-} , ClO_3^{1-} , SO_4^{2-} , CrO_4^{2-} , BF_4^{1-} , Glycollate acetate, lactate, propionate, aceto acetate, α hydroxy butyrate, chloroacetate, isobutyrate, butyrate (as Ruthenium 11, 1, 10 phenanthroline or ruthenium 11, 2, 2' bipyridy ion interaction complexes)	—	—	Non saline	Fluorometric	[46]
F^{1-} , BO_3^{3-} , Cl^{1-} , AsO_4^{3-} , NO_3^{1-} , glycolate, malonate	—	—	Non saline	Two dimension conductiometric detection	[47]
Cl^{1-} , NO_2^{1-} , Br^{1-} , NO_3^{1-} , PO_4^{3-} , SeO_3^{2-} , SO_4^{2-} , lactate, acetate, propionate, butyrate, isobutyrate	—	—	Non saline	—	[48]
NO_2^{1-} , NO_3^{1-} , phenylene, diamine isomers	—	—	Non saline	—	[49]
F^{1-} , BO_3^{3-} , Cl^{1-} , AsO_4^{3-} , NO_3^{1-} , glyoxylate, malonate	—	—	Non saline	—	[50]
<i>Anions</i>	<i>Eluent</i>	<i>Column</i>	<i>Type of sample</i>	<i>Detector</i>	<i>Ref.</i>
PO_4^{3-} , SO_4^{2-} , Cl^{1-}	—	—	Non saline	—	[51]
SO_4^{2-} , Cl	—	—	Raw waters	—	[52]
Glycollate, malonate	—	—	Non saline	Conductiometric	[47]
F^{1-} , BO_3^{3-} , Cl^{1-} , AsO_3^{3-} , NO_3^{1-} , SO_3^{2-} , dithionate	—	—	Mineral leachates	—	[53]
Benzoate, chlorobenzoate anisates, dimiethylbenzoates, sal icy late, hydroxybenzoate, resorcyate, propionate, gallate	—	—	Non saline	—	[54]
Cl^{1-} , NO_2^{1-} , Br^{1-} , NO_3^{1-} , PO_4^{3-} , PO_3^{3-} , SeO_3^{3-1} , SO_4^{2-} , acetate, stationary phase lactate, propionate, butyrate and isobutyrate	—	Mixed mode	Non saline	—	[48]

Source: Own files

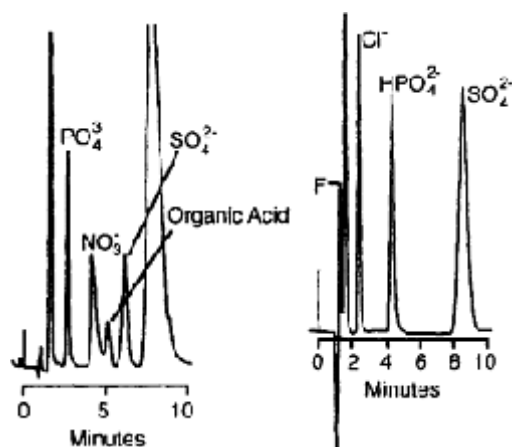


Fig. 12.24 Determination of anions in plant extracts, (a) fresh spinach sample;
 (b) fresh anion sample. Aqueous extracts of macerate samples
 Source: Reproduced with permission from the Royal Society of
 Chemistry [55]

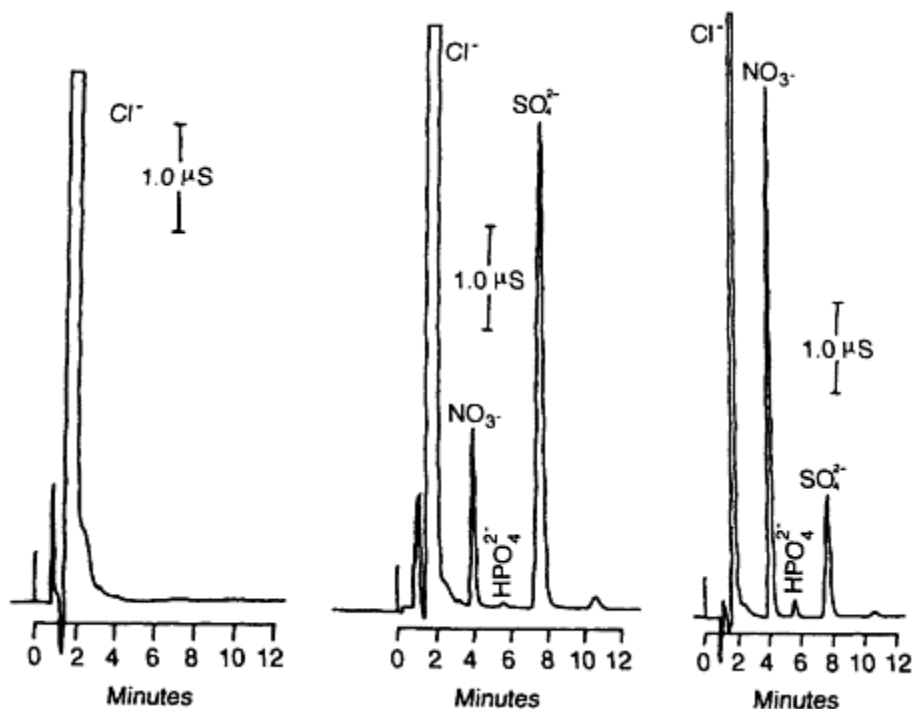


Fig. 12.25 Determination of anions in soil extracts: (a) blank 10mol L⁻¹ KCl;
 (b) soil sample A 10mol L⁻¹ KCl extract; (c) soil sample B 10mmol

L-1 KCl extract 1:5000dil. AMPIC-NGI should also be used in series to remove humic acids

Source: Reproduced with permission from the Royal Society of Chemistry [55]

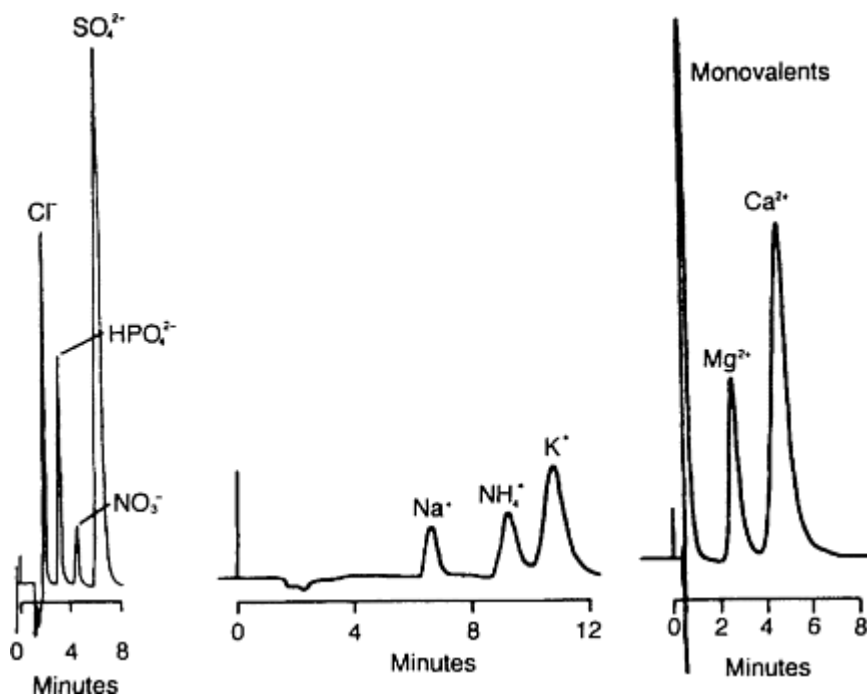


Fig. 12.26 Analysis of granulated fertiliser samples: (a) determination of anions; (b) determination of monovalent cations; (c) determination of divalent cations

Source: Reproduced with permission from the Royal Society of Chemistry [55]

chloride, nitrate, phosphate and sulphate respectively. Recoveries ranged from 84 to 108% with a mean of 97%.

Figs. 12.24–12.26 show chromatograms obtained in the analysis of plant extracts, soil extracts and fertiliser extracts .

12.3 Sea water

12.3.1 Carboxylic acids and amines

Xiao-Hua Yang *et al.* [57] determined nanomolar concentrations of individual low molecular weight-carboxylic acids (and amines) in seawater. Diffusion of the acids across

a hydrophobic membrane was used to concentrate and separate carboxylic acids from inorganic salts and most other organic compounds prior to the application of ion chromatography. Acetic acid, propionic acid, butyric acid-1, butyric acid-2, valeric and pyruvic acid, acrylic acid and benzoic acid were all found in reasonable concentrations in sea water.

12.4 Aqueous precipitation

12.4.1 Chloride, bromide, fluoride, nitrate, nitrite, sulphate, sulphite and phosphate

The application of ion chromatography to the determination of nitrite, nitrate, halogens, sulphate and phosphate (also calcium and magnesium) sodium and potassium in rainwater is discussed below. Wetzel *et al.* [58] used ion chromatography to obtain determinations down to $\mu\text{g L}^{-1}$ concentrations of chloride, phosphate, nitrate and sulphate in rain water samples. Conductivity detector response is linear with concentrations over the mg L^{-1} to $\mu\text{g L}^{-1}$ range for the determinands examined. It was shown that a $3 \times 50\text{mm}$ pellicular anion-exchange resin with tetraethyl ammonium groups attached to a styrene divinyl benzene backbone concentrator column can be loaded remotely and stored for at least 7 days before analysis without significantly affecting ionic determinations.

The response for phosphate, nitrate and sulphate was linear over four orders of magnitude ($2\text{--}10^4 \mu\text{g L}^{-1}$). Response for chloride ion was linear over three orders of magnitude ($2\text{--}10^3 \mu\text{g L}^{-1}$). Correlation coefficients for a linear least squares fit were between 0.9877 and 0.9999.

Oikawa and Saitoh [59] reported studies of the application of ion chromatography to the determination of fluoride, chloride, bromide, nitrite, nitrate, sulphate, sulphite and phosphate ions in 3ml samples of rainwater. The results show that the most suitable eluent for this purpose is 2m mol L^{-1} sodium carbonate/ 5m mol L^{-1} sodium hydroxide. The reproducibility of the determination was satisfactory for standard solutions of all the ions except for nitrite. This problem was solved by preparing standard and sample solutions with the same composition as the eluent.

Apparatus

Model 14 ion chromatograph (Dionex Corp.). Perkin Elmer Model Sigma 10 Data Processor.

Reagents

Sodium carbonate (anhydrous), Merck ultrapure.

Sodium nitrite, Merck Analytical grade. Water, deionised and distilled.

Procedure

Filter the rainwater sample with a membrane filter having a pore size of $0.45\mu\text{m}$. Use the filtrate as the sample for the test. Inject approximately 2ml of the sample into a microloop with a syringe. Table 12.10 lists the determination conditions. Obtain the peak areas of

the chromatogram by the half value width method (width mm) in half value of peak height $\times$ peak height (mm) and prepare a calibration curve.

Table 12.10 Anion determination conditions by ion chromatography

Separator column	3 $\times$ 500mm, filled with low-capacity anion exchange resin
Suppressor column	6 $\times$ 250nm, filled with high-capacity cation exchange resin
Eluent	Mixture of 2m mol L ⁻¹ Na ₂ CO ₃ +5m mol L ⁻¹ NaOH
Pumping speed	156ml h ⁻¹
Sample loop	100 μ L

Source: Reproduced with permission from Elsevier Science [59]

In the sodium carbonate-sodium bicarbonate eluent system, four kinds of eluent were tested by Oikawa and Saitoh [59] 2m mol L⁻¹ sodium carbonate, 2m mol L⁻¹ sodium carbonate, 2m mol L⁻¹ sodium bicarbonate, and 3m mol L⁻¹ sodium bicarbonate.

Fig. 12.27(a) shows the results. The higher the concentration of sodium bicarbonate, the closer the peaks of fluoride, chloride and nitrite ions approach one another. This trend was more significant in sulphite and sulphate and the elution time was shorter. When a combination of 2m mol L⁻¹ sodium carbonate/1m mol L⁻¹ sodium bicarbonate was used, the ions could not be determined because the peak of phosphate was not separated from that of nitrate and sulphite. The ions also could not be determined when the peak of sulphite overlapped when 2m mol L⁻¹ sodium carbonate/1m mol L⁻¹ sodium bicarbonate and 2m mol L⁻¹ sodium carbonate/3m mol L⁻¹ sodium bicarbonate eluents were used. These results show that the sodium carbonate-sodium bicarbonate eluent system is not suitable when simultaneous determination of fluoride, chloride, nitrite, bromide, phosphate, nitrate, sulphite and sulphate is required in samples containing all of these ions.

Fig. 12.27(b) shows the results of ion determinations using the sodium carbonate sodium hydroxide system. The pH of this eluent system was high, 10–12. When 2m mol L⁻¹ sodium carbonate alone (pH 10.12) and a mixture of 2m mol L⁻¹ sodium carbonate/2.5m mol L⁻¹ sodium hydroxide were used, the peak of nitrate overlapped with that of sulphite and that of sulphate overlapped with that of phosphate. Therefore these eluents are not suitable for determination of those ions.

When the 2m mol L⁻¹ sodium carbonate (5m mol L⁻¹ sodium hydroxide (pH 11.63) was used, all the ions were well separated. When the pH was further increased, that is, the 2m mol L⁻¹ sodium carbonate 10m mol L⁻¹ sodium hydroxide eluent was used, the elution time of ions other than phosphate decreased and the peaks approached one another. Conversely, the elution time of phosphate increased; therefore, this eluent is also not suitable.

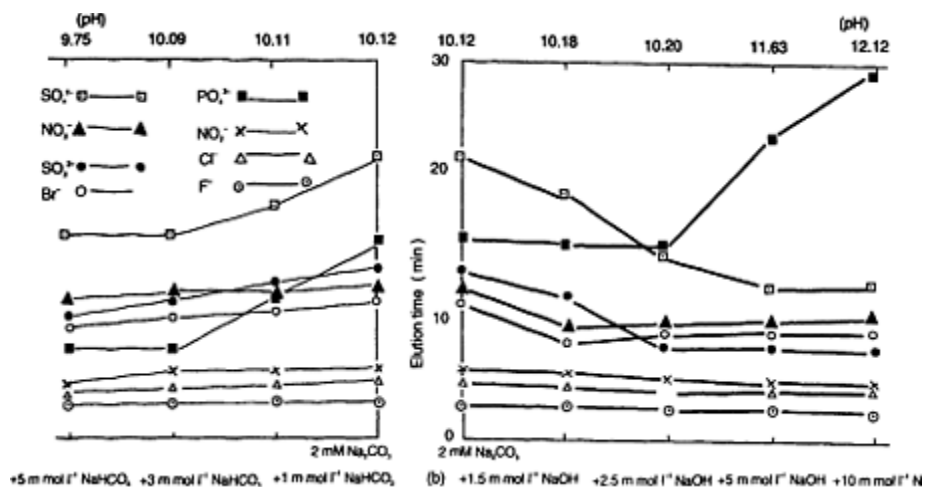


Fig. 12.27 Relationships between concentrations of eluent elements and elution time: (a) mixture of $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$; (b) mixture of $\text{NaCO}_3 + \text{NaOH}$

Source: Reproduced with permission from Elsevier Science [59]

Table 12.11 Reproducibility of determination of anions in standard mixed solution

Ion No	F^- 3mg L ⁻¹	Cl^- 5mg L ⁻¹	NO_2^- 10mg L ⁻¹	NO_3^- 30mg L ⁻¹	SO_3^{2-} 20mg L ⁻¹	SO_4^{2-}
1	16.4	11.2	10.0	4.3	3.1	9.4
2	7.0	11.5	10.5	4.4	3.2	9.9
3	16.7	11.3	10.9	4.6	3.2	10.5
4	16.9	11.5	11.0	4.4	3.2	9.7
5	16.1	11.8	11.3	4.5	3.3	10.6
6	17.1	11.9	11.6	4.6	3.3	10.7
7	17.4	12.3	11.8	4.6	3.3	10.3
8	16.8	12.1	11.9	4.5	3.2	10.6
9	16.9	11.9	11.9	4.6	3.2	10.3
X	16.8	11.7	11.2	4.5	3.2	10.2
CV%	2.3	3.2	6.0	2.5	2.0	4.5

Source: Reproduced with permission from Elsevier Science [59]

These results show that the 2m mol L⁻¹ sodium carbonate/5m mol L⁻¹ sodium hydroxide

eluent is the most suitable when simultaneous determination of fluoride, chloride, nitrite, bromide, sulphite, nitrate, sulphate and phosphate is required or when the sample is considered to contain all of these ions. Further studies were therefore made using this eluent.

Fig. 12.27(a)(b) shows that an optimum eluent for the determination of anions can be selected, and that information to determine the interfering ions and the best conditions can be obtained.

Using this procedure, except for nitrite, the coefficient of variation for each ion was less than 5%, and reproducibility was relatively good (Table 12.11). The peak height of nitrite was elevated as the number of sample injections were increased, and after nine tests the increase in peak height was as high as 20%.

The separation of chloride, nitrite, nitrate, sulphite and sulphate ions in an actual rainwater sample was repeatedly carried out using the procedure. Table 12.12 shows the results, which indicate that the peak height of nitrite tended to increase as the number of times the determination was repeated, showing a coefficient of variation of 13.3%. The coefficient of variation of other anions was less than 10% as was the reproducibility test of the standards.

The detection limit of each ion was obtained from the peak of the chromatogram and the noise of the base line when 100 μ L samples containing fluoride (0.1mg L⁻¹), chloride (0.2mg L⁻¹), nitrite (0.5mg L⁻¹), nitrate (1mg L⁻¹), sulphite (5mg L⁻¹) and sulphate (3mgL⁻¹) were used.

Table 12.12 Reproducibility of anions in actual rainwater samples

Ion no	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₃ ²⁻	SO ₄ ²⁻
1	2.47	0.78	0.43	1.04	0.83
2	2.32	0.79	0.48	1.09	0.84
3	2.24	0.87	0.48	1.31	0.87
4	2.18	0.95	0.42	1.15	0.86
5	2.11	0.95	0.38	0.98	0.81
6	2.15	0.97	0.46	1.09	0.81
7	2.15	0.99	0.49	1.09	0.86
8	2.10	1.13	0.48	1.20	0.83
9	2.12	1.13	0.46	1.20	0.86
X	2.20	0.95	0.45	1.12	0.84
CV%	2.5	13.3	8.1	8.8	2.7

Source: Reproduced with permission from Elsevier Science [59]

When the detection limit was twice the signal to noise ratio of the base line these limits were 0.01mg L⁻¹ for fluoride, 0.02mg L⁻¹ for chloride, 0.05mg L⁻¹ for nitrite, 0.0mg L⁻¹

for nitrate, 0.5mg L^{-1} for sulphite and 0.1mg L^{-1} for sulphate.

Little change was found in the concentration of anions during 3d storage when the sample was kept at 25°C in a refrigerator.

Fig. 12.28 shows an example of an ion chromatogram of rainwater. Using the following conditions, Schwabe *et al.* [60] determined chloride, fluoride, nitrate, phosphate and sulphate in 20min in rainwater and potable water in amounts down to 0.5mg L^{-1} .

Type	Dionex D12
Sensitivity	1ks
Analytical column	Fast run anion separator
Suppressor column	Anion suppressor
Sample loop	$100\mu\text{L}$
Pump flow	115ml h^{-1}
Pressure	22 bar
Run time	11min per sample
Eluent	$0.0048\text{mol L}^{-1} \text{NaHCO}_3$ $0.0023\text{mol L}^{-1} \text{Na}_2\text{CO}_3$

Fig. 12.29 shows the results for chloride, fluoride, nitrate and sulphate in Berlin rainwater. The month of March shows significantly higher loads than the other months, caused by high rainfall. There is also a high load of sulphate and nitrate for October and November.

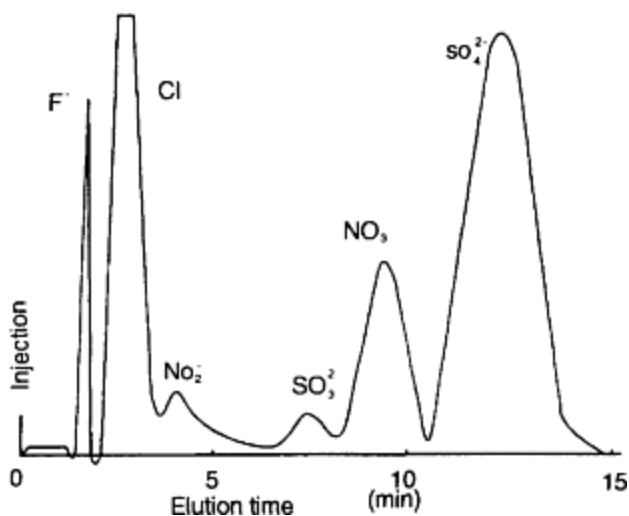


Fig. 12.28 Example of ion-chromatogram of rainwater

Source: Reproduced with permission from Elsevier Science [60]

Buchholz *et al.* [61] have described a procedure for the determination of less than $1\mu\text{g L}^{-1}$ of chloride, nitrite and sulphate in 2ml of rainwater sample using non-suppressed ion chromatography. Detection limits are less than 0.1mg L^{-1} for chloride and nitrate and 0.25mg L^{-1} for sulphate. The method can accomplish the simultaneous analysis of chloride, nitrate, nitrite and sulphate in less than 25min (see Fig. 12.30).

Apparatus

Model 110 A high performance liquid chromatograph (Beckman) equipped with a 2ml constant volume sample loop and a $4.6\times 250\text{mm}$ Wescan 269-001 anion column with guard column. Detection of anions from column eluent is by measurement of conductivity change as eluent flows at 1.8ml min^{-1} through the conductivity cell of a conductivity detector (Wescan Model 213 A). The chromatograms, including peak area data for each anion, were obtained on a reporting integrator (Hewlett Packard 3390A). The anion calibration standard was prepared to contain 1.49, 1.64, and 1.52mg L^{-1} chloride, nitrate and sulphate respectively. The eluent buffer consisted of 2m mol L^{-1} potassium hydrogen phthalate adjusted to pH 4.5 with potassium hydroxide. All standards, buffers and other chemicals were certified A.C.S. grade (Fisher). The handling of all samples, standards, and buffers was accomplished with rubber gloves to prevent anion contamination due to contact with hands.

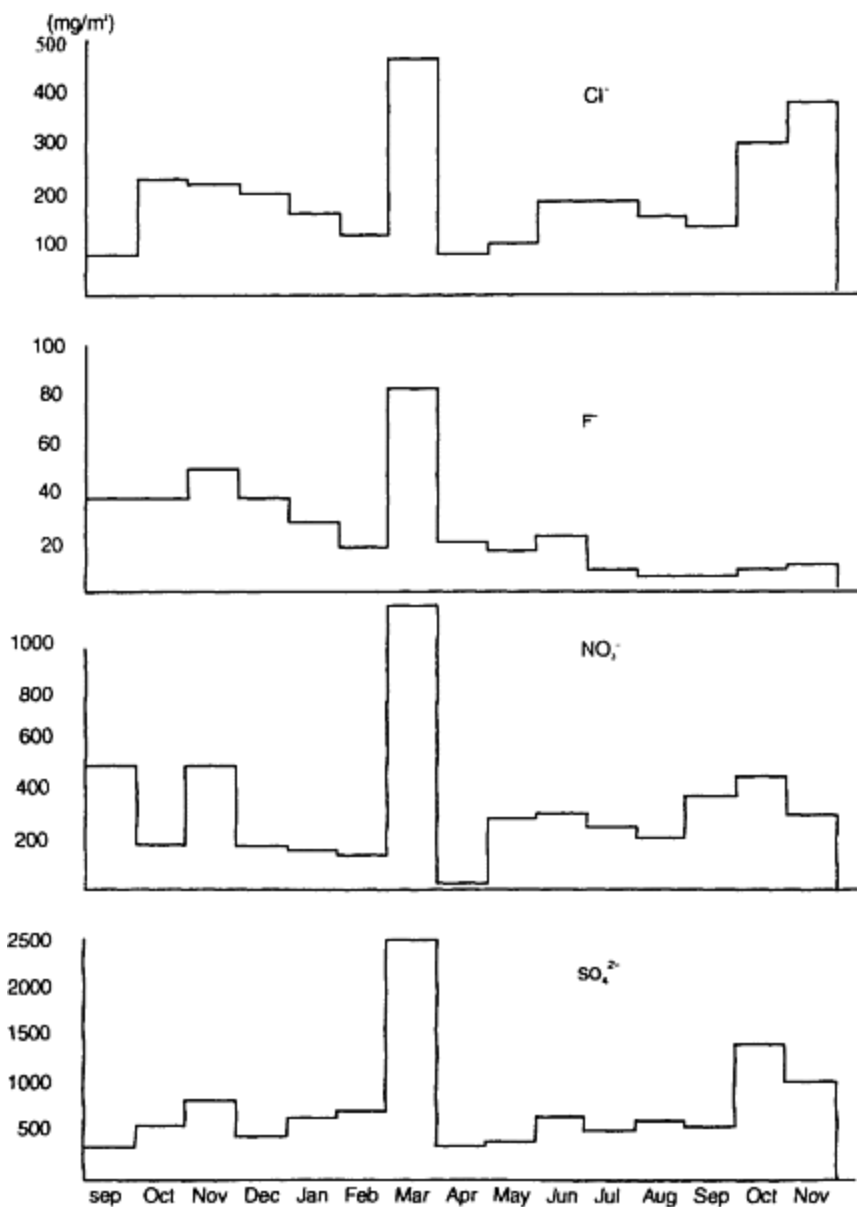


Fig. 12.29 Rainwater analysis (Berlin Marienfelde)

Source: Reproduced with permission from Elsevier Science [60]

The injection of a 2ml sample greatly improved detection sensitivity. However, the injection of a sample of this magnitude onto a column with a bed volume of only 4ml did present a problem. The reduced conductivity of the sample, compared to the eluent

buffer, resulted in a

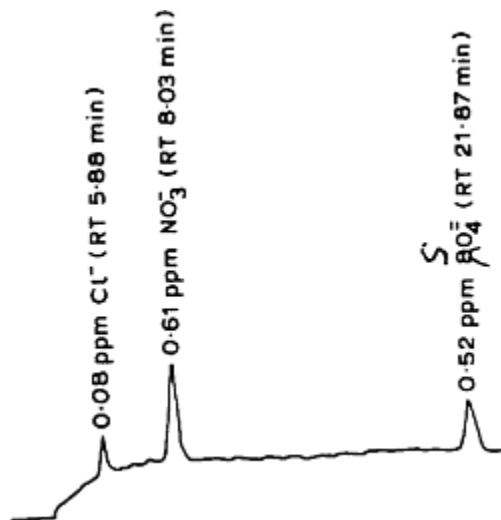


Fig. 12.30 Ion chromatogram of rainwater sample with relatively low concentrations of Cl^- , NO_3^- and SO_4^{2-}

Source: Reproduced with permission from the Journal of Oceanographic Science [61]

large drop in the baseline as the sample front entered the conductivity cell. At a recommended eluent buffer concentration of 4m mol L^{-1} potassium hydrogen phthalate (pH 4.5) as suggested by the manufacturer, the chloride and nitrate peaks were on an upward sloping baseline, which prevented accurate determination of the peak area with the reporting integrator. The sulphate peak, whose retention time was much longer than that of the other two anions, always exhibited a baseline suitable for accurate quantitation. The chloride and nitrate peaks were shifted from the sloping portion of the baseline by a reduction in the concentration of the eluent buffer. Reduction in buffer concentration increased the retention time of all the anion peaks. All peaks also experienced broadening and, in the case of sulphate, this was significant enough to limit the reduction in buffer concentration to 2m mol L^{-1} potassium hydrogen phthalate (pH 4.5). At this concentration the chloride and nitrate peaks were shifted from the sloping baseline for more accurate quantitation, while the sulphate peak had not broadened to the point where detection sensitivity was too greatly diminished.

To test the precision of this method, the calibration standard was diluted 1:2, 1:4 and 1:8. The standard and each dilution were then analysed for anions. The results are summarised in Table 12.13. To verify that detection response was linear for each anion in the concentration range desired for these studies, graphs of peak area vs concentration were prepared.

Table 12.13 Concentrations of calibration standard and various dilutions determined by ion chromatography method

	Concentrations (mg L ⁻¹)		
	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻
A. Laboratory Standard	1.49	1.64	1.52
Concentration by ion chromatography method	1.42	1.57	1.56
	1.48	1.57	1.40
	1.48	1.62	1.53
	1.47	1.62	1.51
Mean	1.46	1.62	1.50
Standard deviation	0.03	0.03	0.07
B. Laboratory standard	0.75	0.82	0.76
(1:2 dilution) concentration by	0.76	0.80	0.73
ion chromatography method	0.74	0.80	0.81
	0.74	0.80	0.78
	0.74	0.79	0.81
Mean	0.75	0.80	0.78
Standard deviation	0.01	0.01	0.04
C. Laboratory standard	0.37	0.41	0.38
(1:4 dilution) concentration	0.36	0.37	0.51
ion chromatography method	0.36	0.38	0.45
	0.34	0.40	0.43
Mean	0.36	0.38	0.45
Standard deviation	0.01	0.01	0.05
D. Laboratory standard	0.19	0.21	0.19
1:8 concentration	0.19	0.18	0.12
by ion chromatography method	0.17	0.21	0.23
	0.18	0.20	0.22
	0.17	0.18	0.19
Mean	0.18	0.19	0.19
Standard deviation	0.01	0.02	0.05

Source: Reproduced with permission from the Journal of Oceanographic Science [61]

The accuracy of the method was considered by determination of the concentration of chloride, nitrate and sulphate in an EPA nutrient/ mineral standard. The results are shown

in Table 12.14. The proximity of the chromatographic values to the EPA values indicates that corrections for matrix effects, due to additional constituents present in this standard, are unnecessary.

The use of concentration columns in conjunction with ion chromatography is one means of improving the sensitivity of this procedure. Wetzel *et al.* [58] used this procedure to obtain determinations down to $\mu\text{g L}^{-1}$ concentrations of chloride, phosphate, nitrate and sulphate in rainwater

Table 12.14 Comparison of anion concentrations: chromatographic values vs EPA values

	Concentrations (mg L^{-1})		
	Cl^-	NO_3^-	SO_4^-
1. EPA value	4.6	0.34	1.8
Chromatography value			
Run 1	5.0	0.32	1.83
Run II	4.84	0.34	1.72
Mean	4.93	0.33	1.78
2. EPA value	2.3	0.17	0.09
Chromatography value			
Run 1	2.27	0.16	0.88
Run II	2.39	0.14	0.89
Mean	2.33	0.15	0.89

Source: Reproduced with permission from the Journal of Oceanographic Science [61]

samples. Conductivity detector response is linear with concentrations over the mg L^{-1} to $\mu\text{g L}^{-1}$ range for the determinands examined. It was shown that a $3 \times 50\text{mm}$ peculiar anion exchange resin with tetraethyl ammonium groups attached to a styrene divinyl benzene backbone concentrator column can be loaded remotely and stored for at least 7 days before analysis without significantly affecting ionic determinations.

Sample loading can be performed with the concentrator replacing the injection loop; sample is then loaded by syringe or by pump. Concentration may also be loaded off line, disconnected from the ion chromatograph. In the former case, activation of the injection valve automatically places the concentrator column in line with the separator column. In the latter case, the concentrator must be manually connected to the flow path before the separator. After injection, sample ions are separated and detected in the usual manner. Normal multispecies analysis often requires less than 5min per ion; trace analysis requires the same time as routine analysis once the concentrator is loaded. Concentrator loading requires 5–15min per sample.

Reagents

Standard solutions of 1000mg L^{-1} . Prepare for individual species (chloride, phosphate, nitrate and sulphate) from reagent grade chemicals and triply distilled water. Then dilute solutions to 10 or 1mg L^{-1} before further dilutions to 20 or $2\mu\text{g L}^{-1}$

Apparatus

Model 14 Ion Chromatograph (Dionex Corporation, Sunnyvale,

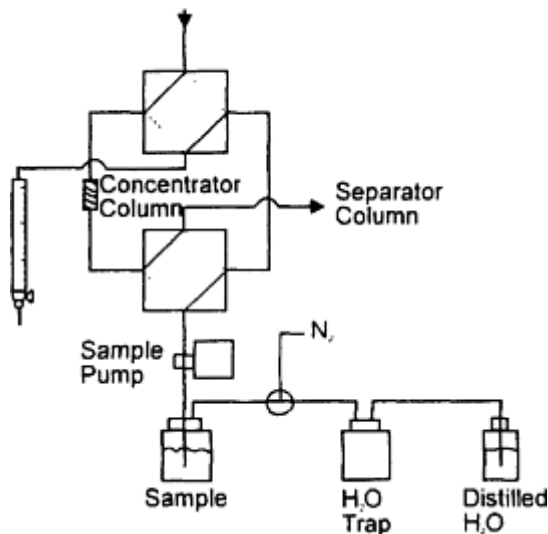


Fig. 12.31 Sample loading and injection flow system

Source: Reproduced with permission from the American Chemical Society [58]

California, 94086). Linear Instruments strip chart recorder was used to monitor the analyses. Instrumental conditions were: eluent, 0.003mol L^{-1} , $\text{NaHCO}_3/0.0024\text{mol L}^{-1}$, Na_2CO_3 ; flow rate, $30\% \times 460\text{ml/h} = 138/\text{h}$; separator column, $3 \times 500\text{mm}$ anion separator; suppressor column, $3 \times 250\text{mm}$ anion suppressor; conductivity meter setting; variable; sample volume, variable; recorder speed, 0.5cm/min^{-1} .

Pump loading of concentrator columns

To eliminate any possibility of sample contamination, samples to be loaded by pump were placed in a Wheaton flask under a purified nitrogen atmosphere. As supplied, the ion chromatograph has two analytical systems, including two eluent pumps. One of the eluent pumps was used to load the concentrator columns while the other was used to load the chromatographic separation. The concentrators were loaded at a rate of 7ml min^{-1} as determined by measuring the effluent from the concentrator wasteline. The sample loading and injection flow system is shown in Fig. 12.31. The two valves constitute one injection valve (upper and lower halves). Solid lines indicate liquid flow connections; dotted lines indicate alternate flow paths used when the valve is in the load position.

During trace analyses, the sample flask always contains water of extremely low ionic content. Attempts to clean the flask often resulted in contamination. All glassware used should be thoroughly rinsed and then soaked for a minimum of 24h with triple distilled water.

Remote loading of concentrator columns

All concentrators were flushed with eluent for 4min before loading. A 10ml glass syringe with a stainless steel Luer adaptor was used for remote loading of concentrator columns. A female Luer adaptor was attached to the column and the sample was forced through the column by manual pressure. Excessive force resulted in leakage along the plunger and through the Luer fitting. Remote loading by pump is also possible. Loaded concentrators were then placed in line before the separator column using the flared Teflon tubing connectors provided with each column.

Suppressor column use for trace determinations

Ion chromatography suppressor columns are used to remove highly conductive eluent ions from the separator column effluent before entering the conductivity cell. During anion determinations, the suppressor exchanges H^+ for Na^+ thus converting the highly conductive sodium bicarbonate, sodium carbonate eluent to a weakly conductive, dilute carbonic acid solution. One consequence of suppressor column use is that solutions with lower conductance than the carbonic acid exiting the suppressor column cause a negative inflection in the detector output or base line. Because sample water is less conductive than the carbonic acid solution, it causes such a negative deflection or water dip approximately 2min after injection during anion determinations.

In order to obtain reproducible results, trace sample ions of interest must be separated from the water dip. Using the sodium bicarbonate sodium carbonate eluent listed above a chloride peak will not separate from the dip when using a concentrator column in conjunction with a fully regenerated (100% H^+ form) $6 \times 250\text{mm}$ suppressor column. Acceptable precision is obtained, though, by converting approximately 50% of the H^+ form suppressor resin to the sodium form. This causes the water dip to become narrower and to elute earlier, thus separating the dip from the chloride peak.

Another method which permits chloride trace determination is to decrease the volume of the suppressor column. As with the partially exhausted larger suppressor, the water dip is separated from the chloride peak. Smaller columns naturally have less capacity than larger columns; in order to avoid delays due to frequent regeneration of these smaller columns, a dual suppressor system was used. One suppressor may be regenerated while the other is used for analysis. Fig. 12.32 shows the flow system used for the dual suppressor column flow system.

Adjust the conductivity cell and meter to a reading of $147\mu\text{mho cm}^{-1}$ at 25°C using a 0.001mol L^{-1} potassium chloride solution.

Procedure

Load various sample volumes onto concentrator columns by glass syringe or by pump. Concentrators loaded by syringe were placed before

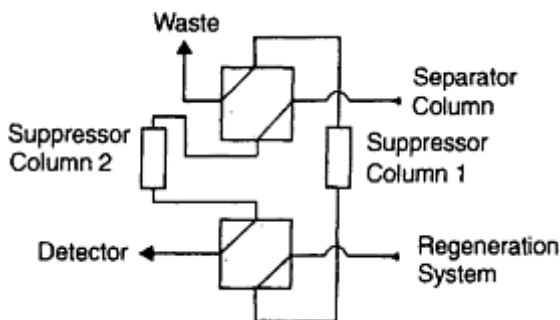


Fig. 12.32 Dual suppressor column flow system

Source: Reproduced with permission from the American Chemical Society [58]

the separator column of the ion chromatograph, those loaded by pump having replaced the injection loop and remained in place during loading and analysis.

Studies on this method have shown the following.

- (1) Sample ions are quantitatively retained ($<7\%$ RSD) in the concentrator, both when large volumes of $\mu\text{g L}^{-1}$ levels or small volumes of mg L^{-1} levels are loaded. Only the total number of milliequivalents is important.
- (2) Detector response is linear over a large range ($2\text{--}103\mu\text{g L}^{-1}$) of ion concentration.
- (3) Reproducibility for identical samples in the $5\text{--}20\mu\text{g L}^{-1}$ range loaded remotely on different concentrators is 18% RSD for phosphate and nitrate and 25% RSD for chloride and sulphate.
- (4) Concentrators can be loaded and then stored for at least 7 days at room temperature before analysis without significantly affecting results.

Tables 12.15–12.18 show that response for phosphate, nitrate and sulphate was linear over four orders of magnitude ($2\text{--}10^4\mu\text{g L}^{-1}$). Responses for chloride ion was linear over three orders of magnitude ($2\text{--}10^3\mu\text{g L}^{-1}$). Correlation coefficients for a linear least squares fit were between 0.9887 and 0.9999.

Table 12.19 lists the results obtained from remotely loaded concentrators analysed immediately after loading vs 7 days after loading. Results show that samples can be stored for at least 7 days without significantly affecting accuracy. The difference in determined concentrations between the immediate and the postponed analyses is less than the RSD for the remotely loaded concentrators.

Table 12.15 Chloride response using a concentrator column

Concentration ($\mu\text{g L}^{-1}$)	Sample vol. (mL)	Micro-equivalents	Scale $\mu\text{mho cm}^{-1}$	Response $\mu\text{mho cm}^{-1}$
1000	5	14.1×10^{-1}	100	758.46

900	5	1.27×10^{-1}	100	691.13
800	5	1.13×10^{-1}	100	609.85
700	5	9.87×10^{-2}	100	534.34
600	5	8.46×10^{-2}	100	463.16
500	5	7.05×10^{-2}	100	387.65
400	5	5.64×10^{-2}	30	310.19
300	5	4.23×10^{-2}	30	235.04
200	5	2.82×10^{-2}	30	150.44
100	5	1.41×10^{-2}	30	75.32
70	5	9.87×10^{-3}	10	55.12
50	5	7.05×10^{-3}	10	41.26
40	5	5.64×10^{-3}	10	30.73
30	5	4.23×10^{-3}	10	21.99
20	5	2.82×10^{-3}	10	14.87
10	5	1.41×10^{-3}	30	7.96
5	5	7.05×10^{-4}	3	3.75
4	5	5.64×10^{-4}	3	3.12
3	5	4.23×10^{-4}	3	2.08
2	5	2.82×10^{-4}	3	1.50

Source: Reproduced with permission from the American Chemical Society [58]

Table 12.16 Actual and equivalent response of phosphate using a concentrator column

Concn. $\mu\text{g L}^{-1}$	Sample vol. ml	Micro- equivalents	Scale μmho cm^{-1}	Actual response $\mu\text{mho cm}^{-1}$	Response equivalent to 5ml
10000	1	.667	30	24.56	122.8
2000	5	.667	30	21.75	21.75
1000	5	.333	30	8.070	8.070
500	5	.1667	30	3.508	3.508
500	5	.1667	3	3.86	3.86
100	5	.0333	3	.702	.702
50	5	.01667	3	.318	.318
20	50	.0667	3	1.648	.1684

15	50	.0500	3	1.228	.1228
10	50	.0333	3	.8070	.0807
8	50	.0267	3	.6140	.0614
5	50	.01667	3	.3509	.0351
2	50	.00667	3	.1228	.0123

Source: Reproduced with permission from the American Chemical Society [58]

Table 12.17 Actual and equivalent response of nitrate using a concentrator column

Concn. $\mu\text{g L}^{-1}$	Sample vol. ml	Micro-equivalents	Scale $\mu\text{mho cm}^{-1}$	Actual response $\mu\text{mho cm}^{-1}$	Response equivalent to 5ml
10000	1	.161	30	18.42	92.10
2000	5	.161	30	17.19	17.19
1000	5	.0806	30	7.368	7.368
500	5	.0403	30	3.508	3.508
500	5	.0403	3	3.930	3.930
100	5	.00806	3	.7018	.7018
50	5	.00403	3	.2807	.2807
20	50	.0161	3	1.912	.1912
15	50	.0121	3	1.386	.1386
10	50	.00806	3	.9474	.0947
8	50	.00645	3	.7719	.0772
5	50	.00403	3	.5965	.0597
2	50	.00161	3	.3684	.0368

Source: Reproduced with permission from the American Chemical Society [58]

Table 12.18 Actual and equivalent response of phosphate using a concentrator column

Concn. $\mu\text{g L}^{-1}$	Sample vol. ml	Micro-equivalents	Scale $\mu\text{mho cm}^{-1}$	Actual response $\mu\text{mho cm}^{-1}$	Response equivalent to 5ml
10000	1	.239	30	19.29	96.49
2000	5	.239	30	15.79	15.79

1000	5 .119	30 6.140	6.14
500	5 .0597	30 2.807	2.81
500	5 .0597	3 3.158	3.16
100	5 .0119	3 .579	.579
50	5 .00597	3 .281	.281
20	50 .0239	3 1.491	.149
15	50 .0179	3 1.105	.111
10	50 .0119	3 .754	.075
8	50 .00955	3 .579	.058
5	50 .00597	3 .351	.035
2	50 .00239	3 .158	.016

Source: Reproduced with permission from the American Chemical Society [58]

Yamamoto *et al.* [2] and Matsuchita [62] have described a method for the determination of chloride, phosphate, nitrate, nitrite, sulphate, calcium and magnesium in rainwater. They used 1m mol L⁻¹ EDTA as an eluent and a silica based anion exchange column.

Table 12.19 Comparison of trace samples analysed immediately after loading and after 7 days storage

<i>Ion</i>	<i>Concn. µg L⁻¹</i>	<i>Peak height^a After 0 days (mm)</i>	<i>Peak height? After 7 days (mm)</i>	<i>RSD (%)</i>
Cl ⁻	5	147	165	12.7
PO ₄ ³⁻	20	23	22	0.7
NO ₃	20	24	21	2.0
SO ₄ ²⁻	20	23	27	2.8

^aComposite standard of 100ml was loaded on each concentrator

Source: Reproduced with permission from the American Chemical Society [58]

Table 12.20 Adjusted retention times

<i>Anions</i>	<i>Rt/min⁻¹</i>	<i>Cations</i>	<i>Rt/min⁻¹</i>
Cl ⁻	3.4	Ca ²⁺	7.4

H_2PO_4^-	3.6 Mg^{2+}	9.0
NO_2^-	3.8	
NO_3	5.0	
SO_4^{2-}	14.2	

Source: Reproduced with permission from the American Chemical Society [2]

Apparatus

Ion chromatographic system consisting of a Toyo Soda Model HLC-6DL ion chromatograph [62]. A Toyo Soda Model CM-8 conductivity detector with a range of $5\mu\text{s cm}^{-1}$. The sample loop volume was 0.1ml and a flow rate of 1.0ml min^{-1} was employed. The separation column, 4.6mm id 50mm long, made of Teflon, was packed with porous silica based anion exchanger of TSK gel 1C–Anion SW (Toyo Soda, particle size $5\pm 1\mu\text{m}$ capacity 0.1mequiv g^{-1}). The column and the conductivity detector was maintained at $27\pm 1^\circ\text{C}$.

EDTA eluent (1mi mol L^{-1}) was prepared by dissolving ethylene diaminetetraacetic acid disodium salt in deionised water and adjusting to pH 6.0 with 0.1mol L^{-1} sodium hydroxide.

Table 12.20 shows the retention times of chloride, phosphate (H_2PO_4), nitrite, nitrate, sulphate, calcium and magnesium. All of these ions were eluted within 15min. The calibration curves of these ions by peak height measurements were linear up to the concentration of 20mg L^{-1} . The detection limits defined as the concentration corresponding to twice the

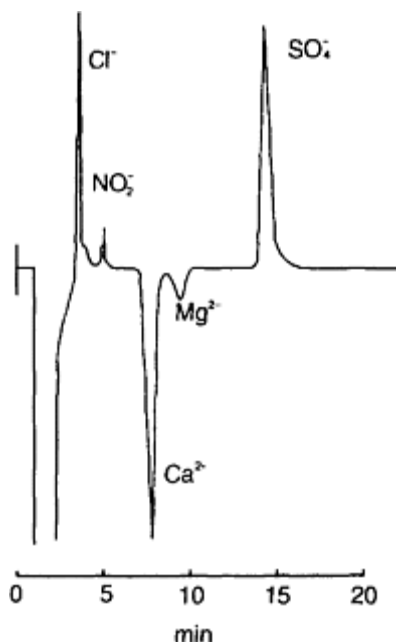
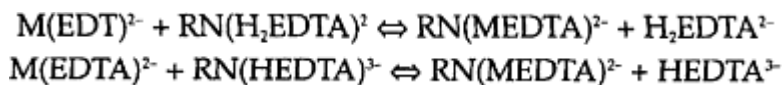


Fig. 12.33 Chromatogram of water

Source: Reproduced with permission from the American Chemical Society [2]

value of noise of the base line were 0.04mg L^{-1} for chloride 0.05mg L^{-1} for nitrite, nitrate, magnesium and calcium and 0.1mg L^{-1} for phosphate and sulphate.

The retention times observed for calcium and magnesium injected as metal cations and those injected as EDTA chelate anions were not significantly different. Therefore, an alkaline earth metal (M^{2+}) forms a chelate anion ($\text{M}(\text{EDTA})^{2-}$) immediately upon contact with EDTA eluent and is then separated according to the following exchange reactions. In this case, the $\text{H}_2\text{EDTA}^{2-}$ and HEDTA^{3-} anions were assumed to present nearly equimolar concentrations in the eluent at pH 6.0:



Using the EDTA eluent, magnesium and calcium chelate anions were eluted between nitrate and sulphate as shown in Table 12.20 and also in Fig. 12.33. Negative peaks of chelate anions might be caused by the lower conductivity of the chelate anion relative to that of the EDTA eluent anion.

The analytical results are given in Table 12.21.

Table 12.21 Analytical results on rain water

mg L ⁻¹	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺
	2.5	1.1	0.38	0.9	0.5

Source: Reproduced with permission from the American Chemical Society [2]

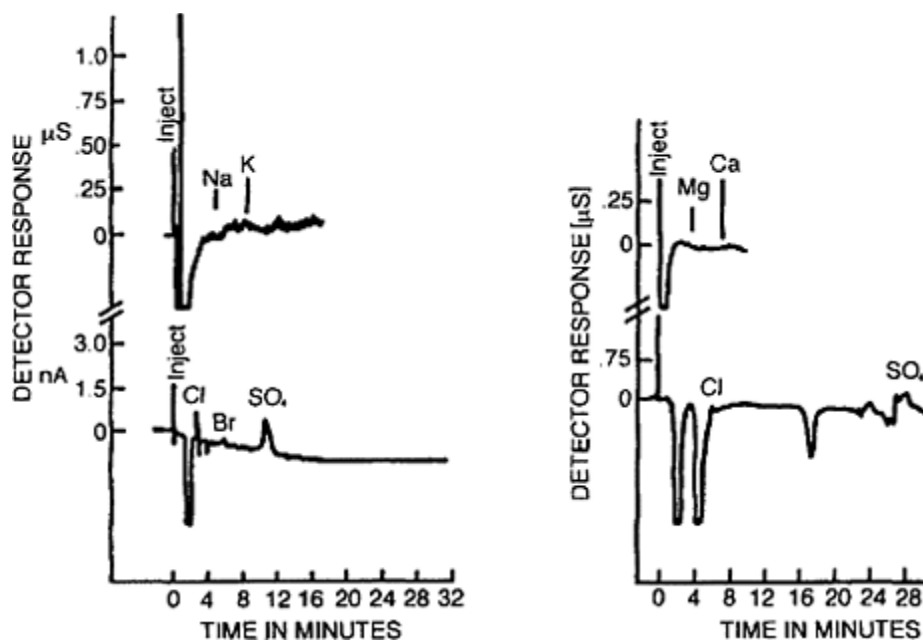


Fig. 12.34 Chromatograms of rainwater (Fort Worth, Texas) monovalent cations and anions and divalent cations and anions

Source: Reproduced with permission from the American Chemical Society [63]

Ion chromatographic methods have been described for the co-determination of anions and cations in rainwater. Thus Jones and Tarter [63], using the conditions given in Table 12.22 reported determinations down to 1 mg L^{-1} of anions (chloride, bromide and sulphate) and cations (sodium, potassium, magnesium and calcium) in rainwater (Fig. 12.34) without converting the cations to anion complexes prior to detection [64]. The technique uses a cation separator column, a conductivity detector, an anion suppressor column, and either a second conductivity detector or an electrochemical detector in sequence. The use of different eluants provides a means for the detection of monovalent cations and anions and divalent cations and anions in each of the samples. Using an eluant with

Table 12.22 Instrumental conditions

Instruments	Dionex model 20 1 0i ion chromatograph Dionex electrochemical detector Houston Instrument Omniscrite chart recorder
Electrochemical applied potential	0.4V
Chart recorder speed	0.25cm min ⁻¹
Flow rate	1.5ml min ⁻¹
Suppressor column	Dionex AMS, preproduction prototype, Membrane suppressor
Injection volume	0.1 0ml
Eluant	0.0016mol L ⁻¹ , Li ₂ CO ₃ +0.0024mol L ⁻¹ LiCOOH.H ₂ O pH=10.4 Monovalent cations and anions
Separator columns	
Anion separator	150×4mm id Dionex HPIC-AS3 anion
Cation separator	200×4mm id Dionex HPIC-CSI cation 0.0033mol L ⁻¹ Cu phthalate divalent cations and anions
Eluant	
Separator columns	
Anion separator	250×4.6mm id Vydac 3021C4.6 anion
Cation separator	200×4mm id Dionex HPIC-CSI cation

Source: Reproduced with permission from International Scientific Communications Inc [63]

a basic pH, it is possible to separate simultaneously and detect the monovalent cations (with the exception of the ammonium ion) and anions, while an eluant with an acidic pH allows for the separation and detection of divalent cations and anions.

The equipment and operating conditions used by Jones and Tarter [63] are described below. The instrumental set-up consists primarily of two separator columns, two detectors and one suppressor column. The analyte flows through the injection valve into the cation separator, where the cations are separated. The separated cations are then detected using a conductivity detector (this is, in effect, a single column ion chromatographic analysis at this stage). The anions, which are essentially unretained on the cation column, are separated on the anion separator column. The ions then travel through the anion suppressor column, where the previously separated and detected cations are removed. Finally, the separated anions pass through the second detector, which may be a conductivity detector or an electrochemical detector. The electrochemical detector responds to pH changes in the eluant as the dissociated acids pass through the detector.

Apparatus

Dionex 2010i ion chromatograph, Dionex electrochemical detector, Houston Instrument Omniscribe chart recorder.

Conditions

Electrochemical applied potential	0.4V
Chart recorder speed	0.25cm min ⁻¹
Flow rate	1.5ml min ⁻¹
Suppressor column	Dionex 4M S ₁ membrane suppressor
Injection volume	0.1mL

Reagents

For monovalent ions: Eluant	0.0016mol L ⁻¹ Li ₂ CO ₃ +0.0024mol L ⁻¹ LiCOOH, H ₂ O pH=10.4 monovalent cations and anions
Separator columns	
Anion separator	150×4mm id Dionex HPLC-A 53 anion
Cation separator	200×4mm id Dionex HPLC-CS 2 cation
For divalent ions: Eluant	0.0033mol L ⁻¹ copper phthalate divalent cations and anions
Separator columns	
Anion separator	250×4.6mm id Vydac 3021 C 4.6 anion
Cation separator	200×4mm id Dionex HPLC-CS 1 cation

All standard anion and cation solutions were prepared by the appropriate dilution of standard stock solutions using distilled deionised water. The salts used to prepare these solutions were ACS Certified quality.

Two different eluants were used, lithium carbonate-lithium acetate dihydrate, and copper phthalate. A stock solution of the lithium carbonate lithium acetate dihydrate eluant was prepared from ACS Certified salts using distilled deionised water with the appropriate dilution to obtain the working eluant.

The copper phthalate eluant was prepared by mixing a solution of cupric acetate with an excess of potassium hydroxide and filtering the resulting cupric hydroxide precipitate. The cupric hydroxide precipitate was then mixed with an equimolar amount of phthalic acid and heated gently overnight to produce copper phthalate.

Procedure

All water samples were injected and analysed as received without prior preparative steps. If dirty samples had been analysed filtering is necessary to remove the solid particles prior to injection on the ion chromatograph.

The normal procedure for the use of the ion chromatograph was followed, with the

exception of the use of the electrochemical detector after the anion suppressor. The solutions were injected and the detector and chart recorder were adjusted to provide peaks of appropriate height.

Simultaneous analysis of both anions and cations indicates that water samples from various localities contain many of the same ions but in differing amounts.

A comparison of ion chromatography and a wet chemical method, EDTA titration, for calcium and magnesium shows good correlation between the two methods. With ion chromatography, the total calcium and magnesium is approximately 42mg L^{-1} while the EDTA titration indicates a total hardness of approximately 49mg L^{-1} with calcium assumed to be the major contributor.

The retention times and detection limits change according to the eluant selected but, under normal daily operating conditions, detection limits will be less than 2mg L^{-1} and retention times will range from 0.5 to 25min for most species.

Wagner *et al.* [65] and Rowland [66] have also determined chloride, nitrate and sulphates in amounts down to 0.5mg L^{-1} .

Rowland [66] pointed out that before the installation of the chromatograph, some of the solutions might contain substances that could reduce the ion exchange efficiency of the column. In particular, in the studies on the effects of acid rain on conifer species, rain collected beneath the dense tree canopy (through-fall) and solutions running down the tree stems (stemflow), was found to contain colourless soluble organic compounds that gradually fouled the column. Such a sample may influence the chromatogram obtained for the subsequent sample. The 'pseudo carry-over' was eliminated by passing these sample types through a clean-up cartridge (Sep-pak C18, Waters Associates). It was found that the guard column protects the separator column from long-term contamination and an initial clean-up is not required. Leachates from the lower mineral soil horizons may contain iron and aluminium colloidal complexes, but column efficiency does not appear to be adversely affected by these solutions.

Despite some gradual deterioration in guard and separator efficiency with time, it is possible to maintain analytical quality with careful monitoring and sample handling techniques, and effective column cleanup procedures. Typically, within a 24h run, the precision was of the order of 0.5%, whereas day to day precision ranged from 0.5 to 1.3%. To maintain good precision, the operating pressure and separating efficiency of the guard column were monitored daily, and remedial action taken immediately when required to minimise the contamination of the separator column. Several recommended clean-up procedures were evaluated and 0.5M sodium nitrate was found to be the most effective

Table 12.23 Determination of halide mixtures in non saline waters by ion chromatography

Type of water	Co-determined anions	Ref.
Natural	Cl, Br, F	[10,11]
Natural	F, Br	[68]

Source: Own files

Table 12.24 Determination of halide mixtures in rainwater by ion chromatography

Type of water	Co-determined anions	Ref.
Rain water	Cl, F, Br	[59,69]
Rain water	Br, Cl	[63,64]
Rain water	Cl, F	[63,64]

Source: Own files

treatment. Hydrochloric acid (0.5M) was also useful, but slightly less effective. It was also found to be essential to use high quality water for eluent preparation, and to remove particulate matter from both the eluent and the sample with an in-line filter.

Using these procedures, 4A-type columns have operated for 8 months and processed approximately 6000 samples. Guard columns remained effective for about 2000 samples and the original separator column for even more samples.

Xiang *et al.* [67] have described an ion chromatographic method for the determination of fluoride, chloride, nitrate and sulphate in acid rainwater with detection limits of 0.03, 0.04, 0.10 and 0.25mg L⁻¹, respectively.

12.4.2 Chloride, bromide and iodide

Ion chromatography has been extensively applied to the determination of mixtures in non saline water. Methods are reviewed in Table 12.23. It has also been applied to the determination of mixed halides in rainwater. Methods are reviewed in Table 12.24.

12.5 Surface waters

12.5.1 Chloride, fluoride, nitrate, nitrite, orthophosphate and sulphate

The standard Environmental Protection Agency Method [16] discussed in section 12.2.1 has been applied to the determination of these anions in surface waters.

12.5.2 Miscellaneous

Iegras [70] has discussed the ion chromatography of various anions and divalent cations in Australian surface waters.

12.6 Potable waters

12.6.1 Chloride, fluoride, nitrate, nitrite, phosphate and sulphate

The method [60] described in section 12.4.1 for the determination of these anions in rainwater has also been applied to the analysis of potable water, as has the Environmental Protection Agency Standard method described in section 12.2.1 [16].

12.6.2 Chloride, bromide, nitrate, phosphate and sulphate

The techniques described respectively, in sections 12.2.1 and 12.4.1 for the determination of these anions in non saline waters [10] and rainwater [60] have been applied to the analysis of potable waters.

12.6.3 Bromide, nitrite, nitrate and sulphate

In studies of the formation of bromoforms produced during the disinfection of water supplies it is necessary to have a method capable of determining bromide ion at the $\mu\text{g L}^{-1}$ level. Morrow and Minear [71] have developed an ion chromatographic procedure using a concentrator column to improve sensitivity. This analysis was carried out on a Dionex model 125 ion chromatograph equipped with concentrator column in place of an injection loop, coupled with an autosampler, which allowed detection at the $\mu\text{g L}^{-1}$ level. A concentrator column is a short separator column used to strip ions from a measured volume of matrix leading to a lowering of detection limits by several orders of magnitude.

To initiate an analysis the system lines were flushed with sample for 2min prior to loading via the auto sampler. A 50ml volume of sample was then loaded onto the concentrator, via the autosampler, at 100% A (7.67ml min^{-1}). The concentrated sample was then flushed (injected) into the

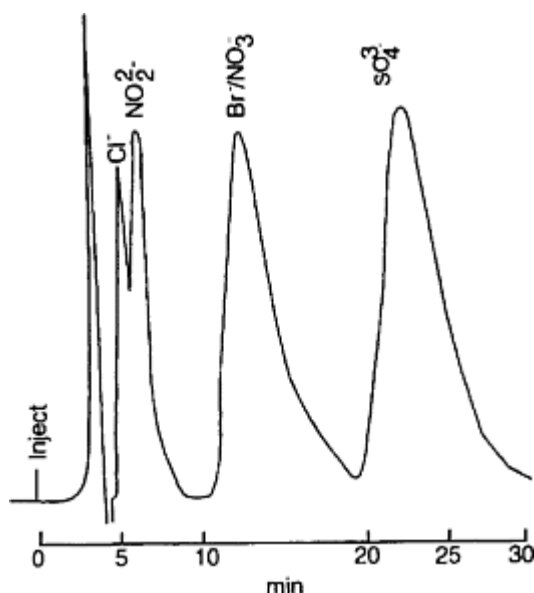


Fig. 12.35 Simultaneous elution of bromide and nitrate using standard eluent
Source: Reproduced with permission from Elsevier Science [71]

system using slightly weakened standard eluent (0.003mol L^{-1} sodium bicarbonate/ 0.0024mol L^{-1} sodium carbonate) at 30% Q (2.3ml min^{-1}). The auto sampler was programmed to allow the ion chromatograph to remain in the inject position for the remainder of each sample elution, after injection of the sample, so that a continual flushing of the concentrator was accomplished prior to loading of the next sample.

When using conventional ion chromatographic separation techniques, it is possible that other matrix anions also common to non saline waters may coelute with bromide. For example, bromide and nitrate elute simultaneously using a standard anion separator column (No. 30065), standard anion suppressor (No. 30366) and standard eluent (0.003mol L^{-1} sodium bicarbonate/ 0.0024mol L^{-1} sodium carbonate at 30% flow (7.67ml min^{-1})). A representative chromatogram is shown in Fig. 12.35.

Separation of bromide from all other matrix anions was shown to be possible using a trace anion separator (No. 30827), a standard anion suppressor, and slightly weakened standard eluent, at 30% flow.

Chloride, nitrate and sulphate were the only ions found to be present in any significant quantities in the representative raw waters analysed. To determine whether response for bromide remained the same regardless of the concentration of these anions, recovery tests were performed on bromide standard solutions of $80\mu\text{g L}^{-1}$ spiked with varying concentrations of chloride, nitrate and sulphate, using the concentrator found to have the highest μ -equivalent capacity.

Table 12.25 Comparison of ion chromatographic and spectrophotometric analyses for bromide

City I.D. No	Date	Bromide ($\mu\text{g L}^{-1}$)	
		<i>Ion chromatography</i>	<i>Spectrophotometer</i>
1	3/27/81	7.5	11.6
2	9/22/81	29.6	30.9
3	12/17/80	104.7	109.8
4	10/16/80	42.6	42.9
5	7/24/81	55.8	55.4

Source: Reproduced with permission from Elsevier Science [71]

In the presence of 100mg L^{-1} chloride, there was 100% recovery of $80\mu\text{g L}^{-1}$ bromide. Chloride was not expected to interfere with the elution of bromide at any concentration since bromide is held preferentially over chloride by the concentrator column. In the presence of 100mg L^{-1} nitrate only 16.2% of the bromide was recovered indicating the concentrator's preference for the nitrate ion. There was no response for $80\mu\text{g L}^{-1}$ bromide in the presence of 1000mg L^{-1} sulphate, indicating 0% recovery.

Evaluation of μ -equivalent concentrator capacity yielded 8.5, 10.6, 6.8, 13.9, 11.7 and 14.6 for the 6 columns subjected to analysis. Evaluation of the concentrator found to possess the highest μ -equivalent capacity (14.6) for percent recoveries of $80\mu\text{g L}^{-1}$ bromide in the presence of varying amounts of nitrate and sulphate revealed that nitrate in excess of 17mg L^{-1} was found to interfere with the elution of bromide and that sulphate in excess of 25mg L^{-1} was found to interfere with the elution of bromide.

Table 12.25 shows a comparison of bromide determinations obtained by the ion chromatographic method and a spectrophotometric method based on the catalytic effect of bromide on the oxidation of iodide or iodine to iodate by potassium permanganate in acidic solution.

A direct statistical comparison of the two methods reveals that, for standard solutions of 20, 60 and $100\mu\text{g L}^{-1}$, the spectrophotometric method produces standard deviations of 0.37, 0.97 and 0.21 and RSDs of 1.9, 1.6 and 0.2%, while the ion chromatography method produces a standard deviation of 1.5 and a RSD of 3.0% for $50\mu\text{g L}^{-1}$ bromide.

Analysis of several raw waters by both methods yielded comparable results on four out of five samples.

Detection by the ion chromatographic method is subject to interference by excessive levels of nitrate and sulphate but this is readily avoided by altering the concentration volume accordingly.

12.6.4 Sulphide and cyanide

Bond *et al.* [21] have described a method for the simultaneous determination of down to 1mg L^{-1} free sulphide and cyanide by ion chromatography, with electrochemical detection. These workers carried out considerable exploratory work on the development of ion chromatographic conditions for separating sulphide and cyanide in a basic medium (to avoid losses of toxic hydrogen cyanide and hydrogen sulphide) and on the development of a suitable amperometric detector.

Reagents

Distilled deionised water, to prepare all standards and eluents.

Sulphide and cyanide standards. Prepare daily by dissolving sodium sulphide and potassium cyanide respectively in 0.005mol L^{-1} sodium hydroxide. Prior to use filter the eluents through a $0.45\mu\text{m}$ filter. Then degas before and during chromatographic runs with high purity nitrogen.

Apparatus

Dionex (Sunnyvale, California) Model 10 ion chromatograph with supplied detector or replaced by an electrochemical (amperometric) detector. A waters (Milford, MA) Model 6000A pump in conjunction with a Model U6K injector. Separator column, a Dionex anion exchange column (internal diameter=3mm, length=250mm). Amperometric detector, Tacussel (Villeurbanne, France) DELC-1 detector cell. Dropping mercury electrode (preferred) and a mercury coated platinum working electrode. Mercury was plated onto the platinum at -1.00V vs Ag/AgCl for 5min and then the electrode was dipped into a mercury pool. Glassy carbon auxiliary and Ag/AgCl (3mol L^{-1} NaCl) reference electrodes. Cathode ray oscilloscope to trace current time curves and hence determine the drop time in the Tacussell cell F.G. & G.Princeton Applied Research Corp., (P.A.R) Princeton, NJ. Model 310 polarographic detector cell with Model 303 static mercury drop electrode with auxiliary and reference electrodes as above.

Polarographic data recovered by use of a PAR Model 174A polarographic analyser, with a PAR Model 303 static mercury drop electrode.

Voltammograms in a conventional electrochemical cell recorded by using 'mini electrodes' obtained from Metrohm (Herisau, Switzerland) Gold working electrode, glassy carbon auxiliary and Ag/AgCl (3mol L^{-1}) reference electrode for voltammetry.

Procedure

All experiments were carried out in a controlled temperature laboratory at $22\pm 1^\circ\text{C}$

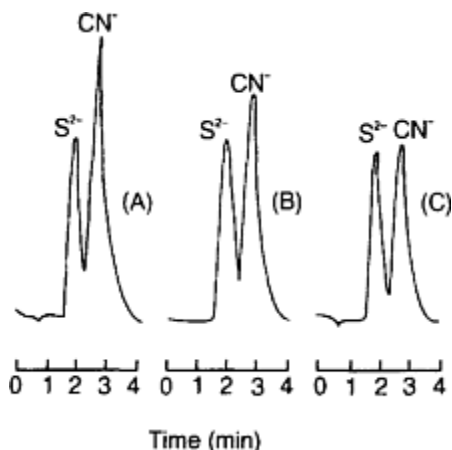


Fig. 12.36 Chromatograms for sulphide and cyanide in deionised water and potable water: (A) deionised water; (b) potable water sample containing 260ng of sulphide and 850ng of cyanide; (c) potable water sample as in (B) spiked with copper ions (2mg L^{-1}) and the decrease in the cyanide response can be seen

Source: Reproduced with permission from the American Chemical Society [21]

Despite a higher sensitivity, the mercury film electrode has some disadvantages compared to the dropping mercury electrode. Day to day reproducibility of the mercury film and hence the analyte signal is harder to maintain than at the dropping mercury electrode. If the film layer is too thin, bad tailing occurs (electrode saturates); the electrode can also eventually become poisoned. The length of time it lasts will depend on the nature and content of samples injected. Consequently more frequent calibration is required than at a dropping mercury electrode.

Fig. 12.36 shows that the response in this water is not the same as in deionised water, suggesting that only free sulphide and cyanide are being determined. This is not surprising and is characteristic of most methods for determining sulphide or cyanide. Since the drinking water was known to contain a significant amount of copper, some of the cyanide may be bound to the metal. Deliberate addition of copper to the water reduced the cyanide peak, supporting this hypothesis. The non-zero intercept for cyanide calibration curves is believed to be a result of complexation by impurities.

Essentially identical results were obtained by using short drop times at the dropping mercury electrode, dc mode (0V) or using the mercury coated platinum electrode, normal pulse mode (pulse -0.80 to 0V , pulse delay= 1s , pulse width= 20ms .) Examination of industrial effluents known to contain sulphide and cyanide demonstrate that the proposed method works extremely well and that free cyanide rather than total is being determined.

12.6.5 Sulphite and cyanide

Goodwin *et al.* [72] determined traces of sulphite in clear or turbid potable waters by a procedure based on gas dialysis/ion chromatography. The detection limit was $2\mu\text{g L}^{-1}$. Ascorbic acid was required as an antioxidant to obtain good recoveries for potable and well waters.

12.6.6 Arsenate, selenate and selenite

The procedure described in section 12.2.2 for the determination of arsenate, selenate and selenite in non saline waters [22] has also been applied to potable waters.

12.6.7 Chlorite and chlorate

Chlorine dioxide (ClO_2) is a widely used disinfectant and bleaching agent that is currently being used by many drinking water treatment utilities in the United States, Canada and Europe for oxidation and disinfection. It is frequently applied as an initial oxidant during treatment, followed by chlorination (gaseous Cl_2 or HOCl) as a final disinfectant. When used as an oxidant, chlorine dioxide reacts to form chlorite (ClO_2^-) and chlorate (ClO_3^-) which have been shown to cause haemolytic anaemia in laboratory animals. Both ClO_2^- and ClO_3^- concentrations are currently under consideration for regulation by EPA and because of possible adverse health effects will likely be regulated with a maximum contaminant limit of $<1.0\text{mg L}^{-1}$ for combined chlorine dioxide, chlorite and chlorate.

Because regulations are imminent and the need exists to protect human health, accurate methods for monitoring these compounds in drinking waters are needed.

In response to these needs Dietrich *et al.* [73] used flow injection analysis with iodometric detection and ion chromatography with conductimetric detection in two methods for the determination of chlorite and chlorate in chlorinated and chloroaminated potable water.

The two methods were accurate and effective for reagent water. The ion chromatographic method was accurate for measurement of chlorite and chlorate concentrations in drinking water even in the presence of other oxidants including chloramines. However, flow injection analysis was affected by chloramines and other oxidants in drinking water, resulting in inaccurate determinations. While chlorite concentrations were unstable in chlorinated drinking water, addition of sodium oxalate increased the stability to up to 3 days and addition of ethylenediamine increased stability up to 18 days. Chlorate concentrations were stable in drinking water for up to 18 days with or without a preservative.

12.7 Waste waters

12.7.1 Bromide, chloride, fluoride, nitrate, nitrite, sulphate and phosphate

Green and Woods [74] have described a method employing a hydrogen form cation exchange column for the analyses of mixtures of chloride, fluoride, sulphate and phosphate in waste waters.

The standard US Environmental Protection Agency Method [16] for the determination of chloride, fluoride, nitrate, nitrite, phosphate and sulphate in non saline waters has been applied to waste waters (see section 12.2.1).

Cameron and Pohlandt [75] determined fluoride, chloride, bromide, nitrate, nitrite, sulphate and phosphate ions, individually or simultaneously, in water and wastewater by suppressed ion chromatography. For simultaneous determination of the anions in the mg L⁻¹ concentration range, the time per analysis was less than 8min. Relative standard deviations were 1.0%, 0.9%, 0.3%, 1.6% 0.3%, 0.8% and 0.3% respectively, for the ions listed above.

12.7.2 Miscellaneous

Ion chromatography has also been applied to the analysis of mixtures of chloride and sulphite [76], fluoride, chloride, phosphate and sulphate and halides, nitrate, sulphate, sulphite, thiosulphate and thiocyanate [77].

12.8 Industrial effluents

12.8.1 Chloride, bromide, fluoride, nitrite, nitrate, sulphate and phosphate

The work of Mosko [78] is important in that he is one of the few workers who have given serious consideration to the determination of nitrite in water. His paper is concerned with the determination of chloride, sulphate, nitrate, nitrite, orthophosphate, fluoride and bromide in industrial effluents, waste water and cooling water. Two types of analytical columns were evaluated (standard anion and fast run series). Chromatographic conditions, sample pretreatment and the results of interference, sensitivity, linearity, precision, comparative and recovery studies are described. The standard column provided separation capabilities which permitted the determination of all seven anions. The fast run column could not be used for samples containing nitrite or bromide owing to resolution problems.

Reagents

Low conductivity water (1–1.5µmho cm⁻¹) prepared by polishing demineralised water with a strong mixed bed resin exchanger used to prepare all standards and eluents.

Standard eluent (0.005mol L⁻¹ NaHCO₃/0.0024mol L⁻¹ Na₂ CO₃). (Periodic conditioning and regeneration of the separator columns and suppressor column employed the use of 0.1mol L⁻¹ sodium carbonate and 1N sulphuric acid solutions, respectively.)

1+1 solution of sodium bicarbonate/sodium carbonate (50g L⁻¹ solutions) appropriate volume added to standards and samples to produce a matrix background similar to the eluent. This minimised interference from the 'water dip' that is common to ion chromatography analyses.

Apparatus

Dionex Auto Ion System 12 Analyzer (Dionex Corp., Sunnyvale, California) consisting of a Model 12 ion chromatograph (Dionex Corp.) coupled with a Gilson autosampler, a Columbia Scientific Industries Supergrator 3-A integrator and a Gilford Instrument Laboratories dual pen strip chart recorder. A concentrator/precolum (4×50mm, Dionex 30825) and separator column (4×250mm, Dionex 30827) were used for the standard seven anion determination. Two anion concentrator precolumns (4×50mm Dionex 30825) connected in series (fast run series) were employed for the five anion analyses. A high capacity suppressor column (9×100mm Dionex 30828) containing a strong acid cation exchange resin in the hydrogen form was used for all chromatography. The ion chromatograph was equipped with a 250pL sample loop. A conductivity full scale sensitivity setting of 30μmho was routinely used.

Eluent pump flow rate of 35–40% (161–184ml h⁻¹) maintained system pressure between 500 and 700psi. Both the sample and regeneration pumps were operated at 50% flow rate (230ml h⁻¹).

Procedure

Filter 10ml of sample through a 0.22μm membrane and collect the filtrate in a 15ml capacity polystyrene vial containing 100μL of 1+1 sodium bicarbonate/sodium carbonate solution. Calibration was established initially and after every six sample analyses by using the combination anion solution indicated in Table 12.26. The calibration standard were prepared fresh daily from separate 1000mg L⁻¹ stock solutions, fortified in the same manner as the samples with bicarbonate/carbonate solution.

Analysis time per run (seven anion determination) was about 24min. Table 12.27 contains information on the calibrated range of the automated method.

Table 12.26 Typical retention times and peak heights of the calibration standard

Concn. mg L ⁻¹ Anion	Approx retention time, min	Approx peak height μV
5.0 fluoride (F)	2.1	54,000
5.0 chloride (Cl)	3.5	30,000
20.0 nitrite (NO ₂)	4.5	50,000
25.0 orthophosphate (PO ₄)	7.0	24,000
25.0 bromide (Br)	9.0	24,300
5.0 nitrate (NO ₃)	11.0	5,000
50.0 sulphate (SO ₄)	15.5	50,700

Source: Reproduced with permission from the American Chemical Society [78]

Table 12.27 Detection limits and calibrated range for sequential seven anion determinations

Anion	Detection limit, mg L^{-1}	Calibrated range, mg L^{-1}	Limit of linearity, mg L^{-1}
Fluoride (F)	0.02	0.1–15.0	>20 ^a
Chloride (Cl)	0.02	0.1–30.0	>20°
Nitrite (NO ₂)	0.25	0.5–30.0	50
Orthophosphate (PO ₄)	0.1	0.2–50.0	50–60
Bromide (Br)	0.1	0.5–50.0	>200>
Nitrate (NO ₃)	0.1	0.2–30.0	150
Sulphate (SO ₄)	0.2	0.5–100.0	120

^aMaximum concentration level tested

Source: Reproduced with permission from the American Chemical Society [78]

A variation in sensitivity of orthophosphate was noted with relation to concentration range. Linear responses were obtained for concentration ranges 0–25mg L^{-1} phosphate and 30–80mg L^{-1} phosphate. However, at a concentration between 25 and 30mg L^{-1} phosphate, the sensitivity changed. To establish a broad linear range, the data were evaluated by using the method of linear regression. Up to a concentration of 55mg L^{-1} phosphate the actual phosphate values did not vary significantly from the linear regression plot. Attempting to quantitate phosphate at concentrations above the 55mg L^{-1} level would result in significant positive error. The degree of error would increase as the phosphate concentration increased. Because of the linearity problem the dynamic range of the method was limited to 0–50mg L^{-1} phosphate. Calibration of the system was established by using a concentration of phosphate standard (25mg L^{-1} phosphate) which was mid-range for the method. Also, the phosphate concentration used for calibration fell within the range where the change in sensitivity occurred. Precision and accuracy data confirmed accurate calibration over the 0–55mg L^{-1} range, using a 25mg L^{-1} phosphate standard.

A decrease in retention time as concentration increased was noted for nitrate. The average retention times observed during development of precision data are listed in Table 12.28. This phenomenon (peak migration) was a source of concern in the automated method because the integrator identifies peaks on the basis of retention time. The program entered into the integrator permitted only a 10% maximum deviation in retention time between the sample peak and a standard calibration peak. If the sample peak retention time deviated more than 10% from that of the calibration standard, the sample peak would be identified by the integrator as an extraneous peak or would possibly be incorrectly identified as some other anion having a similar retention time. A minimum

reporting limit of 0.2mg L^{-1} nitrate was a pre-established requirement for the automated ion chromatographic method. The concentration of nitrate used to establish calibration had to possess a retention time with a 10% window that encompassed the retention time of a 0.2mg L^{-1} nitrate peak. Calibration with a 5.0mg L^{-1} nitrate standard provided a reasonable compromise whereby the widest dynamic range in which identification of the required minimum reporting limit (0.2mg L^{-1} nitrate) was attainable. With this concentration of nitrate used for calibration the range of the method was $0.2\text{--}30\text{mg L}^{-1}$ nitrate. Concentrations of nitrate $>30\text{mg L}^{-1}$ nitrate resulted in retention times outside the 10% window and were identified by the integrator as extraneous peaks or sometimes incorrectly as bromide (anion eluting immediately before nitrate).

Table 12.28 Change in retention time with concentration of nitrate

Nitrate, mg L^{-1}	Retention time, min	Retention time normalised to $5.0\text{mg L}^{-1} \text{NO}_3^-$, min
0.2	12.4	+1.2
5.0	11.2	0
20.0	10.9	-0.3
25.0	10.9	-0.3
45.0	9.2	-2.0

Source: Reproduced with permission from the American Chemical Society [78]

Table 12.29 Comparison of results (mg L^{-1}) obtained with automated ion chromatography vs results obtained with traditional methods

Water type	Fluoride (F)	Chloride (Cl)	Nitrite (NO_2^-)		Orthophosphate (PO_4^{3-})	Bromide (Br)	
	1C	Electrode 1C	Wet chem	1C	Wet chem 1C	Wet chem	1C
Boiler feed	0.1	16	16	<0.5	<0.2	<0.05	0.5
Boiler	0.2	1.2	1.5	<0.5	11	9.9	<0.5
Boiler	1.2	140	125	<5	14	14.4	<0.5
Cooling	4.0	20	24	<0.5	2.0	2.5	1.4
Cooling	0.4	23	28	<0.5	4.2	4.2	<0.5
Zeolite softened	0.1	18	18	<0.5	<0.2	<0.05	<0.5

Softened	0.2	0.2	40	38	<05	0.4	0.2	<0.5
Nitrite treated	<0.5		15	16	<2.5	<100 <10		<25
Nitrite treated	5.0		13	16	<2.5	<100 0.6	0.55	<2.5
City make-up	1.0	1.0	16	16	<0.5	<0.2	<0.05	<0.5
Well water	0.6	0.6	2.2	3.0	<0.5	<0.2	<0.05	<0.5
Waste effluent	<1	0.1	260	280	<5	16	16.1	150

Source: Reproduced with permission from the American Chemical Society [78]

Reproducibility of nitrite with relation to suppressor column capacity was investigated by continuous analysis of a 20mg L⁻¹ nitrite solution over a 6h period. During this period a 24% increase in sensitivity was observed. However, it was noted that satisfactory results (within 10% deviation) were obtained if calibration were re-established after every six sample analyses. Partial exhaustion (after 2h of operation) of the suppressor column was required to achieve sufficient sensitivity for measurement of the desired 0.5mg L⁻¹ nitrite minimum reporting level. Since use of a strong eluent to exhaust partially the suppressor column would also decrease operating time, it was decided that any sample requiring nitrite quantitation would be analysed after the second calibration of the system (calibration performed after every six samples). No nitrite data were reported for samples analysed by using a freshly regenerated suppressor column.

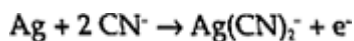
Table 12.29 contains some examples of comparative data. Most results agreed within experimental limits for the specific concentration range and test method used. Traditional methods of analysis used for comparison purposes were as follows: fluoride, ion selective electrode method; chloride, automated mercuric thiocyanate colorimetric method; nitrite, permanganate titration method; orthophosphate, automated ascorbic acid reduction colorimetric method; nitrate automated copper-cadmium reduction colorimetric method. Sulphate was measured with a barium methylthymol blue colorimetric automated method.

12.8.2 Cyanide, sulphide, iodide and bromide

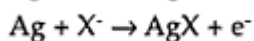
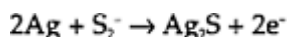
Rocklin and Johnson [23] also used an electrochemical detector in the ion chromatographic determination of cyanide and sulphide. They showed that by placing an ion exchange column in front of an electrochemical detector, using a silver working electrode, they were able to separate cyanide, sulphide, iodide and bromide and detect them in water samples at concentrations of 2, 30, 10 and 10µg L⁻¹ respectively. Cyanide and sulphide could be determined simultaneously. The method has been applied to the analysis of complexed cyanides and it is shown that cadmium and zinc cyanides can be

determined as total free cyanide while nickel and copper complexes can only partially be determined in this way. The strongly bound cyanide in gold, iron or cobalt complexes cannot be determined by this method.

This method is based on the work of Pihlar and Kosta [19,20] who showed that a silver working electrode has the ability to produce a current that is linearly proportional to the concentration of cyanide in an amperometric electrochemical flow through cell. The reaction for cyanide is



Under these conditions sulphides and halides produce insoluble precipitates rather than soluble complexes:



Rocklin and Johnson [23] overcame the latter problem by placing an ion exchange column in front of the electrochemical detector. Cyanide and sulphide are separated and are thus determined simultaneously. Although bromide and iodide can be determined by ion chromatography with conductivity detection, the use of electrochemical detection results in greater selectivity as well as increased sensitivity.

Reagents

Cyanide standard solution. Prepare from a 1000mg L⁻¹ sodium cyanide stock solution, standardised by argentometric titration.

Sulphide standards. Prepare by diluting 21% (NH₄)₂S ammonium sulphide. K₃Fe(CN)

6⁻

Ni(CN)₄²⁻. Prepare from sodium cyanide and nickel acetate.

Cd(CN)₄²⁻. Prepare from 1000mg L⁻¹ solutions of cadmium chloride and sodium cyanide.

Copper cyanide solutions. Prepare by adding stoichiometric quantities of sodium cyanide to a 1.0×10⁻⁵mol L⁻¹ cuprous cyanide solution.

Apparatus

Dionex System 2010 (P/B 352OL) ion chromatograph with sample loop size 50μL and eluent flow 2.5ml min⁻¹. Cyanide and sulphide separated on an HPIC-AS3 (P/N 35311) anion exchange column using an eluent consisting of 14.7mmol L⁻¹ ethylenediamine, 10mmol L⁻¹ NaH₂BO₃ (prepared from H₃BO₃ and NaOH) and 1.0mmol L⁻¹ sodium carbonate. The eluent pH is 11.0. Chromatography of iodide was performed by using an HPIC-ASI (P/N 30827) column with an eluent consisting of 2mol L⁻¹ sodium nitrate. Chromatography of bromide was performed using an HPIC-AS3 (P/N 30985) column with an eluent consisting of 2mmol L⁻¹ sodium carbonate.

Electrochemical detection performed with an Ion Chrom/Amperometric Detector (P/N 35221). The cell (Fig. 12.37) consists of a silver rod working electrode 1.3cm long×0.178cm in diameter, an Ag/AgCl reference electrode separated from the flowing

stream by a Nafion cation exchange membrane and platinum counter electrode. (Nafion is a registered trade mark of E.I. du Pont de Nemours & Co.) The cell geometry is based on one previously reported by Lown *et al.* [79]. The working electrode was occasionally cleaned by mechanical

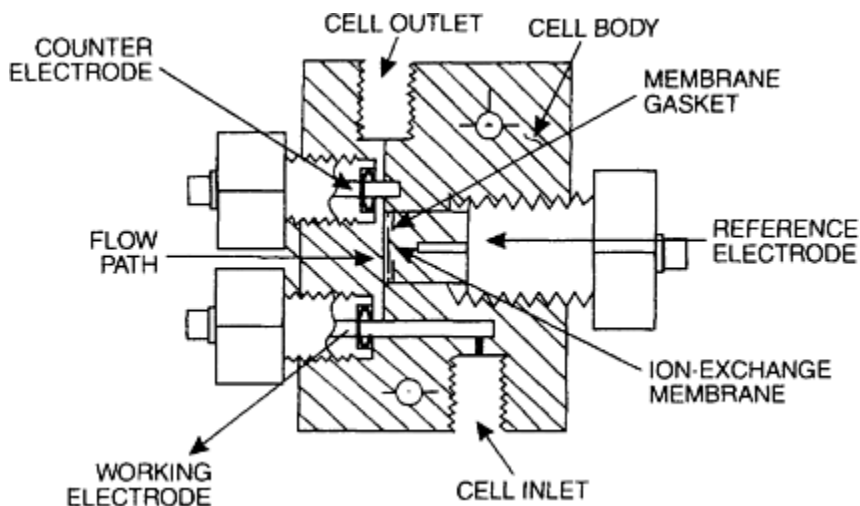


Fig. 12.37 Diagram of amperometric flow through cell

Source: Reproduced with permission from the American Chemical Society [23]

polishing. The applied potential was 0.V for cyanide and sulphide, 0.20V for iodide, and 0.30V for bromide.

Fig. 12.38 shows the separation achieved on a 12 anion standard by this procedure. Sulphide, cyanide, bromide, and sulphite are detected at the silver electrode while nitrite, nitrate, phosphate and sulphate produce no response. Due to the low dissociation of hydrogen sulphide and hydrogen cyanide following protonation by the suppressor column, they are not detected by the conductivity detector.

The major advantage of ion chromatography over other analytical methods is its ability to separate interferences. With one exception, the determination of one of the four ions is not affected by the presence of the others. For example, a solution containing 2500 times as much chloride as bromide has little effect on the determination of bromide (Table 12.30) even though chloride elutes first. Since E_0 for the oxidation of silver to silver chloride is with respect to the value of E_0 for the oxidation of silver to silver bromide, at a potential just on the diffusion controlled plateau for bromide, the current response for bromide will be much greater than that for chloride. This can be exploited in order to determine small quantities of bromide in a large excess of chloride, a difficult process using other methods of analysis due to the similar chemical properties of the two halides.

In the determination of $50\mu\text{g L}^{-1}$ bromide present in 1000mg L^{-1} of chloride the large negative dip following the chloride peak is caused by the reduction of the silver chloride deposited on the electrode. Since there is no longer chloride in the solution next to the

electrode (as it has all

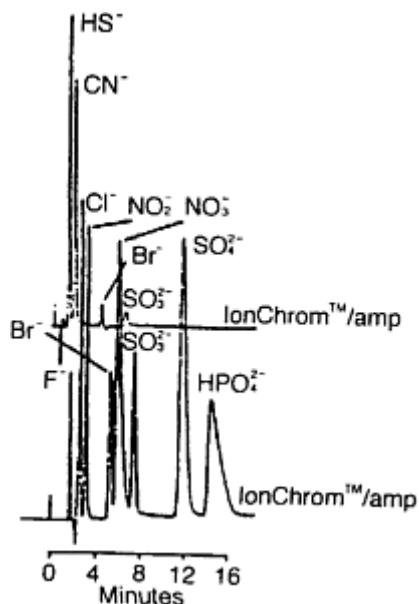


Fig. 12.38 Simultaneous analysis by using electrochemical and conductivity detection. Concentrations are $300\mu\text{g L}^{-1}$ sulphide, $500\mu\text{g L}^{-1}$ cyanide, 1 mg L^{-1} fluoride, 4 mg L^{-1} chloride, 10 mg L^{-1} nitrites, 10 mg L^{-1} bromide, 25 mg L^{-1} nitrate, 30 mg L^{-1} sulphite, 25 mg L^{-1} sulphate and 50 mg L^{-1} phosphate

Source: Reproduced with permission from the American Chemical Society [23]

Table 12.30 Determination of 1 mg L^{-1} cyanide in the presence of sulphide

Amt of added S^{2-} , mg L^{-1}	Recovery of CN^- , %, $\pm 2\%$
0	100
0.10	109
1.00	112
10.0	104

Source: Reproduced with permission from the American Chemical Society [23]

eluted) and since the applied potential is below the diffusion controlled plateau, silver chloride reduction is favoured in order to satisfy the Nernst equation. A small dip

following the bromide peak can also be seen.

The determination of cyanide is affected by the presence of sulphide in the sample as shown in Table 12.31. Since sulphide elutes before cyanide (Fig. 12.38), cyanide does not interfere with the analysis of sulphide. The addition of 0.1mg L^{-1} sulphide enhances the cyanide peak by 9%. This effect can be minimised or eliminated by using the standard addition method or by matching the cyanide standards as closely as possible to the

Table 12.31 Determination of $400\mu\text{g L}^{-1}$ bromide in the presence of chloride

<i>Amt of added Cl^-, mg L^{-1}</i>	<i>Recovery of Br^-, %, $\pm 2\%$</i>
0	100
10	104
100	100
1000	115 ^a

^aThe 100mg L^{-1} chloride solution contains $50\mu\text{g L}^{-1}$ bromide, accounting for 12.5% of the 15% excess

Source: Reproduced with permission from the American Chemical Society [23]

sample. For example, if the sample is known to contain approximately $10\mu\text{g L}^{-1}$ sulphide, then this amount should be added to the standards. In general, plots of the log peak height as a function of the log of concentration are linear at low concentration. At high concentrations an increase in concentration produces a smaller increase in current as shown by the plateau for each ion. This plateau (also observed in flow injection analysis studies) is caused by uncompensated resistance in the cell. The upper limit of linearity can be extended by increasing the applied potential or by decreasing the size of the injection loop. With a $100\mu\text{L}$ injection loop, the detection limit for cyanide is $2\mu\text{g L}^{-1}$, for sulphide $30\mu\text{g L}^{-1}$, for iodide $10\mu\text{g L}^{-1}$ and for bromide $10\mu\text{g L}^{-1}$.

12.8.3 Metal cyanide complexes

The cyanide ion in inorganic cyanides can be present as both complexed and free cyanide. In order to study the chromatography of metal cyanides, Rocklin and Johnson [23] prepared and assayed solutions of cadmium, zinc, copper, nickel, gold, iron and cobalt cyanides. Table 12.32 lists the percentage of total cyanide detected.

The results suggest that the complex cyanides can be grouped into three categories depending on the cumulative formation constant and stability of the complex.

Category 1 includes the weakly complexed and labile cyanides $\text{Cd}(\text{CN})_4^{2-}$ ($\log \beta_4=18.78$) and $\text{Zn}(\text{CN})_4^{2-}$ ($\log \beta_4=16.7$). These complexes completely dissociate under the chromatographic conditions used, the cyanide being indistinguishable from free cyanide.

Category 2 includes the moderately strong cyanide complexes $\text{Ni}(\text{CN})_4^{2-}$ ($\log \beta_4=31.3$) and $\text{Cu}(\text{CN})_4^{3-}$ ($\log \beta_4=30.3$). Although the complexes are labile, they are

retained on the column and slowly dissociate during the

Table 12.32 Percentage of total cyanide in metal complexes determined as 'free' cyanide

Metal complex	$\log \beta_t$	%
$\text{Cd}(\text{CN})_4^{2-}$	18.8	102
$\text{Zn}(\text{CN})_4^{2-}$	16.7	102
$\text{Ni}(\text{CN})_4^{2-}$	31.3	81
$\text{Cu}(\text{CN})_4^{3-}$	30.3	52
$\text{Cu}(\text{CN})_3^{2-}$	28.6	42
$\text{Cu}(\text{CN})_2^-$	24.0	38
$\text{Au}(\text{CN})_2^-$	38.3	0
$\text{Fe}(\text{CN})_6^{3-}$	42	0
$\text{Co}(\text{CN})_4^{3-}$	64	0

Source: Reproduced with permission from the American Chemical Society [23]

chromatography. This slow dissociation produces tailing which lasts for several minutes as the free cyanide elutes and is detected. As the results presented in Table 12.32 demonstrate, the tailing and the non-quantitative recovery of cyanide preclude the use of direct injection to determine total cyanide in samples containing copper and nickel. These samples may be analysed after acid distillation and caustic trapping. The cyanide in the caustic solution can then be determined by ion chromatography with electrochemical detection.

Category 3 includes those cyanides which are inert and therefore totally undissociated, such as $\text{Au}(\text{CN})_2^-$ ($\log \beta_2 = 38.3$), $\text{Fe}(\text{CN})_6^{3-}$ ($\log \beta_6 = 42$) and $\text{Co}(\text{CN})_4^{3-}$ ($\log \beta_4 = 64$). No free cyanide was detected for these complexes. Although these complexes do not elute under the chromatographic conditions used, they can be eluted and determined by using different chromatographic conditions and conductivity detection.

Samples containing both free cyanide (or weakly complexed strongly complexed cyanide can be analysed for free cyanide by direct injection. The determination of total cyanide (both free and strongly complexed) requires distillation of the sample with caustic trapping.

12.8.4 Sulphite and dithionate

Petrie *et al.* [53] have determined sulphite and dithionate in mineral leachates by ion chromatography.

12.9 High purity water

12.9.1 Chloride, sulphate, nitrite

Roberts *et al.* [80] have described a single column ion chromatographic method for the determination of chloride and sulphate in steam condensate and boiler feed water. This was shown to be a valuable technique for analysing $\mu\text{g L}^{-1}$ levels of chloride and sulphate in very pure waters. The anions are concentrated on a short precolumn, separated on a low capacity ion exchange column and detected by an electrical conductivity detector. The apparatus is simple and no 'suppressor' column is needed. Adaptation to on-line analysis would be inexpensive and automation would require control of only the load/ inject valve.

The preliminary work by Roberts *et al.* [80] was carried out using a resin of very low exchange capacity ($0.003\text{mequiv g}^{-1}$) and a $7.5 \times 10^{-4}\text{M}$ solution of benzoic acid as the eluant. Unusually good sensitivity can be obtained in single column anion chromatography using this eluant. To increase the sensitivity further, the size of the sample loop was increased to $500\mu\text{L}$ from the usual $100\mu\text{L}$. This method adequately separated chloride and sulphate with detection limits of 10mg L^{-1} chloride and 100mg L^{-1} sulphate. However, a prolonged dip in the base line occurred sometime after the sulphate peak and made this procedure inefficient for repetitive analyses. Chloride must be separated from the water dip before it can be analysed reliably in the same run with a sulphate. This was accomplished by carefully constructing a concentrator column and by careful choice of the column dimensions, resin capacity and eluant strength. The effect of column and eluant parameters on anion retention times has been discussed previously by Gjerde *et al.* [81,82]. If eluant flow rate and anion selectivity coefficients are taken to be constant then the effects of column resin weight w , resin capacity i_c , and eluant concentration $[E]$ on the adjusted retention time of anions, t' , are shown by the following equation where y is the sample anion charge and x is the eluant anion charge.

$$\log t' = \log w + y/x \log c - y/x \log [E] - \text{constant}$$

It can be seen that the log of column resin weight can be directly proportional to log adjusted retention time regardless of the anionic charges. Increasing the weight of resin in a column will shift both chloride and sulphate to later retention times. However, lowering the resin capacity and/or increasing the eluant concentration will shift the sulphate faster relative to chloride to shorter retention times. These parameters were adjusted until chloride eluted away from the water dip and sulphate still eluted in a reasonable amount of time. The determination of chloride and sulphate in one run greatly reduced the time needed to do the analysis. Sample concentrations for which peaks were at least three times the background signal were $3\text{--}5\mu\text{g L}^{-1}$ chloride and $1\text{--}2\mu\text{g L}^{-1}$ sulphate with this procedure.

A chromatogram of the determination of chloride and sulphate in a single run is shown in Fig. 12.39. Data from 20ml injections of $5\text{--}100\mu\text{g L}^{-1}$

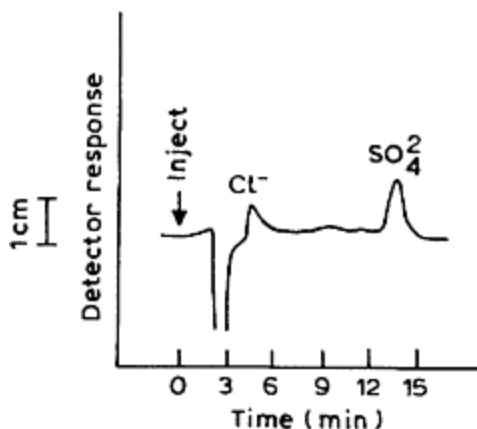


Fig. 12.39 Standard containing $19\mu\text{g L}^{-1}$ chloride and $22\mu\text{g L}^{-1}$ sulphate concentrated from 20.0ml; eluant, 2.0×10^{-4} potassium phthalate, pH 6.2; concentrator column resin, XAD-4 0.5mequiv g^{-1} ; separator column resin, XAD-1 $0.013\text{mequiv g}^{-1}$, $44\text{--}57\mu\text{m}$
 Source: Reproduced with permission from the American Chemical Society [80]

chloride and sulphate in 'pure' water were used to plot standard addition calibration graphs. A straight line of the form $y=0.401x+1.56$ and a correlation coefficient of 0.997 were obtained for chloride and $y=0.516x+3.70$ and a correlation coefficient of 0.995 were obtained for sulphate. Extrapolation of these plots showed a $4.0\mu\text{g L}^{-1}$ chloride concentration and $6.5\mu\text{g L}^{-1}$ sulphate concentration for this sample of 'pure' water. Detection limits under these conditions were $3\text{--}5\mu\text{g L}^{-1}$.

Ion chromatography has been employed to analyse mixtures of chloride, nitrite and sulphate in amounts down to $1\mu\text{g L}^{-1}$ in high purity waters [83].

12.10 Boiler feed waters

12.10.1 Chloride, sulphate and nitrite

The Roberts [80] procedure described in section 12.9.1 has been applied to the analysis of boiler feed waters.

12.10.2 Sulphate and orthophosphate

Ion chromatography has been used to analyse mixtures of sulphate and orthophosphate in boiler blow down water [84].

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Chapter 13

Multianion analysis, application of high performance and related chromatographic techniques

This chapter discusses the applications to natural and treated water analysis of the following techniques:

- high performance liquid chromatography;
- post-suppression ion exchange chromatography;
- ion pairing chromatography;
- suppressed ion chromatography;
- micelle exclusion chromatography;
- ion exclusion chromatography

13.1 High performance liquid chromatography

13.1.1 *Non saline waters*

13.1.1.1 Chloride and sulphate

Takeuchi *et al.* [1] described an indirect photometric detection method for anions in micro high performance liquid chromatography. Micro anion exchange octadecylsilica columns permanently coated with the hydrophobic cetyltrimethylammonium ion (cetrimide) were used in the high performance liquid chromatography of chloride, nitrate and sulphate contained in potable water. Indirect detection of analyte anions was achieved with an ultraviolet detector. The breakthrough volume of the anion-exchange column was measured with aqueous sodium salicylate (1mM). Retention times of analyte anions in an artificial mixture were longer when aqueous sodium salicylate (1mM) containing acetonitrile (5%) was used as the mobile phase.

13.1.1.2 Chloride, bromide, iodide, nitrate and thiocyanate

High performance liquid chromatography with a variable, wavelength ultraviolet detector is a sensitive and precise method for the simultaneous measurement of chlorides, bromides, iodides, nitrates and thiocyanates in non saline water samples. Stetzenbach and Thompson [2] applied the

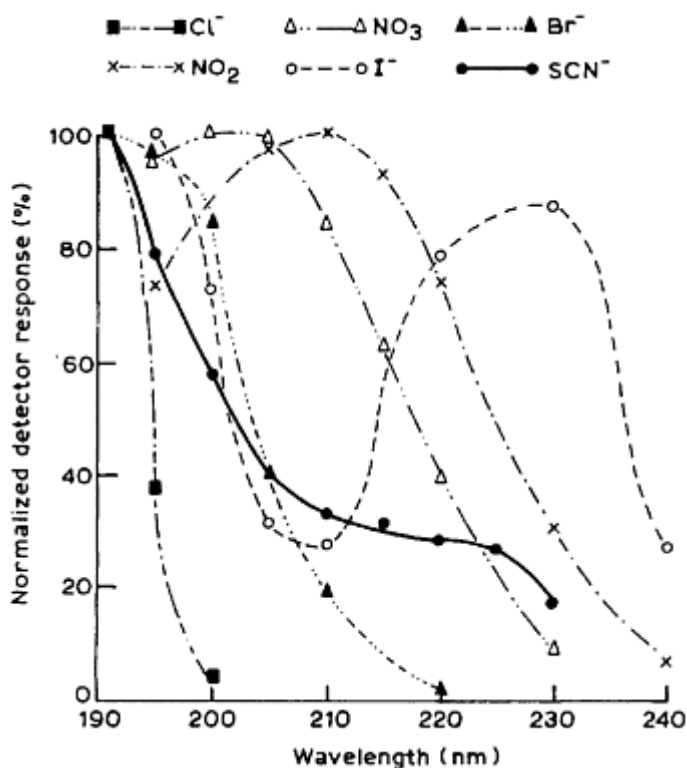


Fig. 13.1 Normalised detector response versus wavelength for Br^- , Cl^- , NO_2^- , NO_3^- and SCN^- showing the optimum absorption wavelengths
Source: Reproduced with permission from Groundwater Publishing Co., Dublin, US [2]

method employing anion-exchange columns to ground water samples achieving detection limits of $50\mu\text{g L}^{-1}$ for these ions.

Thiocyanate, bromide, iodide, nitrate and nitrite have large enough extinction coefficients at 194–215nm to make ultraviolet absorption detection useful for trace analysis at these wavelengths. An eluant of phosphate buffer prepared with high performance liquid chromatography grade water has no significant background absorption to 190nm and could be used over the entire functional pH range of silica based stationary phases. The choice of a suitable wavelength is generally limited only by the purity of the eluant and the limits of the detector. Fig. 13.1 shows the area responses of a 10mg L^{-1} bromide sample at several wavelengths. Wavelengths longer than 220nm are not suitable for trace bromide analysis while those below 195nm show only marginal increases in sensitivity. Thiocyanate demonstrates a similar wavelength absorptivity relationship but its usable wavelengths limit extends to 235nm. The absorption spectrum for the remaining anions are also shown in Fig. 13.1. Fig. 13.2 shows the results of the analysis of a water sample containing chloride at

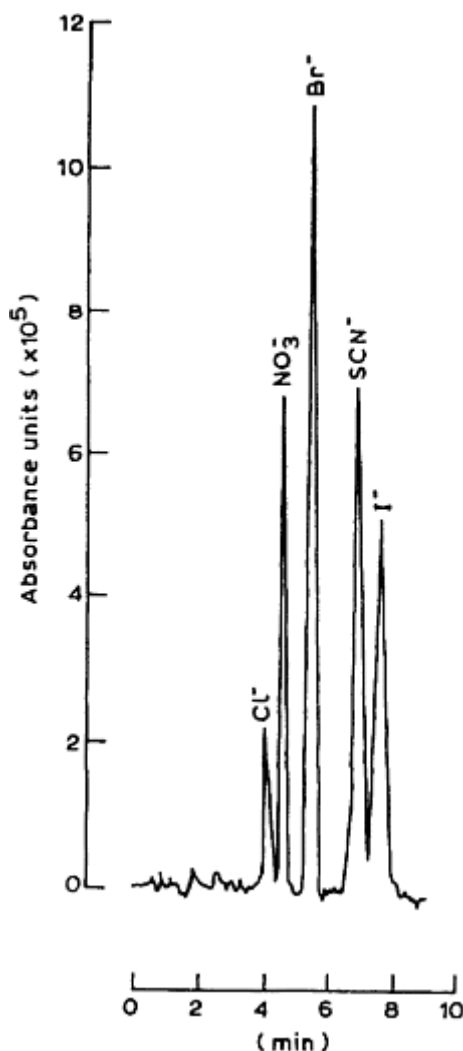


Fig. 13.2 Chromatogram of Cl⁻ at 4.4mg L⁻¹, NO₃⁻ at 0.85mg L⁻¹, Br⁻ at 0.73mg L⁻¹ and SCN⁻ at 0.88mg L⁻¹ in water; column Partisil 10 SAX 25cm, solvent 0.15 KH₂PO₄, detector Scheoffel UV 195nm, sample 50μL and flow 3.0ml min⁻¹

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4.4mg L⁻¹ and sub mg L⁻¹ concentrations of nitrate, bromide and iodide. These results indicate the sensitivity of the measurement method and the time required to analyse all five anions. The practical limit of detection is about 50mg L⁻¹ for all of the anions except chloride which is about 1mg L⁻¹.

Nitrite and nitrate are also easily separated and measured by this method. Fig. 13.3 shows these species measured in a surface water sample.

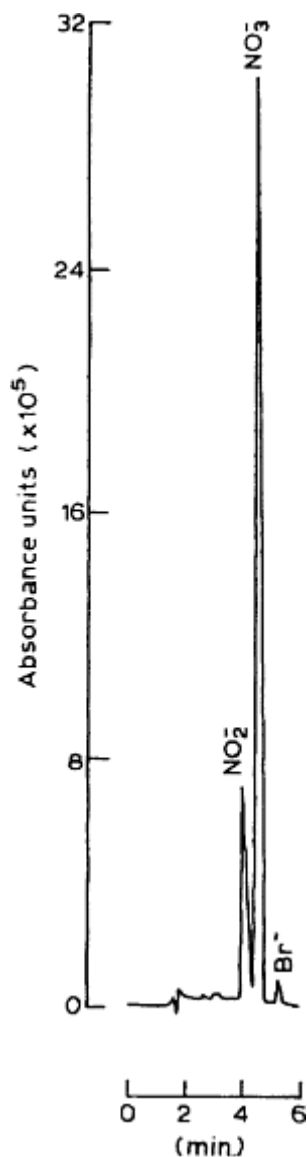


Fig. 13.3 Surface water from Safford, Arizona; column Partisil-10 SAX 25cm, solvent 0.1M KH_2PO_4 , 205nm, 5 μL sample, flow 3.0ml min⁻¹

Source: Reproduced with permission from Groundwater Publishing Co., Dublin, US [2]

13.1.1.3 Nitrite, nitrate, thiosulphate and iodide

Lee and Field [3] have discussed a technique of post column fluorescence detection of nitrite, nitrate, thiosulphate and iodide anions in high performance liquid chromatography. These anions reacted with cerium (IV) to produce fluorescent species in a post column packed bed reactor.

13.1.1.4 Nitrite, bromide, nitrate, sulphate, iodide and thiocyanate

Maki and Danielson [4] have described in indirect photometric chromatographic determination of these anions using sodium naphthalene trisulphonate. The detection limits were in the range 0.1–0.4ng absolute.

13.1.1.5 Fluoride, perchlorate, chloride, nitrite, phosphite, arsenate, nitrate, chlorate, sulphate, chromate, borofluoride, glycollate, acetate, lactate, propionate, aceto-acetate, hydroxybutyrate, chloroacetate, isobutyrate and butyrate

Rigas and Pietrzyk [5] studied ruthenium(II) complexes as ion interaction reagents for the liquid chromatographic separation and indirect fluorometric detection of these organic and inorganic anions. Ruthenium(II-1), 10-phenanthroline and ruthenium(II)-2,2'-bipyridine were used as mobile phase additives for the liquid analytes.

13.1.1.6 Palmitate, pyrenylpalmitate, lactate, propionate and formate

Nimura *et al.* [6] used 1-pyrenyldiazomethane as fluorescent labelling reagent for the liquid chromatographic determination of the above carboxylates. Excitation was carried out at 395nm and fluorescence measurements made at 340nm. Down to 20–30fmol of the above organic anions were determined.

13.1.1.7 Chlorate, chloride, bromide, iodate, bromate and iodide

Salov *et al.* [7] determined chlorate, also chloride, bromide, iodate, bromate and iodide in non saline waters by high performance liquid chromatography with an inductively coupled argon plasma mass spectrometric detector.

13.1.2 Potable waters

13.1.2.1 Chloride, bromide, iodide, chlorate, iodate and bromate

Salov *et al.* [7] have described a method for the determination of these anions in potable waters based on high performance liquid chromatography coupled with an inductively coupled argon plasma mass spectrometric detector.

13.1.3 Aqueous precipitation

13.1.3.1 Chloride, bromide, iodide, nitrate, nitrite and thiocyanate

The procedure described by Stetzenback and Thompson [2] discussed in section 13.1.1.2 has been applied to the determination of these anions in rainwater.

13.1.3.2 Nitrate and nitrite

Imanari *et al.* [8] describe a method for determining nitrate and nitrite in rainwater by separation with high performance liquid chromatography followed by electrochemical detection. The eluate from the column was passed through a reductor column which converted the nitrate to nitrite and the two peaks were then measured electrochemically. The recoveries were $99.7 \pm 2.6\%$ for nitrate and $100.5 \pm 3.0\%$ for nitrite. A similar technique for determining nitrate and nitrite in water was reported by Ishigami *et al.* [9].

13.1.3.3 Chloride, bromide and iodide

Moss and Stephen [10] determined chloride, bromide and iodide in rainwater by converting them to alkylmercury(II) halides and measurement by high performance liquid chromatography.

13.1.4 Trade effluents

13.1.4.1 Thiosulphate and polythionates

Takana *et al.* [11] used high performance liquid chromatography on an anion-exchange column with differential pulse polarographic detection to the determination of thiosulphate and tri-, tetra-, penta- and hexa-thionates in trade effluents. The method is accurate to within 10% at the $0.001\text{--}1\text{m}^M$ concentration range.

13.2 Ion exclusion chromatography

13.2.1 Non saline waters

13.2.1.1 Sulphide and sulphite

The ion chromatographic determination of weak acid anions is complicated by ion exclusion in the suppressor column, resulting in faster elution and sharper peaks, directly proportional to the degree of exhaustion of the suppressor column [12]. A 10mg L^{-1} nitrite standard showed a 37% increase in peak height over an 8h period when monitored

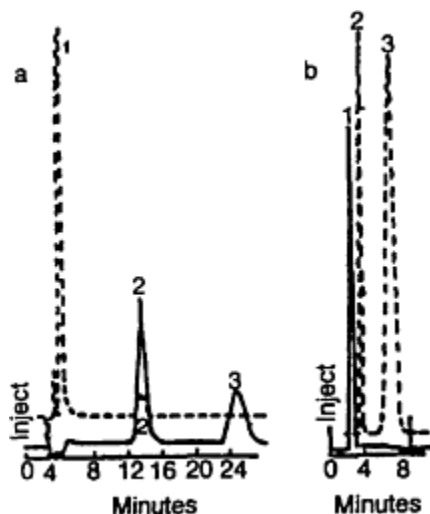


Fig. 13.4 Sulphide separator (a) ion chromatographic conditions conductivity detector (—), UV detector (---) at 215nm position 1; peak 1, $10\text{mg L}^{-1} \text{S}^{2-}$; peak 2, SO_3^{2-} ; peak 3, SO_4^{2-} ; (b) ion exclusion chromatographic conditions 4, conductivity detector (—), UV detector (---) at 192nm; position 1; peak 1, SO_3^{2-} and SO_4^{2-} ; peak 2, SO_3^{2-} ; peak 3, 15mg L^{-1}

Source: Reproduced with permission from Elsevier Science [12]

with the conductivity detector while on only a minor 2% increase in peak height was observed over the same time period by using the ultraviolet detector after the separator column.

The ultraviolet detector can also be used in some cases to resolve overlapping peaks. Determination of the nitrite peak by using the conductivity detector is complicated by both the ion exclusion effect and the incomplete resolution between the large chloride peak and the much smaller nitrite peak.

The ion exclusion interference can be eliminated for ultraviolet active anions by placing the ultraviolet detector between the separator and suppressor columns (position 1). In addition, the problem of overlapping peaks can sometimes be resolved spectrophotometrically by proper choice of wavelength.

Sulphide cannot be detected under normal ion chromatographic conditions. It is converted into hydrogen sulphide in the suppressor column. Hydrogen sulphide acid is a very weak acid that does not ionise sufficiently to be detected with the conductivity detector. The ultraviolet detector, however, is able to detect sulphide at low levels, as is illustrated in Fig. 13.4.

Since sulphide is a weak acid anion, the ultraviolet detector was placed between the separator and suppressor columns. Fig. 13.4 also shows the presence of sulphite and sulphate due to oxidation of the sulphide ion.

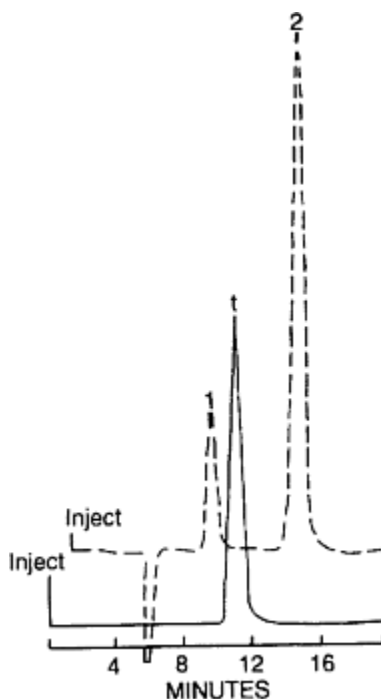


Fig. 13.5 Separation of arsenite and arsenate by ion exclusion chromatography; conductivity detector (—); UV (---) at 200nm, position 1; peak 1, 15mg L⁻¹ AsO₄²⁻; peak 2, 30mg L⁻¹ AsO₃²⁻
Source: Own files

Ion exclusion, besides being a source of chromatographic interference, can also be used to separate weak acids. Fig. 13.4 shows the separation of sulphide by ion exclusion chromatography using a strong cation exchange column and water as the eluent. Peak 1 is a combined peak resulting from both sulphite and sulphate, as monitored with the conductivity detector. Peaks 2 and 3 correspond to sulphite and sulphide respectively, as monitored using the ultraviolet detector. Since sulphide can be separated by either ion chromatography or ion exclusion chromatography, the choice of separation mode will depend on the sample matrix.

13.2.1.2 Arsenate and arsenite

Fig. 13.5 shows the separation of arsenite and arsenate by ion exclusion chromatography using 0.01mol L⁻¹ hydrochloric acid as the eluent. Arsenious acid is a very weak acid and cannot be detected at low levels by the conductivity detector. However, like sulphide, it is easily detected with the ultraviolet detector. The simultaneous determination of arsenite and arsenate is possible.

Arsenite can also be separated by ion chromatography using standard conditions. It

elutes early, near the carbonate dip. For these applications the ultraviolet detector should be placed between the separator and suppressor columns.

13.2.1.3 Phosphate, chloride, sulphate, condensed phosphates

Ion exclusion chromatography provides a convenient way to separate molecular acids from highly ionised substances. The separation column is packed with a cation exchange resin in the H^+ form so that salts are converted to the corresponding acid. Ionised acids pass rapidly through the column while molecular acids are held up to varying degrees. A conductivity detector is commonly used.

Tanaka *et al.* [12–14] have reported that the separation of phosphate from chloride, sulphate and several condensed phosphates $P_2O_7^{4-}$, $P_3O_{10}^{2-}$ and $P_3O_9^{3-}$ could be achieved by ion exclusion chromatography on a cation exchange resin in the H^+ form by elution with an acetone water and dioxan water mixture. As the separation mechanism of the ion exclusion chromatography by elution with water alone for numerous anions or their respective acids is based on the Donnan membrane equilibrium principle (ion exclusion effect) it is a highly useful technique for the separation of non-electrolytes such as carbonic acid from electrolytes such as hydrochloric acid and sulphuric acid [15]. Ion exclusion chromatography has also been coupled to ion chromatography to determine simultaneously both weak and strong acids [16]. The ion exclusion chromatography separation of orthophosphate from the strong acid anions by elution with organic solvent water described above is based on this ion exclusion effect and/or the partition effect between the cation exchange resin phase (water rich) and the mobile phase (organic solvent rich) owing to the hydration of the resin [12] and phosphate has been monitored as the corresponding acid (H_3PO_4) with a flow coulometric detector for the detection of H^+ ion and a conductometric detector.

13.2.1.4 Organic anions, tartrate, maleate, malonate, citrate, glycollate, formate and fumarate

Okada [17] employed a Redox suppressor in his ion exclusion chromatographic determination of tartrate, maleate, malonate, citrate, glycollate, formate and fumarate in non saline waters. A conductimetric detector was employed.

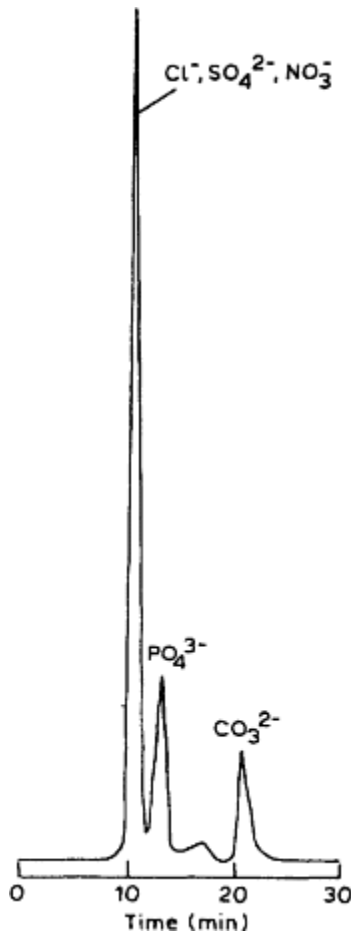


Fig. 13.6 Ion exclusion chromatogram of mixture of 10mg L^{-1} each of Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} and CO_3^{2-} obtained by elution with 60% acetone-water. Detected with FCD (100mV full scale)

Source: Reproduced with permission from Elsevier Science [11]

13.2.2 Waste waters

13.2.2.1 Chloride, sulphate, carbonate and phosphate

Tanaka and Ishizuka [11] have investigated the possibility of determining orthophosphate in waste waters by ion exclusion chromatography on a cation exchange resin in the H^+ form by elution with acetone water. They discuss optimal conditions for the separation of phosphate from chloride, sulphate, carbonate, etc. which are always present in waste water and sewage samples.

Fig. 13.6 shows the chromatogram of a mixture of 10mg L^{-1} of chloride sulphate, nitrate, phosphate and carbonate obtained with the flow colorimetric detector by elution with 60% acetone water. As can be seen from Fig. 13.6 phosphate could be separated from the strong acid anions and carbonate. The RS value between the strong acid anions and phosphate was about 1.7. This RS value suffices for the quantitation of phosphate by the peak area measurement with a computing integrator.

In Fig. 13.6 an unknown peak was observed between phosphate and carbonate. This peak was due to water in the sample solution introduced into the chromatograph. However, the peak did not interfere with the quantitation of phosphate.

13.3 Ion exchange chromatography

13.3.1 Non saline waters

13.3.1.1 Miscellaneous

Shintani and Dasgupta [18] have reported that post suppression membrane-based ion exchange chromatography with fluorescence detection permits detection limits superior to those obtained by conductivity detection in hydroxide eluent suppressed anion chromatography.

13.3.2 Aqueous precipitation

13.3.2.1 Chloride and bromide

Akaiwa *et al.* [19] have used ion exchange chromatography on hydrous zirconium oxide combined with a detection based on direct potentiometry with an ion selective electrode for the simultaneous determination of chloride and bromide in non saline waters (Table 13.1).

Table 13.1 Accuracy tests

Sample	Calibration curve method		Standard addition method	
	Br^- , $\mu\text{g L}^{-1}$	Cl^- , $\mu\text{g L}^{-1}$	Br^- , $\mu\text{g L}^{-1}$	Cl^- , $\mu\text{g L}^{-1}$
Pond water (Gunma Univ)	27	8.6	27	9.0
Pond water (Kozouji Park)	31	19.3	35	18.5
Tap water (NittaTown)	–	38.5	–	39.0
Tap water (Gunma Univ)	–	9.5	–	9.0

Source: Reproduced with permission from Elsevier Science [19]

13.4 Ion pairing chromatography

13.4.1 Non saline waters

Bidling Meyer *et al.* [20] have studied the ion pairing chromatographic determination of anions using an ultraviolet absorbing co-ion in the mobile

Bidling Meyer *et al.* [21] have also discussed the ion pair chromatographic determination of anions using an ultraviolet absorbing co-ion in the mobile phase. The separation and spectrophotometric determination of otherwise non-ultraviolet absorbing anions is possible. Spectrophotometric detection was comparable to conductimetric detection at nanogram levels for the eight anions investigated.

13.5 Micelle exclusion chromatography

13.5.1 Non saline waters

13.5.1.1 Thiocyanate, sulphite and sulphide

Gonzalez *et al.* [22] have applied micelle analysis in the kinetic multicomponent analysis for the simultaneous determination of thiocyanate, sulphite and sulphide in non saline waters. The method involved reaction of the anions with S,S' dithiobis(2-nitrobenzoic acid) in aqueous cetyltrimethyl ammonium bromide micelles. Cyanide, sulphide and sulphite were determined at concentrations, respectively, down to $0.5\text{--}1.5 \times 10^{-4}\text{M}$, $0.2\text{--}1 \times 10^{-4}\text{M}$ and $0.2\text{--}1.5 \times 10^{-3}\text{M}$ with a relative error of less than 5%.

13.5.1.2 Nitrite, nitrate, bromide, iodide and iodate

Okada [23] has applied micelle exclusion chromatography to the determination of nitrite, nitrate, bromide, iodide and iodate in non saline waters.

13.5.1.3 Thiosulphate, cyanide and thiocyanate

Jones [24] carried out a simultaneous separation of non-organic cations (eg calcium, potassium and sodium) and anions (eg nitrate, thiosulphate, cyanide and thiocyanate) by ion chromatography using a single column coated with weak/strong charged three walterionic bile salt micelles.

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Chapter 14

Multianion analysis, miscellaneous methods

14.1 Gas chromatography

14.1.1 Non saline waters

14.1.1.1 Carboxylic acids, malonate, hexabenzene carboxylate, octanoate, octandioate

Olsen *et al.* [1] determined carboxylic acids by isotope dilution gas chromatography Fourier transform infrared spectroscopy. The carboxylic acids were first converted to their methyl esters. Carboxylates studied include malonate, hexabenzene carboxylate, octanoate and octandioate.

14.1.1.2 Bromide and iodide

Bromide and iodide occur as trace elements in non saline waters in the concentration range 10^{-4} to 10^{-8} M.

For the selective and highly sensitive simultaneous determination of bromide and iodide Maros *et al.* [2] suggest a gas chromatographic separation combined with electron capture detection of the acetone derivatives. The method for iodide determination based on oxidation with iodate in the presence of acetone followed by an extraction of iodoacetone with n-hexane gives inaccurate results, especially if other reductive substances are present that reduce iodate to iodide or iodine. The quantitative oxidation of iodide and bromide in the presence of acetone to iodo- and bromoacetone can be performed by chromate and permanganate, without the interference of other reducing substances. Instead of n-hexane, benzene was found to be more convenient for the extraction of bromo- and iodoacetone from aqueous solutions, due to the significantly higher solubilities of these compounds in benzene. The sample preparation for the gas chromatographic analysis consists of the oxidation of bromide and iodide in the presence of acetone and of a single-step extraction of the derivatives with benzene.

In this method [2] oxidation of bromide and iodide ions in acidic solutions in the presence of acetone forms the corresponding acetone derivatives. Iodate was reduced with thiosulphate prior to the determination. After extraction with benzene the bromo- and iodoacetone were measured by gas chromatography using electron capture detection. The bromide and iodide contents of rainwater, drinking water, river water and sea water, were all determined. The relative standard deviations for bromide at 10^{-7} M and for iodide at 10^{-8} M concentration were 1.9% and 3% respectively, using a 10mL sample for the determination without preconcentration.

14.1.2 Aqueous precipitation

14.1.2.1 Nitrate, sulphate and phosphate

Faigle and Klockow [3] applied gas chromatography to the determination of traces of nitrate, sulphate and phosphate in rain water. The dissolved salts are freeze-dried and converted to the corresponding silver salts. These are then converted to *n*-butyl esters with the aid of *n*-butyl iodide, the *n*-butyl esters being determined by direct injection into a gas chromatographic column. Sulphate and phosphate may be determined simultaneously on a column containing 3% OV-17 on Chromosorb G, while nitrate is determined separately with 3% tri-*p*-cresylphosphate as the stationary phase on a similar support.

14.1.2.2 Chloride, bromide and iodide

Mack and Grimsrud [4] have described a photochemical modulated pulsed electron capture detector suitable for the gas chromatographic determination of chloride, bromide and iodide in rainwater.

14.1.3 Potable waters

14.1.3.1 Chloride, bromide and iodide

Bachmann and Matusca [5] have described a gas chromatographic method for the determination of $\mu\text{g L}^{-1}$ quantities of chloride, bromide and iodide in potable water. This method involves reaction of the halide with an acetone solution of 7-oxabicyclo-(4.1.0) heptane in the presence of nitric acid to form halogenated derivatives of cyclohexanol and cyclohexanol nitrate. The composition of the reagent is 1% 0.1N nitric acid 7-oxabicyclo-(4.1.0) heptane, 25% water, 75% acetone. The column effluent passes through a pyrolysis chamber at 800°C and then through a conductivity detector. The solution is injected onto a gas chromatographic column (OV-10-Chromosorb W-HPI 80–100 mesh), 150cm long, 0.2cm diameter, operated at 50°C Hydrogen is used as carrier gas. Chloride contents determined by this method were $5.0 \pm 1.5 \mu\text{g L}^{-1}$ in potable water.

Grandet *et al.* [6] have described a method for the determination of traces of bromide (and iodide) in potable water which permits determination of $50 \mu\text{g bromide L}^{-1}$ and $5 \mu\text{g iodide L}^{-1}$ without preconcentration of the sample, or $0.5 \mu\text{g bromide L}^{-1}$ and $0.2 \mu\text{g iodide L}^{-1}$ after preconcentration. The method is based on the transformation of the halides into 2-bromo- or 2-iodo-ethanol. These derivatives are extracted with ethyl acetate and determined with an electron capture detector. The difference in the retention periods enables both halides to be determined simultaneously in one sample. The method is substantially free of interferences and is suitable for use on many types of water.

14.2 Spectrophotometric methods

14.2.1 Non saline waters

14.2.1.1 Phosphate, nitrate and nitrite

Skjemstad and Reeve [7] have reported three automated procedures for the simultaneous determination of phosphate, ammonia and nitrate plus nitrite at $\mu\text{g L}^{-1}$ levels in non saline waters. Phosphate is estimated by reaction with molybdate and reduction to molybdenum blue with ferrous ammonium sulphate. Ammonia is determined by the salicylate/ dichloroisocyanurate reaction in the presence of nitroprusside after in-line distillation. Nitrate plus nitrite is estimated by using an in-line copperised cadmium reductor, diazotising the nitrite with sulphanilamide and coupling with *N*-1-naphthylethylenediamine. Mercuric chloride used as a preservative does not interfere in these procedures.

14.2.2 Potable water

14.2.2.1 Phosphate and arsenate

Matsubara *et al.* [8] determined trace amounts of phosphate and arsenate in potable water by Spectrophotometric detection at 627nm of their heteropoly acid-malachite green aggregates following preconcentration by nitrocellulase membrane filtration.

14.2.3 Waste waters

14.2.3.1 Chlorite, nitrite and nitrate

Canelli [9] has described an autoanalyser-based procedure for the simultaneous determination of chlorite (and nitrite and nitrate) in waste water.

14.2.3.2 Thiocyanate, cyanate and cyanide

Luthy *et al.* [10] have described a spectrophotometric method for the determination of thiocyanate and cyanide in coal gasification waste waters. They showed that the copper pyridine method with pre-extraction was applicable but that high concentrations of carbonate and sulphide must first be removed from the sample.

Botto *et al.* [11] used *p*-phenylenediamine as the chromogenic reagent in the spectrophotometric determination of thiocyanate and uncomplexed cyanide in waste water.

14.2.3.3 Sulphide, sulphite and sulphate

Bhat *et al.* [12] reported methods for the determination of low levels of sulphides, sulphites and sulphates in waste waters. The method for sulphite and sulphide involves the reduction of the bis-2, 9-dimethyl-1-10-phenanthroline copper(II) ion by sulphide in the presence of formaldehyde and by sulphite in its absence. In the method for sulphate, stannous chloride in hydrochloric acid is used to reduce sulphate ions to hydrogen sulphide which is reacted with bis-2, 9-dimethyl-1-10-phenanthroline copper(II) ion.

All analyses are completed by measuring the absorbances due to the coloured copper(I) complex formed by chemical reduction. While the methods are less than ideal from the point of view of sensitivity, simplicity and freedom from interferences, the colours formed are stable and the sulphate reduction system can be used repeatedly.

14.3 Titration methods

14.3.1 Potable water

14.3.1.1 Chlorite, hypochlorite and chlorate

Oxidising agents such as chlorine and hypochlorite ion are widely used in drinking water disinfection [13,14] in the United States. Recently, chlorate ion and possibly chlorite ion have been suggested to exist in drinking water at measurable levels when hypochlorite ion is used as the sole chlorinating agent. Chlorite and chlorate ions may be a potential health hazard, and their low-level toxicity is controversial. The US EPA is considering regulating [15,16] the amount of chlorite and chlorate permitted in drinking water. The most likely source of [17,18] these ions is the decomposition of concentrated aqueous sodium hypochlorite stock solutions or solid calcium hypochlorite during storage before being applied as the disinfectant. Thus, an analytical methodology is needed for the direct and selective determination of hypochlorite, chlorite and chlorate in concentrated sodium hypochlorite or $\text{Ca}(\text{OCl})_2$ solutions.

In solution chloride and hypochlorite have similar reactivities, and both ions react with the reagents typically used for their determination, such as iodide and thiosulphate. The various difficulties of other methods used to analyse solutions containing chloride and hypochlorate have been summarised [19]. Freshly produced concentrated solutions of commercial grade sodium hypochlorite (ie 5–15wt% measured as chlorine) contain levels of chlorite and chlorate ions which range from 200 to 2000 times less than the concentration of hypochlorite. Due to this large concentration difference, the analysis of each ion is not straightforward. The primary objective of the work of Adam and Gordon [20] was to demonstrate a selective technique for the determination of hypochlorate at high concentration and chlorite and chlorate at low concentrations when these species are present in solution.

These workers [20] developed a selective potentiometric technique for the determination of hypochlorite at high concentration (eg 1–3M) and chlorite and chlorate

at comparatively low concentrations (eg 50–150mg L⁻¹) when these species are present together in solution. The method uses sulphite ion as a mask to selectively and quantitatively remove hypochlorite at pH 10.5. Thus hypochlorite is measured and masked at the same time. At pH 10.5, sulphite does not react with chlorite and chlorate. The remaining sulphite is quantitatively removed with triiodide ion. Following the masking procedure, the sequential determination of chlorite and chlorate is carried out either by iodometric titration at the appropriate pH or by ion chromatography. The results from the direct potentiometric titration using sulphite are compared to those of an indirect reference method.

Adam and Gordon [20] prepared high purity sodium hypochlorite by a previously described procedure [21,22].

Gordon [23] has described a procedure for the determination of down to 0.1mg L⁻¹ of chlorite and hypochlorite by a modified iodometric technique.

14.3.2 Trade effluents

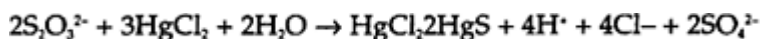
14.3.2.1 Thiosulphates and polythionates

Makhija and Hitchen [24] determined these anions in mining effluents by an acidimetric method. It involves sodium hydroxide titration of the acid liberated on addition of mercuric chloride (which oxidises thiosulphate and polythionates to sulphuric acid), after adjustment of the initial pH value to either 4.3 (using methyl orange) or 8.2 (using phenolphthalein).

In this method a suitable portion of the solution containing a polythionate having 3, 4 or 5 sulphur atoms is acidified to either pH 4.3 or pH 8.9 with 0.005N sulphuric acid and sodium hydroxide and mercuric chloride is added to release acid quantitatively. The stoichiometric equation is:



A similar equation applies for the thiosulphate:



In both cases the acid generated is titrated with standard sodium hydroxide solution to determine the sum of the concentration of the four sulphur anions: $S_2O_3^{2-}$; $S_3O_6^{2-}$; $S_4O_6^{2-}$; $S_5O_6^{2-}$.

14.3.2.2 Thiocyanates and cyanides

Atkinson *et al.* [25] have described a technique for titrating thiocyanate/ cyanide mixtures in hydrometallurgical effluents. The mixtures are titrated with silver nitrate solution using an automatic potentiometric titration with a silver/glass electrode pair. When thiocyanate is to be determined, cyanide is masked with formaldehyde.

Table 14.1 gives data for the potentiometric determination of thiocyanate in the presence and absence of cyanide. The cyanide added is without effect on the thiocyanate determination when it is masked by formalin.

14.4 Flow injection analysis

14.4.1 Non saline waters

14.4.1.1 Thiosulphate, sulphate, sulphide, polysulphide and sulphite

Sonne and Dasgupta [26] carried out a simultaneous photometric flow injection analysis of thiosulphate, sulphate, sulphide, polysulphide and sulphite.

14.4.1.2 Bromide, iodide and pseudohalides

Carlsson *et al.* [27] have described a flow injection spectrophotometric method for determining bromide and iodide in river waters with a detection limit of 15M for bromide.

Frenzel *et al.* [28] used flow injection analysis with electrochemical detection for determining halide and pseudohalide ions in non saline water, with a relative standard deviation of essentially 1.5%.

14.4.1.3 Silicate and phosphate

Linares *et al.* [29] discussed a flow injection analysis method for the simultaneous determination of silicate and phosphate, based on the

Table 14.1 Potentiometric determination of thiocyanate in the presence and absence of cyanide

An initial nitration volume of 1 35ml was used

Thiocyanate/mg		Cyanide present/mg	Absolute error/mg	Recovery, %
Taken	Found			
25.18	25.46	—	0.28	101.1
25.18	25.50	10.0	0.32	101.3
12.50	12.65	—	0.15	101.2
12.50	12.66	10.0	0.16	101.3
9.47	9.52	—	0.05	100.5
9.47	9.58	20.0	0.11	101.2

4.74	4.76	—	0.02	100.4
4.74	4.76	100.0	0.02	100.4
1.26	1.14	—	-0.12	90.5
1.26	1.13	50.0	-0.13	89.7
0.625	0.565	—	0.06	90.4
0.625	0.578	50.0	-0.047	92.2
0.252	0.241	—	0.0 11	85.6
0.252	0.249	100.0	0.003	98.8
0.125	0.121	—	-0.004	96.8
0.125	0.109	100.0	-0.016	87.2

Source: Reproduced with permission from the Royal Society of Chemistry [25]

formation rates of phosphate heteropolyacid being higher than that of the corresponding silicate acid. The heteropolyacid was detected by its oxidation of a buffered solution of thiamine to trichrome which was measured fluorometrically. The apparatus configuration allowed two measurements at different times on each injected sample. The analytical range was 30–600 µg L⁻¹ in ratios 1:10 and 10:1 phosphate:silicate. Phosphate and sulphide interfered with the determination of silicate when in similar concentrations to the analyte. Hypochlorous acid and iodide were tolerated in 5:1 and 15:1 ratio to silicate. Arsenite and sulphite were tolerated in 50:1 ratio to analyte. Sulphide and copper(II) interfered with the determination of phosphate when present in similar concentrations to the analyte. Iron(II) and iron(III) were tolerated in 1:1 ratio and hypochlorite and carbonate in 25:1 ratio. Up to 60 samples per hour could be analysed.

14.4.1.4 Sulphate, silicate, cyanide, sulphide, chloride, nitrite, nitrate, phosphate and alkalinity

Van Staden [30] reviewed flow injection analysis methods for the determination of sulphate, sulphide, chloride, residual chlorine, nitrite, nitrate, phosphate, silicate, cyanide and alkalinity in water and waste water. Sampling rate, concentration range, precision, sample volume, chemistry, manifold technique and detection methods are summarised for each procedure.

14.4.1.5 Arsenate, arsenite and phosphate

The influence of the chemical form of a given compound on its toxicity has a representative example in arsenic; thus, As(III) is more toxic than As(V), the latter exhibiting higher toxicity as arsenate than as monomethylarsonic acid (and this, in turn, exhibiting higher toxicity than dimethylarsonic acid). This tradition of toxicity accounts for the interest in the speciation of these compounds; there are some conventional methods for speciation of arsenic in the literature (eg that based on its selective

transformation into hydride and subsequent measurement by atomic absorption spectrometry).

The simultaneous presence of arsenic, generally as arsenate and phosphate in non saline water (the arsenate/phosphate ratio being usually high) has given rise to the development of manual conventional methods for determination of these species with or without a prior separation process. The reaction on which these determinations are based is in most cases the formation of a heteropolyacid with molybdate, with photometric detection of Mo(V), molybdenum blue, generated with the aid of a suitable reductant, or voltammetric detection, taking advantage in this case of the modification of the redox potential of Mo(VI) caused by the formation of the heteropoly acid.

Flow injection analysis has proved to be a suitable technique for speciation as well as for simultaneous determinations; however, it has found very limited use for the determination of phosphate and arsenate (voltammetric detection), but not for the resolution of ternary mixtures of this type or for arsenic speciation.

Linares *et al.* [31] have suggested several photometric flow injection methods for arsenic speciation (as AsO_2^- and arsenate) and resolution of binary (arsenate-phosphate) and ternary (AsO_2^- -arsenate-phosphate) mixtures based on heteropoly acid formation and on the use of a simple flow injection configuration which, by means of a selective valve, allows fixing the most suitable conditions to this end.

In this method [31] the presence of a selecting valve in the flow injection analysis system allows obtaining a suitable medium for the indicator reaction to develop with one, two, or the three species of the mixture. The methods are simple and reliable and cover wide ratio ranges for mixture resolution, and the errors encountered in their application to real samples are relatively small.

14.4.1.6 Sulphate, orthophosphate and triphosphate

Coetzee and Gardner [32] have described a method for the determination of these anions by flow injection analysis with a lead(II) ion selective electrode as a detector.

The system was optimised for the determination of sulphate ion over the concentration range of 1–1000 mg L^{-1} . This entire range is accessible with a single reagent solution of 10^{-5}M lead perchlorate in ethanol, which is mixed with an aqueous carrier stream, making the method particularly useful for samples containing a wide range of sulphate concentrations. The maximum sampling rate is a function of sulphate concentration; for 100 ppm sulphate, the rate is 20 samples/h. Main interferences are such multicharged anions as phosphates. The same flow system, but with an aqueous rather than ethanolic reagent, was used for the determination of orthophosphate and triphosphate ions. While calibration curves tended to be non-linear for these ions, reproducibility was adequate for many analytical purposes.

One objective of this work was to study the applicability of ion selective electrodes as detectors in flow injection analysis, particularly when potentially complicating factors, such as precipitate formation, are present. The lead(II) ion selective electrode was chosen for this purpose because many anions form sufficiently insoluble lead(II) salts to allow their determination with lead ion. Examples of solubility products (as pK_{sp}) are as follows: SO_4^{2-} , 7.79; CrO_4^{2-} , 12.55; PO_4^{3-} , 43.5 (38°C); $\text{Fe}(\text{CN})_6^{4-}$, 18.02; and MoO_4

²⁻, 13.0 (uncertain). In addition, lead(II) ion forms moderately stable complexes with such anions as $\text{P}_2\text{O}_7^{4-}$ ($\log \beta_1 = 7.3$ at $I = 1\text{M}$) and $\text{C}_2\text{O}_4^{2-}$ ($\log \beta_1 = 6.54$ at 25°C).

A second objective of this work was to explore the potentialities of solvent optimisation in flow injection analysis. In principle, the determination of such anions as sulphate that form only moderately insoluble lead salts can be improved by judicious addition of a cosolvent in order to lower the solubility. In fact, this has been done frequently in classical gravimetric and volumetric determinations. It is necessary, however, to address potential complications introduced by cosolvent addition, such as inadequate electrode response or undesirable precipitation or complexation of analyte or reagent ions with other substances that may be present in actual samples.

Flow injection analysis is rapidly developing into a powerful analytical tool with many merits, such as broad scope, rapid sample throughput, and benefits accruing from controlled dispersion. In such applications ion selective electrodes have been used in a variety of ways, eg in direct sensing of analyte ion activities, in sensing the activities of reagent ions after reaction with analytes, or in enzyme-catalysed reactions producing ions that can be sensed with ion selective electrodes.

In the above work, Coetzee and Gardner [32] developed a simple flow injection analysis system with lead(II) ion as reagent. They studied its applicability to the determination of sulphate ion over a wide concentration range with high sample throughput and made exploratory measurements with orthophosphate and triphosphate ions as well.

14.4.2 Aqueous precipitation

14.4.2.1 Chloride, nitrate, bromide and phosphate

Flow injection analysis has been applied to the determination rain water of chloride, nitrite, nitrate and phosphate [33,34].

14.5 Continuous flow analysis

14.5.1 Aqueous precipitation

14.5.1.1 Nitrate, chloride, sulphate and phosphate

A computer controlled multichannel continuous flow analysis system has been applied to the measurement of nitrate, chloride and ammonium ions in small samples of rainwater [34]. Continuous flow methods (flow injection analysis and continuous flow analysis) have been used [33] to determine the principal constituents of rain water. While the two methods are similar they differ in certain important respects, such as the rate of flow, presence of air bubbles, diameter of the tubes and the reactions which are permissible within the retention period limits set by the physical constraints. They were applied to selected determinands (alkalinity, chloride, nitrite, nitrate, phosphate, sulphate,

ammonium, alkali metals and alkaline earth metals).

Reijnders *et al.* [33] have also used this technique to determine chloride, nitrate sulphate and phosphate in rainwater.

14.6 Column coupling isotachoelectrophoresis

14.6.1 Non saline waters

14.6.1.1 Chloride, fluoride, nitrite, nitrate, sulphate and phosphate

At present, ion chromatography has a dominant position among the separation methods used for the analysis of inorganic anions [35–38]. However, when the separation efficiencies typically achieved by ion chromatography are compared to characterising capillary zone electrophoresis for analysis of a group of analytes, it is apparent that the latter technique has advantages. As the effective mobilities of inorganic anions are sufficiently due to differences in their ionic mobilities they can be influenced in a desired way via appropriately selecting (differences in pK, values) and/or via the use of suitable additives [39], the selectivity factors [40] are also favourable leading to rapid resolutions of the analytes by capillary zone electrophoresis.

Although in some instances it is possible to determine low concentrations of inorganic anions by capillary zone electrophoresis [41], problems arise when the concentrations of the sample constituents vary considerably. This is due to the fact that the determination of microconstituents may require the sample load to have an impact on both the migration velocities and the resolution of analytes [42]. The use of indirect detection, as preferred in the case of inorganic anions [41,43] is also less capable of achieving adequate load capacities.

Of the inorganic anions which are currently monitored chloride, sulphate, and in many instances also nitrate, are considered anionic macroconstituents. These are often accompanied by nitrite, fluoride, and phosphate present in samples at 10^2 – 10^5 -fold lower concentrations. Such a concentration span probably cannot be covered by capillary zone electrophoresis.

This technique offers very similar advantages to ion chromatography in the determination of anions in water, namely multiple ion analysis, little or no sample pretreatment, speed, sensitivity and automation. Very similar advantages are offered by capillary isotachophoresis [44,45]. However, with the exception of the work by Bocek *et al.* [46] in which the determinations of chloride and sulphate in mineral water were demonstrated, little attention has been paid to this subject.

Zelenski *et al.* [47] applied the technique to the determination of 0.02–0.1 mg L⁻¹ quantities of chloride, nitrate, sulphate, nitrite, fluoride and phosphate in river water. Approximately 25 min was required for a full analysis. These workers used a column coupling technique which, by dividing the analysis into two stages, enables a high load capacity and a low detection limit to be achieved simultaneously without an appreciable increase in the analysis time.

The separation unit of the home made capillary isotachophoresis instrument used is

shown in Fig. 14.1. A 0.85mm id capillary tube made of fluorinated ethylene propylene copolymer was used in the pre-separation (first) stage and a capillary tube of 0.30mm id made of the same material served for the separation in the second stage. Both tubes were provided with conductivity detection cells [48] and an ac conductivity mode of detection [44] was used for making the separations visible. The driving current was supplied by a unit enabling independent currents to be pre-selected for the pre-separation and final analytical stages. The run of the analyser was controlled by a programmable timing and control unit. The zone lengths from the conductivity detector, evaluated electronically, were printed on a line printer.

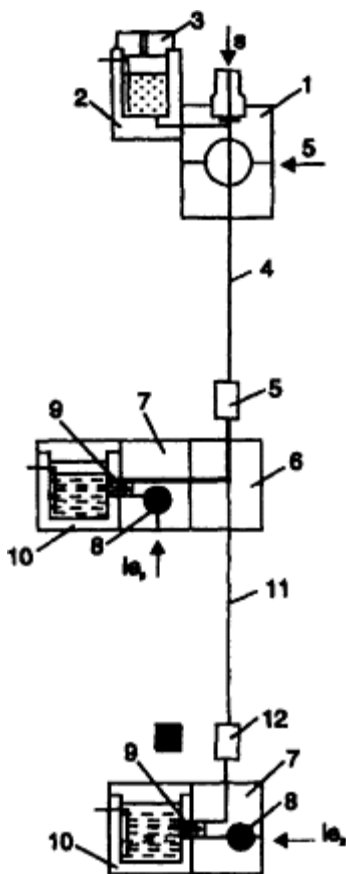


Fig. 14.1 Separation unit in a column coupling configuration as used for the analysis of anions in river water: 1, sampling block with a 30µL sampling valve; 2, terminating electrolyte compartment with a cap (3); 4, 0.85mm id capillary tube (pre-separation column); 5 and 12, conductivity detectors; 6, bifurcation block; 7, refilling block with needle valve (8); 9, mechanically supported membranes; 10, leading electrolyte compartments; 11, 0.30mm id capillary tube; s, positions

for the sample introduction (valve or microsyringe); lep and le, positions for refilling of the columns used for the first and second stages respectively

Source: Reproduced with permission from Elsevier Science [47]

The use of a column coupling configuration of the separation unit provides the possibility of applying a sequence of two leading electrolytes in one analytical run. Therefore, the choice of optimum separation conditions can be advantageously divided into two steps:

- (1) the choice of a leading electrolyte suitable for the separation and quantitation of the macroconstituents in the first stage (pre-separation column) simultaneously having a retarding effect on the effective mobilities of micro constituents (nitrite, fluoride, phosphate); and
- (2) the choice of the leading electrolyte for the second stage in which only micro constituents are separated and quantified (macro constituents were removed from the analytical system after their evaluation in the first stage).

To satisfy the requirements for the properties of the leading electrolyte applied in the first stage and, consequently, to decide its composition, two facts had to be taken into account, ie the pH value of the leading electrolyte needs to be around 4 or less (retardation of nitrite relative to the macro constituents in this stage) and at the same time the separations of the macro constituents need to be optimised by other means than adjusting the pH of the leading electrolyte (anions of strong acids). For the latter reason, complex equilibria and differentiation of anions through the charge number of the counter ions were tested at a low pH as a means of optimising the separation conditions for chloride, nitrate and sulphate in the presence of nitrite, fluoride and phosphate.

The retardation of chloride and sulphate through complex formation with cadmium enabling the separation of anions of interest [45] to be carried out, was found to be unsuitable, as the high concentration of cadmium ions necessary to achieve the desired effect led to the loss of fluoride and phosphate (probably owing to precipitation).

Similarly, the use of calcium and magnesium as complexing co-counter ions [49] to decrease the effective mobility of sulphate was found to be ineffective as a very strong retardation of fluoride occurred.

Better results were achieved when a divalent organic cation was used as a co-counter ion in the leading electrolyte [50,51] employed in the first separation stage when, simultaneously, the pH of the leading electrolyte was 4 or less, and the steady state configuration of the constituents to be separated was chloride, nitrate, sulphate, nitrite, fluoride and phosphate. The detailed composition of the operational system of this type used for quantitative analysis is given in Table 14.2 (system No. 1.)

The choice of the leading electrolyte for the second stage, in which the microconstituents were finally separated and quantitatively evaluated, was straightforward: a low concentration of the leading constituent (low detection limit) and a low pH of the leading electrolyte (separation according to pK values). The operational system used throughout this work in the second stage is given in Table 14.2.

An isotachopherogram from the analysis of a model mixture of anions obtained in the first separation stage is shown in Fig. 14.2. This isotachopherogram merely indicates the

differences in the effective mobilities of the anions of interest, as the concentration of nitrite, fluoride and phosphate in river water are usually too low to be detected in the first stage.

Both the cross sectional area of the capillary tube and the concentration of the leading constituent used in the second stage were optimised with

Table 14.2 Operational systems

System No.	Parameter	Leading electrolytes		
		1st stage	2nd stage	Terminating electrolyte
1	Anion	Cl ⁻	Cl ⁻	CITR ^b
	Concentration (mmol L ⁻¹)	8	1	2
	Counter ion	BALA ^a	BALA ^a	H ⁺
	Co-counter ion	BTP ^c	—	—
	Concentration (mmol L ⁻¹)	3	—	—
	Additive to the leading electrolyte	0.1%HEC ^d	0.1%HEC ^d	—
	pH	3.55	3.55	ca.3
2	Anion	Cl ⁻	Cl ⁻	CITR ^b
	Concentration (mmol L ⁻¹)	1	1	1
	Counter ion	H ⁺	H ⁺	H ⁺
	Additive to the leading electrolyte	electrolyte	0.1%HEC ^d	0.1%HEC ^d
	pH	3.0	3.0	ca.3

^aβ-alanine

^bCitric acid

^cAbbreviations: BALA=β-alanine; CITR=citric acid; BTP=aminopropane, 1, 3-bis-tris(hydroxy-methyl)methyl-aminopropane

^dHEC=Hydroxyethylcellulose

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respect to the determinations of micro constituents. In a search for optimal separating conditions, operational system No.2 (Table 14.2) was used for the determinations of microconstituents.

As only anionic constituents of relatively strong acids can achieve the effective mobilities within the chloride phosphate mobility interval at low pH, the number of possible interfering constituents (eg organic anions associated with biological processes in water) is also reduced using the proposed operational systems.

Some typical results obtained by applying the isotachophoretic technique to river water samples are shown in Tables 14.3 and 14.4.

These results serve as an illustration of the degree of agreement of the quantitative analyses obtained by this technique and classical methods. In several instances the agreement of the results is good. However, large differences found for some sample constituents (especially macro constituents) must be ascribed to a lower accuracy of the classical methods, as is clear from the analyses of model mixtures summarised in Table 14.5.

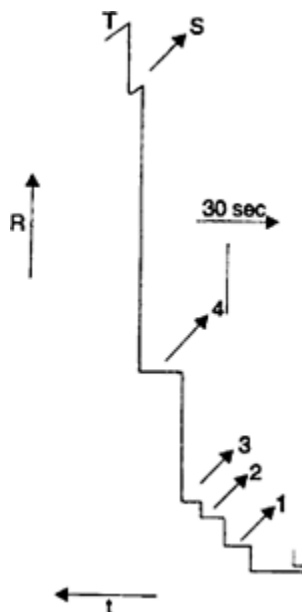


Fig. 14.2 Isotachopherogram for the separation of anions in the first stage using operational system No. 1:1, nitrate (40mg L^{-1}); 2, sulphate (20mg L^{-1}); 3, nitrite (20mg L^{-1}); 4, fluoride (20mg L^{-1}); 5, phosphate (20mg L^{-1}). Driving current $250\mu\text{A}$. L and T= leading and terminating anions, respectively; R=increasing resistance, t=increasing time. The sample was introduced with the aid of a $30\mu\text{L}$ valve

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Table 14.3 Determinations of inorganic anionic macro constituents present in river water

Sample No.	Sulphate (mg L^{-1})		Nitrate (mg L^{-1})		Chloride (mg L^{-1})	
	ITP	Titrimetry ^a	IPT	Spectro-photometry ^b	ITP	Titrimetry ^c
1	36.6	41.6	13.2	11.7	18.9	31.2
2	40.8	34.4	13.6	12.3	23.0	33.2

3	38.9	42.5	13.3	11.3	20.6	33.2
4	57.6	56.9	13.3	9.0	26.3	39.2
5	50.9	54.4	12.4	10.3	22.2	35.5
6	43.7	55.2	13.3	9.4	22.8	34.6

^aThe procedure described in [51]

^bFor details, see [52]

^cMercurimetric determination [52]

The relative standard deviations for ITP determinations were better than 2% whereas for the classical methods they varied within the range 2–15%.

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Table 14.4 Determination of inorganic anionic micro constituents present in river water

Sample No. ^a	Nitrite (mg L ⁻¹)		Fluoride by ITP (mg/L) ^c mg L ⁻¹	Phosphate (mg L ⁻¹)	
	ITP	Spectro-photometry ^b		ITP	Spectro-photometry ^d
1	0.25	0.13	0.17	0.61	0.55
2	0.29	0.13	0.18	0.56	0.5 1
3	0.33	0.11	0.18	0.49	0.44
4	0.33	0.16	0.14	0.23	0.16
5	0.33	0.16	0.13	0.27	0.22
6	0.22	0.13	0.10	0.34	0.27

^aSamples as in Table 14.3

^bThe procedure described in [51]

^cNot determined by a classical method as only a very labour-consuming distillation method [51] was available

^dFor details see [52]

The relative standard deviations for both ITP and classical were typically 5% or less

Source: Reproduced with permission from Elsevier Science [47]

Kaniansky *et al.* [53] have also reported on a method for the determination of nitrate, sulphate, nitrite, fluoride and phosphate by capillary zone electrophoresis coupled with capillary isotachoelectrophoresis in the column coupling configuration. Such distributions of these anions are typical for many environmental matrices, and it is shown that capillary isotachophoresis-capillary zone electrophoresis tandem enables the capillary isotachoelectrophoresis determination of the macroconstituents, while capillary isotachophoresis-preconcentrated microconstituents cleaned up from the macroconstituents can be determined by capillary zone electrophoresis with a conductivity detector. This approach was effective when the concentration ratio of macro-microconstituents was less than $(2-3) \times 10^4$. The limits of detection achieved for

the microconstituents (200, 300 and 600 ppt for nitrite, fluoride and phosphate, respectively) enabled their determinations at low parts per billion concentrations in instances when the concentrations of sulphate or chloride in the samples were higher than 1000 ppm. Although in such situations the load capacity of the capillary isotachophoresis column was not sufficient to provide the quantitations of the macroconstituents, the capillary isotachophoresis sample cleanup enabled the capillary zone electrophoresis determinations of the microconstituents present in the samples at 10^5 – 10^6 -fold lower concentrations. Experiments with samples of such extreme compositions showed that anionic impurities from the capillary isotachophoresis electrolyte solutions transferred together with

Table 14.5 Determinations of anionic macro constituents present in model mixtures

Sample	Sulphate (mg L ⁻¹)			Nitrate (mg L ⁻¹)			Chloride (mg L ⁻¹)			
	Taken	UP	Titrimetry	Taken	ITP		Spectro- photometry	Taken	ITP	Titrimetry
A	40.0	49.7	32.7	14.0	14.4		14.3	25.0	25.4	29.9
B	100.0	100.5	103.7	30.0	30.2		24.2	50.0	49.8	47.5
C	150.0	149.6	–	45.0	a		44.0	75.0	a	83.7

^aMixed zone of nitrate and chloride for the column used

For further details see notes in Table 14.4 and the text

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the analytes into the capillary zone electrophoresis column are probably the main hindrances in extending this dynamic concentration range by decreasing the limits of the detection to a level associated with the noise characteristics of the conductivity detector.

14.6.2 Aqueous precipitation

14.6.2.1 Chloride and fluoride

Zelenski *et al.* [47] applied column coupling capillary isotachoelectro-phoresis to the determination of chloride and fluoride in rainwater.

14.7 X-ray fluorescence spectroscopy

14.7.1 *Aqueous precipitation*

14.7.1.1 Chloride, bromide and iodide

Yamamoto [54] determined chloride, bromide and iodide in snow by X-ray fluorescence spectrometry after precipitation of their silver salts using silver nitrate. The colloidal silver halides formed were collected on a 0.45 μm filter paper and dried at room temperature. Limits of detection were 0.2 μg for chloride, 0.1 μg for bromide and 0.5 μg for iodide, and the relative standard deviation ($n=5$) was less than 5.0% for 10–80 μg of the chloride and bromide and was 8.2% for 10 μg of the iodide. There were interferences in the presence of ions which can exist in rainwater.

14.8 Anodic stripping voltammetry

14.8.1 *Waste waters*

14.8.1.1 Thiosulphate

Differential pulse anodic stripping voltammetry has been used [55] to detect thiosulphate, a potential substrate for sulphuric acid forming thiobacilli. The method was selective for thiosulphate in the presence of hydrogen sulphide, sulphite, polysulphide and elemental sulphur. Reproducible results were obtained for thiosulphate concentrations of 5 mg L^{-1} to 3 mg L^{-1} .

14.9 Cathodic stripping voltammetry

14.9.1 *Non saline waters*

14.9.1.1 Bromide and chloride

Bromide and chloride have been determined simultaneously in non saline waters [56] by cathodic stripping voltammetry with a mercury-coated platinum wire as the working electrode, a mercury/mercuric sulphate reference electrode, a platinum plate as the auxiliary electrode, and perchloric acid as the supporting electrolyte. Bromide was determined by using the peak at -0.1V and the sum of bromide and chloride was determined by using the peak at 0.0V . The relative standard deviation of the method was less than 10%, and the limit of detection for bromide was $0.4\mu\text{g mL}^{-1}$ and for chloride was $0.43\mu\text{g mL}^{-1}$.

14.9.1.2 Iodide and iodate

Cathodic stripping square wave voltammetry has been used to monitor vertical profiles of iodide, iodate and free iodine in non saline waters periodically during the course of a year [57].

14.10 Polarography

14.1 0.1 Non saline waters

14.10.1.1 Iodide and iodate

Differential pulse polarography has been used [57] to monitor vertical profiles of iodide, iodate and free iodine in non saline waters periodically during the course of a year.

14.10.2 Potable waters

14.10.2.1 Nitrate, perchlorate and iodide

Marecek *et al.* [58] investigated the feasibility of using a hanging drop electrode for the determination of nitrate, perchlorate and iodide in potable water. A three-electrode system was used with a polarographic analyser. The potential range of the method was increased by using crystal violet dicarbollylcobalate electrolyte in the nitrobenzene phase and magnesium sulphate in the aqueous phase, with a lead/lead sulphate reference electrode.

14.11 Ion selective electrodes

14.1 1.1 Mineral waters

14.11.1.1 Sulphide and cyanide

Jovanovic and Jovanovic [59] have described a method for the determination of sulphide and cyanide in spa water using a deposited on wire silver-silver sulphide ion selective electrode.

14.11.2 Waste waters

14.11.2.1 Thiosulphate, sulphide, sulphite, sulphate and polysulphide

Sulphide, thiosulphate, sulphite, sulphate and polysulphide have been determined in

paper mill waste waters [60] using a sulphide ion selective electrode. The electrode is used as an indicator electrode in potentiometric titration with mercuric chloride. In 0.1N sodium hydroxide medium, sulphide and polysulphides are titrated to form mercuric sulphide (and HgSx). Mercuric ions, thiosulphate and sulphite can also be converted into thiosulphate and can be titrated; sulphite can be decomposed with formaldehyde and so thiosulphate can be titrated alone.

14.12 Miscellaneous anions

14.12.1 Non saline waters

Keundler and Reich [61] have characterised electrolyte systems for the isotachopheresis of anions by cluster analysis. The leading electrolyte system with a pH of 3 and one with a pH between 6 and 10 were found, based on hierarchical and a non-hierarchical clustering procedure, to be the most favourable binary combination for anion identification purposes. Ternary combinations were also selected. Other systems studied do not increase the identification power.

Jackson and Haddad [41] have discussed the optimisation of injection techniques in the isotachoelectrophoresis of trace anions in non saline waters in amounts down to low ppb.

Hutta *et al.* [62] studied use of various solid phase adsorbents in the isotachoelectrophoresis of anions in non saline waters.

Preswell *et al.* [63] used capillary electrophoresis to determined sub ppm levels of anions in non saline waters.

Romano and Krol [64] demonstrated the separation of anions using capillary electrophoresis and showed that results obtained agreed well with those obtained by ion chromatography.

14.12.2 Aqueous precipitation

14.12.2.1 Chloride, fluoride, bromide, nitrate and sulphate

Slanina *et al.* [65] have discussed various methods for the determination of anions in rainwater. Methods discussed include ion selective electrodes (chloride, fluoride), neutron activation analysis (chloride, bromide), ultraviolet spectroscopy (nitrate [66]) and nephelometry (sulphate [67]).

14.12.2.2 Miscellaneous

Cox *et al.* [68] discuss the ion exchange treatment of complicated rain water samples prior to ion chromatographic analysis. Such treatment is often preferable to sample dilution as a means of reducing electrolyte concentration.

Cheam and Chau [69] have discussed the automated simultaneous analysis of anions and mono and divalent cations in rain water.

14.12.3 Surface waters

14.12.3.1 Sulphide, sulphite and thiosulphate

Various workers [70–72] have discussed the determination of multiple sulphur anions (sulphide, sulphite and thiosulphate) in non saline waters.

14.12.4 Potable waters

14.12.4.1 Sulphide and cyanide

Jovanovic and Jovanovic [59] determined low levels of sulphide and cyanide using a deposited on wire silver-silver sulphide electrode.

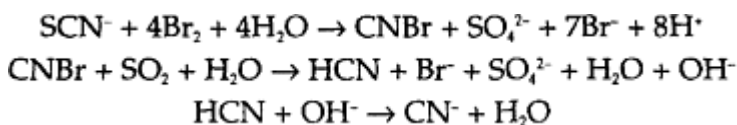
14.12.5 Waste waters

14.12.5.1 Thiocyanate, cyanate and cyanide

Thieleman [73] attempted the separation of thiocyanate, cyanate and cyanide ions by thin layer and paper chromatography. Thin layer chromatography was not successful but these three ions were successfully separated by paper chromatography with the solvent methanol-pyridine-dioxan (7:2:1) in 7–8 h. Cyanide and cyanate were identified by means of bromocresol purple and thiocyanate by 15% ferric chloride solution, as spray reagent. Carbonate ions have the same R_F value as cyanide and cyanate.

Cyanide and cyanate in waste water have also been separated by paper chromatography [74]. Separation is achieved by use of isopropyl alcohol-ethanol-water (9:4:3) as solvent with Filtrak FN 8 paper. After drying, the paper is sprayed with bromocresol green solution. On a green background the ions appear as clear blue spots (R_F values: cyanide, 0.04, cyanate 0.29). The spots may also be located by treating the paper with silver nitrate solution and exposing it to hydrogen sulphide.

Thiocyanate has been determined in waste water using a cyanide selective electrode [75]. In this method thiocyanate is first converted to cyanogen bromide using bromine water. Excess bromine is removed by the addition of phenol. The cyanogen bromide is then converted to cyanide by the addition of sulphurous acid and then sodium hydroxide added. Cyanide was then estimated using the cyanide-selective electrode.



14.12.6 Sewage effluents

14.12.6.1 Phosphate, nitrate, nitrite, chloride and cyanide

King [76] has discussed the application of the Autoanalyser to the determination of ammonia, phosphate, total phosphorus, total nitrogen, nitrite, nitrate, detergents, chloride, toxic metals, cyanide and phenols in sewage.

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Chapter 15

Preconcentration techniques

Despite the great strides forward in analytical instrumentation that have been made in recent years, the analyst working in the fields of potable water analysis and environmental analysis of non-saline and saline waters finds that, frequently, the equipment has insufficient sensitivity to be able to detect the low concentrations of substances present in his samples with the consequence that he has to report less than the detection limit of the method. Consequently, trends upwards or downwards in the levels of background concentrations of these substances in the environment cannot be followed. This is a very unsatisfactory situation which is being made worse by the extremely low detection limits being set in new directives on levels of pollution, issued by the European Community and other international bodies. To overcome the problem, there has been a move in recent years, to apply preconcentration to the sample prior to analysis so that, effectively, the detection limit of the method is considerably reduced to the point that actual results can be reported and trends followed.

The principle of preconcentration is quite simple. Suppose that we need to determine 5ng L^{-1} of a substance in a sample and that the best technique has a detection limit of $1\mu\text{g L}^{-1}$ (1000ng L^{-1}). To reduce the detection limit to 5ng L^{-1} , we might, for example, pass 1L of the sample down a small column of a substance that absorbs the substance with 100% efficiency. We would then pass down the column 5ml of a solvent or reagent which completely dissolves the substance from the column thereby achieving a preconcentration of $1000/5=200$. Thus, if the detection limit of the analytical method without preconcentration were 1000ng L^{-1} then with preconcentration it would be reduced to approximately 5ng L^{-1} .

The use of a column is but one of many possible methods of achieving preconcentration.

A combination of preconcentration with the newest, most sensitive, and, by definition, most expensive analytical techniques now becoming available is achieving previously undreamt of detection limits at the very time when the requirements for such sensitive analysis is increasing at a rapid pace. Thus the combination of preconcentration with these techniques is enabling exceedingly low concentrations of anions in the ng L^{-1} or lower range to be determined. Preconcentration prior to gas or high performance liquid chromatography is achieving similar results in the analysis of organics.

Another aspect of preconcentration is, however, worthy of mention, particularly in the case of smaller laboratories which cannot afford to purchase the full range of modern analytical instrumentation. Using older, less sensitive instrumentation, preconcentration will still achieve very useful reductions in detection limits which will be adequate in many but not all instances. Thus, if conventional atomic absorption spectrometry achieves detection limits of 1 and 5mg L^{-1} for halides in water, then a 200-fold

preconcentration will reduce these limits to approximately 5 and $25\mu\text{g L}^{-1}$ and a 1000-fold preconcentration will achieve 1 and $5\mu\text{g L}^{-1}$.

15.1 Non saline waters

15.1.1 Arsenate and arsenite

Howard *et al.* [1] electively preconcentrated arsenite onto mercapto modified silica gel. Arsenate, monomethylarsonate, and dimethyl arsenite, which commonly occur in arsenic contaminated non saline water samples, do not interfere in this procedure.

15.1.2 Borate

Yoshimura *et al.* [3] have described a highly sensitive method for preconcentrating borate based on adsorption on Sephadex G-25 gel in alkaline medium and reversible desorption acid medium. The borate is then determined spectrophotometrically by the azomethine-4 method.

Jun *et al.* [4] preconcentrated boron from non saline waters as its complex with chromotropic acid and octyltrimethyl ammonium chloride on an anion exchange column (TSK gel, I.C. Anion PW).

The eluted concentrate was analysed by high performance liquid chromatography.

15.1.3 Bromide

Carlsson *et al.* [5] preconcentrated bromide and iodide on an anion exchanger, oxidised by per-oxodisulphate to bromate, treated with iodide and measured the absorbance of the resulting tri-iodide. The sum of bromate and iodate produced in the oxidation was determined by treating the oxidised sample with iodide in hydrochloric acid. The iodate was determined separately by applying the reaction in acetic acid. The working range of the spectrophotometric method was $1\text{--}15\mu\text{M}$, the limit of the determination was $0.7\mu\text{M}$ for iodate and for iodate plus bromate and the enrichment factor in the preconcentration step was 50.

15.1.4 Chromate

The preconcentration of chromium(IV) (chromate) in non saline waters by coprecipitation with barium sulphate has been shown to be a selective and accurate procedure [6]. Analysis of the preconcentrate is carried out by determining down to $0.02\mu\text{g L}^{-1}$ chromium spectrophotometrically. The method is based on the similarity between the solubility products of barium sulphate and barium chromate. Interference from ferric iron, aluminium, and trivalent chromium was overcome by using salicylic acid as a masking agent. The method was used on river water samples and the results obtained were in good agreement with those obtained by an aluminium hydroxide coprecipitation method. In order to prevent contamination, the membrane filter, the sample bottle, and other vessels were carefully precleaned with concentrated

hydrochloric acid and redistilled water. The coprecipitation step for chromium(VI) was carried out as soon as possible after sampling to minimise the sample storage problem.

Cranston and Murray [7,8] took the samples in polyethylene bottles that had been precleaned at 20°C for 4 days with 1% hydrochloric acid. This acid had been previously distilled to reduce metal impurity levels. Total chromium, $\text{Cr(IV)} + \text{Cr(III)} + \text{Cr}_p$ (particulate chromium) was coprecipitated with iron(II) hydroxide and reduced chromium ($\text{Cr(III)} + \text{Cr}_p$) was coprecipitated with iron(III) hydroxide. These coprecipitation steps were completed within minutes of sample collection to minimise storage problems. The iron hydroxide precipitates were filtered through 0.4µm Nuclepore filters and stored in polyethylene vials for later analyses in the laboratory. Particulate chromium, was also obtained by filtering unaltered samples through 0.4µm filters. In the laboratory the iron hydroxide coprecipitates were dissolved in 6mol L⁻¹ hydrochloric acid and analysed by flameless atomic absorption. The limit of detection of this method is about 0.1–0.2nmol L⁻¹. Precision is about 5%.

Alumina has been used to preconcentrate chromate before determination by inductively coupled plasma atomic emission spectrometry [9]. Trivalent chromium is not adsorbed under these conditions. A detection limit of 0.2µg L⁻¹ was achieved by this procedure.

Use of immobilised chelating agents for sequestering trace metals from aqueous and saline media presents several significant advantages over chelation-solvent extraction approaches to this problem [10,11]. With little sample manipulation, large preconcentration factors can generally be realised in relatively short times with low analytical blanks. As a consequence of these considerations Willie *et al.* [12] developed a new approach to the determination of total chromium. This involves preliminary concentration of dissolved chromium from sea water by means of an immobilised diphenyl-carbazone chelating agent, prior to determination by atomic absorption spectrometry. A Perkin-Elmer Model 500 atomic absorption spectrometer fitted with a HGA-500 furnace with Zeeman background correction capability was used for chromium determinations. Chromium was first reduced to Cr(III) by addition of 0.5ml aqueous sulphur dioxide and allowing the sample to stand for several minutes. Aliquots of sea water were then adjusted to pH 9.0 ± 0.2 using high-purity ammonium hydroxide and gravity fed through a column of silica at a nominal flow rate of 10ml min⁻¹.

The sequestered chromium was then eluted from the column with 10.0ml 0.2mol L⁻¹ nitric acid. More than 93% of chromium was recovered in the first 5ml of eluate by this method. Extraction of 80ng spikes of Cr(III) from 200ml aliquots of sea water was semi-quantitative.

Schaller and Neeb [13] extracted di(trifluoroethyl) dithiocarbamate chelates of hexavalent and trivalent chromium and cobalt from aqueous solution at pH 3 using a carbon-18 column. Adsorbed chelates were eluted with toluene before gas chromatographic analysis with electron capture detection. Broadening of the peaks of cobalt and chromium was reduced by arranging that the end of the capillary was 1cm within the detector body, the base of which was isolated with glass wool and aluminium foil. The last 0.2cm of the column was also protected with a sleeve of braided wire. The detection limit for chromium(VI) was 0.05µg L⁻¹. Various ion exchange resins have been used to preconcentrate chromate ions including Dowex AG 1-X4 anion exchange resin

[14].

Parkow [15] acidified water samples containing chromate to pH 5 and passed them upwards through an anion exchange resin, so that the chromate is adsorbed in a narrow zone at the lower end of the resin bed. The chromate is eluted rapidly with small volumes of an acidic reluctant solution which reacts with chromate on the column to form trivalent chromium during elution, thus producing very high concentration factors.

Parkow and Janer [16] acidified water samples containing chromate to pH 5 and then passed them upwards through a Dowex Ag 1-X4 anion exchange resin, so that the chromate was adsorbed in a narrow zone at the lower end of the resin bed. The chromate was eluted rapidly with small volumes of an acidic reluctant solution which reacts with chromate on the column to form trivalent chromium during elution, thus producing very high concentration factors. Amberlite LA liquid anion exchange resin has also been used for this purpose [17].

Farag *et al.* [18] determined chromium(VI) (chromate) in water using 1, 5-diphenylcarbazide-loaded polyurethane foam.

A particularly recent innovation that has been used for metals and also for chromate preconcentration consists of a modification of the flow injection analysis technique whereby the samples pass through a micro-column containing an adsorbent for the ion of interest, thereby achieving a concentration factor. Following an automatic switch to an acidic reagent, the adsorbed anion is desorbed in a sharp pulse of the flowing reagent and then passes on to the detection system. Systems such as this, therefore, combine preconcentration and automation. Syty *et al.* [19] separated chromium(III) from chromium(VI) on a microcolumn of alumina which preconcentrated chromium(VI). Chromium(VI) was then flushed from the column with a small volume of acid before determination by inductively coupled plasma atomic emission spectrometry in amounts down to $0.2\mu\text{g L}^{-1}$.

Hexavalent chromium is reduced by diethyldithiocarbamate to trivalent chromium [20,21], with which it forms an isobutyl methyl ketone soluble complex. Hexavalent chromium is then determined in the solvent extract by atomic absorption spectrometry at 357.9nm.

Music *et al.* [22] used hydrous iron oxides to preconcentrate chromate.

Chromium(VI) has been preconcentrated by procedures based on coprecipitation with ferric hydroxide [23]. The mechanism of the sorption of chromate ions onto amorphous ferric hydroxide, ferric oxide and magnetite particles has been examined and the effects of several variables including the pH of the solution examined and the presence of competing ions (chloride, sulphate, molybdate) determined. The sorption of hexavalent chromium onto hydrous ferric oxide can be explained in terms of ligand exchange hydroxyl ions being released from the surface of the hydrated oxide particles. For magnetic particles, however, the sorption effect was explained by the reduction of traces of hexavalent chromium at the magnetite/water interface, as a result of which a very fine ferric hydroxide/chromium hydroxide coating was produced which exhibited further reduction of hexavalent chromium.

Fung and Dao [2] used Chelex-100 resin to remove anions from non saline waters. They retained chromate. The chromate could then be stripped from the column and determined in sub $\mu\text{g L}^{-1}$ quantities.

15.1.5 Iodide and iodate

Iodide in non saline waters has been determined [24] by ion exchange high performance liquid chromatography using an iodide ion selective electrode as detector. On-line preconcentration of iodide on an anion guard cartridge allowed determinations down to 1nM.

Palagni [25] used the pulsed column bed technique to selectively separate and preconcentrate low levels of iodide-127 in non saline water. The pulsed bed consisted of a syringe containing a scintillation detector and a gamma-ray spectrometer. The adsorbent consisted of open cell polyurethane foam impregnated with long chain tri-*n*-alkylamine which formed a complex with iodide.

Carlsson *et al.* [5] preconcentrated bromide and iodide (and bromide), on an anion exchanger, oxidised by peroxysulphate to bromate, treated with iodide, and measured the absorbance of the resulting triiodide. The sum of bromate and iodate produced in the oxidation was determined by treating the oxidised sample with iodide in hydrochloric acid. The iodate was determined separately by applying the reaction in acetic acid. The working range of the spectrophotometric method was 1–15µM, the limit of detection was 0.7µM for iodate and for iodate plus bromate and the enrichment factor in the preconcentration was 50.

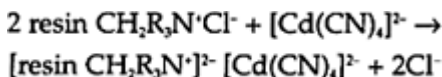
Iodide in non saline waters has been preconcentrated by transport extraction based on solvent sublimation [26].

15.1.6 Metal cyanide complexes

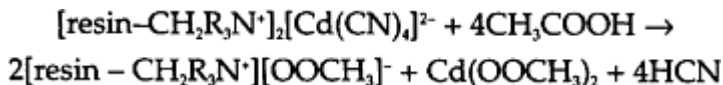
Simple cationic metal species do not react with anion exchange resins. However, if the metal ion M^+ is first reacted with a reagent with which it forms a negatively charged anionic complex, then the resulting negatively charged metal-containing ions are retained on an anion exchange resin. Thus, cadmium(II) forms a soluble anionic complex upon reaction with potassium cyanide:



This complex is retained in a column of strong base anion exchange resin which, for convenience, is represented as follows:

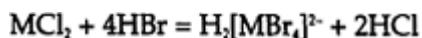


The cadmium complex can then be dissolved off the column with a small volume of aqueous acetic acid to produce the acetate form of the resin and cadmium acetate:

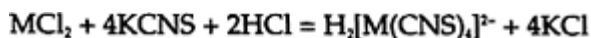


Other examples include the formation of the following.

- (a) Complexes of the type $H_2 [MBr_4]^{2-}$ upon reaction of cadmium, copper or lead with hydrobromic acid:



- (b) Complexes of the type $H_2M(CN_5)_4^{2-}$ upon reaction of cadmium, cobalt or zinc with acidic ammonium thiocyanate:



- (c) Formation of $TlCl_4^{3-}$ by reaction of thallous ion with hydrochloric acid.

High preconcentration factors can be achieved by such techniques, some further examples of which are reviewed in Table 15.1.

15.1.7 Molybdate

Murthey and Ryan [63] used colloid flotation as a means of preconcentration prior to neutron activation analysis for molybdenum. Hydrous iron(III) is floated in the presence of sodium dodecyl sulphate with small nitrogen bubbles from 1L of sea water at pH 5.7. Recoveries of molybdenum were better than 95%. This method has been used [64] to precipitate from water samples traces of molybdenum. The trace element was concentrated by coprecipitation with thionalide at pH 9.1. Co-precipitation with thionalide allowed the concentration of both ions and colloids.

Molybdenum has been determined after preconcentration on Sephadex G.25 gel at pH 3.5. Ethylenediaminetetra acetic acid desorbs molybdenum from the gel. This preconcentration method brings the detection limit for molybdenum in fresh and sea waters down to $1\mu g L^{-1}$ in 250ml samples. The procedure was applied to 100ml solutions containing $1.25\mu mol$ of molybdenum and 1- to 10000-fold amounts of various ions. Interference from vanadium(V) and tungsten(VI) is probably due to complex formation with molybdenum. Iron(III) at a 100-fold level lowered the recovery, probably because its hydroxides or hydroxo complexes adsorb molybdenum, but the interference could be overcome in the presence of $0.5mol L^{-1}$ acetate. The method is suitable for the determination of molybdenum at the levels normally encountered in river water ($0.2-0.6\mu g L^{-1}$) and is particularly effective for sea water.

Vasquez-Gonzalez *et al.* [65] have described a method for preconcentrating and determining molybdate by electrothermal atomisation atomic absorption spectrometry after preconcentration by means of anion-exchange using Amberlite IRA-400 resin in citrate form. The optimal analytical parameters were established by drying, carbonisation, charring, atomisation and cleaning in a graphite furnace. The precision and accuracy of the method were investigated. Less than $0.2\mu g L^{-1}$ molybdate could be determined by this procedure.

Fung and Dao [2] used Chelex-100 resin to remove molybdate from non saline waters prior to desorption and determination at the $\mu g L^{-1}$ level.

15.1.8 Phosphate

15.1.8.1 Complexation-solvent extraction preconcentration

Most spectrophotometric methods of phosphates are based on the formation of heteropoly acid with molybdate. The heteropoly acid formed

Table 15.1 Preconcentration of anionic metal species from non saline water

<i>Metal</i>	<i>Type of water</i>	<i>Resin</i>	<i>Medium</i>	<i>Eluting agent</i>	<i>Detection limit</i>	<i>Analytical finish</i>	<i>R</i>
Al	Potable	Anion exchange	Pyro catechol violet	–	–	–	[2]
Cd	Non saline	Dowex 1-X8	HCl or HBrO	HNO ₃	–	Spectrophotometric	[2]
Cd	Non saline	Amberlite IRA-400	Cyanide	CH ₃ COOH	–	Spectrophotometric	[2]
Cd	Non saline	Biorad 140–1242 A91–X2	8-hydroxy quinoline 5-sulphonic acid	2mol L ⁻¹ HNO ₃	<0.2µg L ⁻¹	AAS	[1]
Cd	Sea water	Anion exchange 1 mol L ⁻¹ thiocyanate	0.1mol L ⁻¹ HCl	2mol L ⁻¹ HNO ₃	–	AAS	[3]
Cd	Sea water	Polyacrylamidoxime Resin	–	1:1 HClH ₂ O	–	AAS	[3]
Cd	Non saline and potable	Dowex 1–X8	MeOH:HBr	aq HNO ₃	–	AAS	[3]
Cd	Sea water	Single bead anion exchange	–	–	–	Mass spectroscopy	[3]
Co	Non saline	Biorad 140-quinoline 1242, A91–X2	8-hydroxy HCl 5-sulphonic acid	12mol L ⁻¹	<0.2µg L ⁻¹	AAS	[1]
Co	Non saline	Dowex A91–X8	HCl-thiocyanate	HCl	–	Spectrophotometric	[3]

Co	Sea water	Anion exchange	0.1 mol L ⁻¹ cyanate 0.1 mol L ⁻¹ HCl	2 mol L ⁻¹ HNO ₃	—	AAS	[1]
Cu	Sea water	Anion exchange	1 mol L ⁻¹ cyanate 0.1 mol L ⁻¹ HCl	2 mol L ⁻¹ HNO ₃	—	AAS	[3]
Cu	Sea water	Polyacryl amidoxime resin	—	1:1 HCl:H ₂ O	—	AAS	[3]
Cu	Non saline and potable	Dowex 1-X8	MeOH: HBr	aqNH ₃	—	AAS	[3]

<i>Metal</i>	<i>Type of water</i>	<i>Resin</i>	<i>Medium</i>	<i>Eluting agent</i>	<i>Detection limit</i>	<i>Analytical</i>
Au	Non saline	Anion exchange	—	—	—	NAA
Au	Sea water	Single bead anion exchange	—	—	—	Mass spect
In	Sea water	Single bead anion exchange	—	—	—	Mass spect
Ir	Sea water	Single bead anion exchange	—	—	—	Mass spect
Ir	Sea water	Single bead anion exchange	—	—	—	AAS
Fe	Sea water	Polyacryl amidoxime	1:1 H ₂ O:HCl	—	—	AAS
Fe	Sea water	Amberlyst A27 (thin layer chromatography)	Bathophenanthroline	HCl NH ₂ OH NH ₄ OH pH 4–5	—	Photodensi
Fe	Non saline	Anion exchange	—	—	1–2 ng	Spectropho
Pb	Non	Biorad 140–	8	2 mol	<0.2 µg L ⁻¹	AAS

	saline	1242 AGI-X2	Hydroxyquinoline- 5-sulphonic acid	L-1 HNO ₃		
Pb	Sea water	Polyacryl amidoxime	–	1:1 HCl:– H ₂ O	–	AAS
Pb	Sea water and non saline	Dowex 1–X8	MeOH: HBR	aq	–	AAS
Pb	Sea water	Single bead anion exchange	–	–	–	Mass spect
Pb	Non saline	Dowex AGX–8	NH ₂ OH NaCl	4N HNO ₃	2ng L ^{–1}	CVAAS
Ni	Mineral water	Dowex A–1	NaOO CCH ₃	HCl	0.5 _{Mg}	Spectropho
Mo	Mineral and potable	Dowex 1–X8	Acid thiocyanate ascorbic acid	–	Spectrophotometric as Tiron complex	[43,103
Mo	Sea water	Amberlite (GC– 400)	Ascorbic acid	4N HNO ₃	10µg L ^{–1}	Spectropho as thiocyan complex

<i>Metal</i>	<i>Type of water</i>	<i>Resin</i>	<i>Medium</i>	<i>Eluting agent</i>	<i>Detection limit</i>	<i>Analytical finish</i>	<i>Ref.</i>
Pt	Sea water	Polyacryl amidoxime	–	1:1 H ₂ O:HCl	–	AAS	[38]
Pu- 239 Pu- 240	Non saline	Anion exchange	–	HF-HCl	–	Deposited on Pt γ-ray spectrometry	[45]
Pu- 240	Sea water	Single bead anion exchange	–	–	–	Mass spectrometry	[34]
Ag	Non saline	Anion exchange	HCl	0.4mol L ^{–1} thiourea	–	NAA	[46]
Ag	Non saline	Dowex Ag 1×8	–	Acetone: HNO ₃ H ₂ O	–	Ammonium pyrrolidone dithiocarbamate	[47]

				(20:1:1)		extraction-AAS	
Tc	Sea water	Single bead anion exchange	–	–	–	Mass spectrometry	[34]
Tl	Non saline	Strongly basic anion exchange	Conversion to TI Cl_4^{3-} ion	H_2SO_3	–	GFAAS	[48]
Tl	Non saline	Anion exchange	Conversion TI Cl_4^{3-} ion with Cr (IV) sulphate	$(\text{NH}_4)\text{SO}_4$	3.3ng L^{-1}	AAS	[49]
Th	Non saline	Dowex AGI-X8	HNO_3	HCl	–	Spectrophotometric	[50]
Sn	Sea water	Dowex IX (CI from)	HCl	2mol L^{-1}	–	Spectrophotometric with catechol violet	[51]
U	Sea water	Basic azide exchange	azide ions	1mol L^{-1}	–	Spectrometric	[52]
U	Non saline	Amberlite LA-1	–	–	$0.04\mu\text{g L}^{-1}$	Fluorometric	[53–55]
U	Non saline	Dowex AGI-X8	H_2SO_4	H_2SO_4	$0.3\mu\text{g L}^{-1}$	Fluorometric	[56]

<i>Metal</i>	<i>Type of water</i>	<i>Resin</i>	<i>Medium</i>	<i>Eluting agent</i>	<i>Detection limit</i>	<i>Analytical finish</i>	<i>Ref.</i>
V	Sea water	Anion exchange	1M thiocyanate 0.1 MHCl	2mol L^{-1} HNO_3	–	AAS	[32]
V	Sea water	Dowex 1–X8 (SCN form)	Thiocyanate-HCl	conc HCl	$1.65\mu\text{g L}^{-1}$	Spectrophotometric as 2-pyridyl azoresorcinol	[57]
V	Sea water	Dowex 1–X8	Thiocyanate-ascorbic acid	–	–	AAS	[58,59]
Zn	Sea water	EDE-10P	HCl	HCl	–	Spectrophotometric	[60]
Zn	Non saline	Biorad 140–1242	8-hydroxyquinoline 5-sulphonic acid	2mol L^{-1} HNO_3	$<0.2\mu\text{g L}^{-1}$	AAS	[16,31]

Zn	Sea water	Anion exchange	1 M thiocyanate 0.1 M HCl	2mol L ⁻¹ – HNO ₃	AAS	[31]
Zn	Sea water	Polyacryl amidoxime resin	–	1:1 HCl:H ₂ O	AAS	[32]
Various radio nucleides	Non saline	Single bead anion exchange	–	–	Point source mass spectrometry	[61]
22 elements	Non saline	Anion exchange	–	–	NAA	[62]

Source: Own files

(molybdophosphate) and its reduction product (so-called molybdenum blue) have been used, as has the yellow vanadmolybdophosphoric acid. The protonated forms of these species have also been extracted into organic solvents for spectrophotometry. It is well known that molybdo-phosphate reacts with cationic dyes and organic bases to form ion pairs.

Shida and Matsuo [66] reported a very sensitive spectrophotometric method based on formation of the ion associate of molybdophosphate with methylene blue, flotation of this ion-pair between the aqueous phase and cyclohexane-4-methylpentan-2-one and displacement of methylene blue from the ion pair by tetradecyldimethylbenzylammonium ion.

In an attempt to improve the extractability of ion pairs of molybdo-phosphate and thus the sensitivity of the determination of phosphate, Motomizu *et al.* [67] examined several cationic dyes and extracting solvents. They found that procedures based on ethyl violet and a cyclo-hexane-4-methylpentan-2-one mixture enabled 10µg L⁻¹ concentrations of phosphate to be determined spectrophotometrically.

In the samples of river water and seawater, the phosphorus content is often in the µg L⁻¹ range. The procedure requires small volumes of sample (below 10ml) and very simple vessels (25ml test tube) which are easily heated in order to hydrolyse any condensed phosphate.

The absorption spectrum of the ion pair formed between molybdophosphate and ethyl violet in the organic phase obtained by the procedure B is shown in Fig. 15.1. Maximum absorbance occurs at 602nm where the absorbance of the reagent blank is about 0.1. The calibration graphs obtained are linear in the range 0–0.6µg of phosphorus and the molar absorptivity calculated from the slope of the curve was 2.7×10⁵L mol⁻¹ cm⁻¹. Silicate, vanadate and tungstate, which may react with molybdate to form heteropoly acids, do not interfere with the determination of phosphorus even at the amounts of 5×10⁻⁵M, 10⁻⁵M and 5×10⁻⁶M respectively. Arsenic(V) causes positive errors because it reacts with molybdate to form the heteropoly acid, which is quantitatively extracted into the organic phase. But in non saline waters such as river water and sea water, the arsenic content is very much smaller than the phosphorus content. Tin(II) and (IV) ions at concentrations

more than 10^{-6} M interfere; large amounts of tin(II) make it impossible to determine phosphate and tin(IV) causes negative errors.

In later work, Motomizu *et al.* [68] point out that in the determination of phosphate at $\mu\text{g L}^{-1}$ levels in waters the above method has certain disadvantages. First the absorbance of the reagent blank becomes too large for the concentration effect achieved by the solvent extraction to be of much use; for example when 20ml of sample solution and 5ml of methyl isobutylketone were used, the absorbance of the reagent blank was 0.14. Secondly, the shaking time needed was long and the colour of the extract faded gradually if the shaking lasted more than 30min. In the

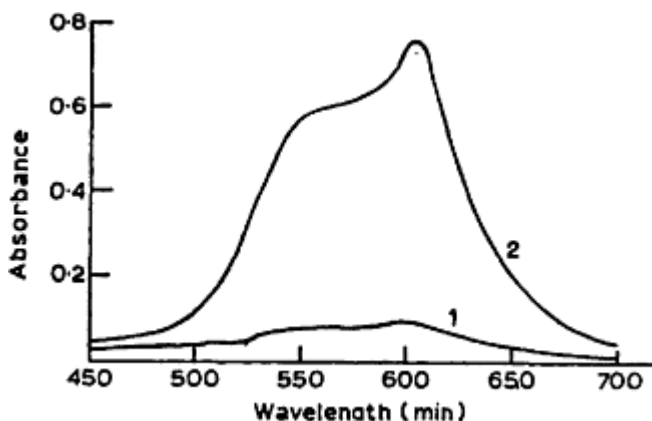


Fig. 15.1 Absorption spectra in the organic phase (procedure B) (1) reagent blank measured against solvent; (2) $0.38\mu\text{g P}$ measured against solvent

Source: Reproduced with permission from the Chemical Society of Japan [66]

course of attempts to improve on this method, they observed that malachite green gave a stable dark yellow species in 1.5M sulphuric acid (probably a protonated one), whereas ethyl violet became colourless within 30min even in only 0.5M sulphuric acid.

Malachite green has several advantages over ethyl violet:

- (1) the absorbance of the reagent blank is very small and 20-fold concentration of phosphate by solvent extraction is possible;
- (2) the reagent solution, which consists of malachite green, molybdate and 1.5M sulphuric acid is stable at least for a month;
- (3) the method is less troublesome and shaking for 5min is enough to complete the extraction; and
- (4) colour fading in the organic phase does not occur during shaking and standing.

The recovery of phosphorus was good, 99–103%. The relative standard deviation for phosphorus was 0.6% for $21.0\mu\text{g L}^{-1}$ in sea water (12 replicates) and 1.1% for $4.3\mu\text{g L}^{-1}$ in potable water (10 replicates).

Molybdenum blue solvent extraction procedures have also been applied to polluted waters [69].

Other molybdenum blue solvent extraction-preconcentration procedures include the use of isoamyl alcohol with a pulse polarographic finish [70] and methyl isobutyl ketone with an inductively coupled plasma atomic emission finish [71,72].

Inductively coupled plasma procedures have the advantage of being applicable to estuarine as well as river waters. Many of the earlier atomic

Table 15.2 Effect of other ions on phosphorus results (sample, 100ml; DIBK, 5ml; P, 10µg)

Other ion	Amount added	Recovery (%)	Other ion	Amount added	Recovery (%)
None	–	100	Fe(III)	1mg	101
As(V)	0µg	100	Cl [–]	2g	101
	50µg	102	I [–]	10mg	102
	100µg	105	Br [–]	10mg	99
As(III)	1mg	104	NO ₂ [–]	10mg	91
Si	10mg	102		10mg	104 ^a
Ge	10mg	101	S ₂ O ₃ ^{2–}	1g	103

^a20mg of sulphamic acid added

Source: Reproduced with permission from Elsevier Science [71]

absorption procedures had the disadvantage that arsenic, silicon and germanium cause positive errors because these elements also form reduced heteropoly acids.

Muyazaki *et al.* [71,72] overcame this problem by determining phosphorus at the P(I) 214.91nm line as the Mo(II) 213.61nm line interferes with the P(I) 213.62nm line.

To achieve the µg L^{–1} sensitivity they required they incorporated a 100-fold preconcentration stage into the method. This involved adding molybdate-vanadate reagent to 500ml water sample, reducing with aconitic acid and extracting to reduced molybdoantimonyphosphoric acid complex with 5ml diisobutyl ketone.

The effects of other ions are summarised in Table 15.2. No interference from silicon and germanium (which cause positive errors in the spectrophotometric method) was observed even at 1000-fold excesses. Arsenic(V) was permissible up to 10 times the weight of phosphorus. Above this amount, a slight upward background shift was observed which caused a positive error exceeding 5%.

However, non saline water containing arsenic(V) in amounts more than 10 times that of phosphorus is rare. Most of the other anions did not show any interference and that of nitrite was decreased by addition of sulphamic acid. There was no interference from peroxodisulphate indicating that pretreatment with peroxodisulphate as used for the determination of total phosphorus in water is also applicable to this method.

The calibration graph obtained by the extraction method was linear for at least three orders of magnitude of concentration above the detection limit. The detection limit, defined as the concentration of phosphorus equivalent to three times the standard deviation of the background signal (3) was $37\mu\text{g L}^{-1}$ phosphorus in the 5ml of extract, hence, the detection limit for the original samples (500ml) was $0.37\mu\text{g L}^{-1}$ phosphorus. Measurements of $5\mu\text{g}$ of phosphorus, extracted from 500ml portions of aqueous solution gave a relative standard deviation of 2.1%.

More recently, Muyazaki *et al.* [72] have extended the detection limit of the inductively coupled plasma emission spectrometric technique down to the sub $\mu\text{g L}^{-1}$ level by measurements of the reduced molybdoantimonic phosphoric acid, not at the phosphorus P(I) 214.91nm line, as in the previous method, but at the more sensitive molybdenum(II) 202.03nm or the antimony(I) 206.83nm lines. This method is simple, sensitive and precise. Washing of the organic phase is not necessary because of the low solubility of diisobutyl ketone in water.

Arsenic(V) caused serious interference but germanium, silicon and arsenic(II) did not interfere in 100-fold amounts. Nitrite seriously interferes in spectrophotometric methods for molybdenum blue. Molybdenum measurements by the inductively coupled plasma method did not suffer from interference by up to 5mg of nitrite (2500-fold excess over phosphorus). In the antimony measurements, nitrite was permissible up to 0.2mg (100-fold amount). Above that amount, the interference decreased with increasing amount of antimony in the molybdenum-antimony reagent, although the interference was not completely suppressed. The addition of sulphamic acid decreased the interference from nitrite. The difference in the interference mentioned above may be related to the mechanism of the reduction of molybdoantimonic phosphoric acid. No interference was observed from peroxodisulphate. Pretreatment with peroxodisulphate as used for the determination of total phosphorus in water, therefore, may be applicable to this method.

Bet-Pera *et al.* [73] have described an alternative phosphate preconcentration procedure in which phosphate is converted to 12-molybdophosphoric acid which is then extracted into isobutyl acetate. After evaporation of the organic solvent the complex is dissolved in alkaline solution and after acidification molybdenum(VI) is reduced to molybdenum(III) using a Jones reductor. The resulting molybdenum(III) is reoxidised with iron(III) to molybdate and the resulting iron(II) is determined spectrophotometrically at 562nm as the iron(II) ferrozine complex.

Phosphates in non saline water samples were determined by this method in amounts as low as $4\mu\text{g L}^{-1}$ in the final solution with a relative precision of 12% at 2α value.

15.1.8.2 Preconcentration on activated carbon

Hashitani *et al.* [74] preconcentrated phosphate in water using activated carbon loaded with zirconium. Activated carbon (10g) was contacted with zirconyl nitrate solution (1g zirconium at pH 1.6) at 25°C for 3 days. After filtration the material was air dried and formed into a bed on a membrane filter, porosity $0.54\mu\text{m}$. A 0.1–10L sample at pH 1.5 was passed through the bed. Phosphate was adsorbed quantitatively and instantly below pH 8 and desorbed above pH 13.5. Pyrophosphate, tripoly-phosphate and metaphosphate behaved as orthophosphate.

15.1.8.3 Preconcentration on inorganic solids

Coprecipitation with aluminium hydroxide has been used to preconcentrate phosphate ion in waters [75]. This method involves coprecipitation with aluminium hydroxide, flotation of the precipitate which is then dissolved in sulphuric acid and determination of phosphate by a conventional molybdenum blue method. Recoveries are better than 95% and the relative standard deviation is 1% with samples in the range 5–150 $\mu\text{g L}^{-1}$.

Khan and Chow [76] have described a method in which the phosphate is converted into phosphomolybdate which is then extracted into polyurethane foam and analysed for molybdenum by X-ray fluorescence spectrometry directly on the foam. A polyether type polyurethane foam disc is squeezed for an hour in a mixture of phosphate solution, sodium molybdate and hydrochloric acid, spiked with phosphorus 32. After washing and drying, the foam disc is placed on plastic foam and stretched across the X-ray source holder. The method is simple and rapid and the precision is 5% for 0.25 $\mu\text{g L}^{-1}$ and 2% for 2.5 mg L^{-1} phosphate. Equimolar amounts of silicon, germanium and arsenic(VI) appear to interfere with the determination.

A preconcentration technique based on nitrocellulose or acetyl cellulose membranes has been described for phosphate [77]. Phosphorus was collected as phosphomolybdate on a nitrocellulose or acetylcellulose membrane in the presence of *n*-dodecyltrimethylammonium bromide. The membrane was dissolved in dimethylsulphoxide and the absorbance of dimethylsulphoxide solution measured. Moderate concentrations of silicate, anionic and non-ionic surfactants and high concentrations of sodium chloride did not interfere. Arsenate interference could be eliminated by reducing arsenate to arsenite. Determination of condensed and organic phosphates was possible following their conversion to orthophosphoric acid. The limit of determination was 0.02 $\mu\text{g L}^{-1}$ phosphate.

15.1.8.4 Coprecipitation with ferric hydroxide

A solution of iron containing ferric chloride and acidified with hydrochloric acid is treated with aqueous ammonia to precipitate ferric hydroxide coprecipitated with ferric phosphate produced by any phosphate ions in the sample [78]. The precipitate is filtered off and dissolved in dilute hydrochloric acid and ammonia and uranyl acetate added to produce uranyl phosphate which is estimated polarographically. To determine phosphate plus arsenate the ferric hydroxide precipitate, containing coprecipitated iron phosphate and arsenite is made acid with hydrochloric acid and potassium iodide added. The arsenic trichloride produced is extracted with carbon tetrachloride and this solution back extracted into hydrochloric acid. Application of the ammonia ferric chloride precipitation technique to this gives a preconcentrate containing arsenic only.

Hori *et al.* [78] also examined the adsorption behaviour of various phosphorus containing anions on ferric hydroxide as a function of solution pH. Adsorbed phosphorus compounds were determined spectrophotometrically and percent adsorption calculated from adsorbed and initial amounts. This was plotted against solution pH. Orthophosphate was adsorbed quantitatively at pH 4.0–8.0; triphosphate and pyrophosphate at pH 4.0–9.3

and monomethylphosphate, phosphite and α and β glycerophosphates at pH 4.0–6.8. Dimethylphosphate and hypophosphite were only slightly adsorbed at all pH values examined. The adsorbed ions were desorbed readily into a small volume of alkaline solution.

A solution of iron containing ferric chloride and acidified with hydrochloric acid is treated with aqueous ammonia to precipitate ferric hydroxide coprecipitated with ferric phosphate produced by any phosphate ions in the sample [79]. The precipitate is filtered off and dissolved in dilute hydrochloric acid and ammonia and uranyl acetate added to produce uranyl phosphate which is estimated polarographically. To determine phosphate plus arsenate the ferric hydroxide precipitate, containing coprecipitated iron phosphate and arsenite, is made acid with hydrochloric acid and potassium iodide added. The arsenic trichloride produced is extracted with carbon tetrachloride and this solution back extracted into hydrochloric acid. Application of the ammonia ferric chloride precipitation technique to this gives a preconcentrate containing arsenic only.

In one procedure [80,81] phosphate is adsorbed onto anion exchange resin. Orthophosphate is quantitatively adsorbed by a A,G Dowex 1–X8 anion exchange resin, then eluted and reacted with an acid molybdate reagent for estimation. Arsenic and organic phosphorus compounds did not interfere with the estimation of orthophosphate while polyphosphates did interfere if present in equal or greater amounts than orthophosphate. It is concluded that the use of the anion exchange technique results in a more valid estimate than direct action with the acid molybdate reagent.

15.1.9 Selenate and selenite

2,2'-Diethylaminocellulose filters enabled selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) to be preconcentrated from non saline water [82,83] at pH 3–6 with a detection limit of $0.05\mu\text{g L}^{-1}$.

Selenite has been preconcentrated on a bismuthiol 1L modified anion exchange resin (Amberlite 1 RA–400) [84] followed by fluorometric estimation using diaminonaphthalene. Selenite adsorbed on the column as selenotrisulphate was desorbed with a small volume of 0.1mol L^{-1} penicillamine or 0.1mol L^{-1} cysteine prior to fluorometric determination of selenium [85].

Selenate and selenite can be determined by energy dispersive X-ray spectroscopy after preconcentration of elementary selenium on activated carbon, ascorbic acid being used to reduce selenium to its elemental form [86–89].

Fung and Dao [2] used Chelex-100 resin to remove selenate from non saline water prior to desorption from the column and determination at the sub $\mu\text{g L}^{-1}$ level.

15.1.10 Silicate

Silicate can be preconcentrated [89] from water in microgram amounts by conversion to molybdosilicic acid in a medium 0.1N sulphuric acid or hydrochloric acid containing ammonium molybdate. The heteropoly acid is extracted into butanol or isoamyl alcohol and reduced to molybdenum blue using stannous chloride prior to spectrophotometric determination.

15.1.11 Sulphide

Sulphide has been preconcentrated on a column of Amberlite IRA 400 [90]. The sulphide is removed from the column with 4M sodium hydroxide and determined spectrophotometrically by the *N,N'*-dimethyl *p*-phenylene diamine method. Down to $0.1\mu\text{g L}^{-1}$ sulphide can be determined by this procedure.

Desalvo and Street [91] preconcentrated sulphide from well water on a column of cadmium exchanged zeolite sorbent prior to determination by visible spectrophotometry. This method had an appreciably lower detection limit than conventional sulphide methods.

Bain [92] preconcentrated sulphide in non saline waters at levels of $1\text{--}1000\mu\text{g L}^{-1}$ at 0.20V (vs Ag/AgCl) and determined by cathodic stripping voltammetry. Over the concentration range of $0\text{--}40\mu\text{g L}^{-1}$ the stripping peak height is linearly proportional to sulphide concentration; over the range of $40\text{--}10000\mu\text{g L}^{-1}$ concentrations are obtained from the calibration plot. The detection limits are 0.20 and $0.10\mu\text{g L}^{-1}$ for dc and differential pulse stripping analysis, respectively, and the coefficients of variation are 3.7% and 2.6% for 10 and $100\mu\text{g L}^{-1}$ sulphide.

A flow injection gas diffusion method has been described [93] for the preconcentration and determination of traces of sulphide. Accumulation and preconcentration of the analyte is accomplished using the acceptor stream of a diffusion unit in a closed-loop recirculating mode. The detection limit from a 5ml sample is $0.15\mu\text{g L}^{-1}$ level is 4%.

15.1.12 Thiosulphate

Chakraborty and Das [94] have described an indirect atomic absorption spectrometric method for determining thiosulphate in photographic processing effluents based on the formation of a stable ion association complex between lead, thiourea and thiosulphate in alkaline medium. The complex is extracted into *n*-butylacetate:*n*-butanol 2:1 and analysed directly by flame atomic absorption spectrometry. Down to $0.2\mu\text{g L}^{-1}$ thiosulphate were determined.

15.1.13 Multianion analysis

Fung and Dao [2] used Chelex-100 resin to preconcentrate selenate, arsenate, molybdate, vanadate, tungstate and chromate from non saline waters. The anions were subsequently desorbed from the Chelex 100 with suitable reagents and determined in $\mu\text{g L}^{-1}$ quantities.

15.2 Potable water

15.2.1 Molybdate

Hidalgo *et al.* [95] preconcentrated molybdenum(VI) in potable water and seawater by co-flotation on iron(III) hydroxide. Co-flotation was achieved by means of surfactants;

octadecylamine for tap water samples, hexa-decyltrimethylammonium bromide for non saline waters, and both hexadecyltrimethylammonium bromide and octadecylamine for sea water samples. Differential pulse polarography using the catalytic wave caused by molybdenum(VI) in nitrate medium was applied to the preconcentrate. Good reproducibility was obtained with mean values of $0.7\mu\text{g L}^{-1}$ and $5.7\mu\text{g L}^{-1}$ for molybdenum(VI) in tap water and sea water, respectively.

15.3 Seawater

15.3.1 Molybdate

Shriadah *et al.* [43] determined molybdenum(VI) in seawater spectro-photometrically after enrichment as the Tiron complex on a thin layer of anion exchange resin. There were no interferences from trace elements or major constituents of sea water except for chromium and vanadium. These were reduced by the addition of ascorbic acid. The concentration of dissolved molybdenum (VI) determined in Japanese sea water was $11.5\mu\text{g L}^{-1}$ with a relative standard deviation of 1.1%.

Kuroda *et al.* [96] preconcentrated trace amounts of molybdenum from acidified sea water on a strongly basic anion exchange resin (Bio-Rad Ag 1-X8 in the chloride form) by treating the water with sodium azide. Molybdenum(VI) complexes with azide were stripped from the resin by elution with ammonium chloride/ammonium hydroxide solution ($2\text{mol L}^{-1}/\text{mol L}^{-1}$). Relative standard deviations of better than 8% at levels of $10\mu\text{g L}^{-1}$ were attained for sea water using graphite furnace atomic absorption spectrometry.

15.3.2 Perrhenate

Matthews and Riley [97] have described the following procedure for determining down to $0.06\mu\text{g L}^{-1}$ perrhenate in sea water. From 6 to $8\mu\text{g L}^{-1}$ rhenium, was found in Atlantic sea water. The rhenium in a 15L sample of sea water, acidified with hydrochloric acid, is concentrated by adsorption on a column of De-Acidite FF anion-exchange resin (Cl^{-} form), followed by elution with 4mol L^{-1} nitric acid and evaporation of the eluate. The residue (0.2ml), together with standard and blanks, is irradiated in a thermal neutron flux of at least $3 \times 10^{12} \text{ neutrons cm}^{-2} \text{ s}^{-1}$ for at least 50h. After a decay period of 2 days, the sample solution and blank are treated with potassium perrhenate as carrier and evaporated to dryness with a slight excess of sodium hydroxide. Each residue is dissolved in 5mol L^{-1} sodium hydroxide. Hydroxylammonium chloride is added (to reduce Tc(VIII)) which arises as $^{99\text{m}}\text{Tc}$ from activation of molybdenum present in the samples, and the Re(VII) is extracted selectively with ethyl methyl ketone. The extracts are evaporated, the residue is dissolved in formic acid:hydrochloric acid (19:1), the rhenium is adsorbed on a column of Dowex 1 and the column is washed with the same acid mixture followed by water and 0.5mol L^{-1} hydrochloric acid; the rhenium is eluted at 0°C with acetone:hydrochloric acid (19:1) and is finally isolated by precipitation as tetraphenylarsonium perrhenate. The precipitate is weighed to determine the chemical yield and the ^{186}Re activity is counted

with an end-window Geiger-Muller tube. The irradiated standards are dissolved in water together with potassium perchlorate. At a level of $0.057 \mu\text{g L}^{-1}$ rhenium the coefficient of variation was $\pm 7\%$.

15.3.3 Phosphate

Mullins [98] has described a procedure for determining the concentrations of dissolved chromium species in sea water. Chromium (III) and chromium(VI) separated by coprecipitation with hydrated iron(III) oxide and total dissolved chromium are determined separately by conversion to chromium(VI), extraction with ammonium pyrrolidinediethyl-dithiocarbamate into a methyl isobutyl ketone and determination by atomic absorption spectroscopy. The detection limit is $40 \text{ ng L}^{-1} \text{ Cr}$. The dissolved chromium not amenable to separation and direct extraction is calculated by difference. In the waters investigated, total concentrations were relatively high ($1\text{--}5 \mu\text{g L}^{-1}$) with chromium(VI) the predominant species in all areas sampled with one exception, where organically bound chromium was the major species. A standard contact time of 4h was found to be necessary for the quantitative coprecipitation of chromium on ferric oxide. The r.s.d values for the determination of chromium(III), chromium(VI) and total dissolved chromium were generally 10.0, 5.0, and 5.0% respectively. From these results, the r.s.d for the calculated concentration of the bound species was 20%.

The sorption of hexavalent chromium (chromate) onto hydrous ferric oxide can be explained in terms of ligand exchange, hydroxyl ions being released from the surface of the hydrated oxide particles. For magnetic particles, however, the sorption effect was explained by the reduction of traces of hexavalent chromium at the magnetite/water interface, as a result of which a very fine ferric hydroxide/chromium hydroxide coating was produced which exhibited further reduction of hexavalent chromium.

Nakayama *et al.* [99] have described a method for the determination of chromium(III), chromium (VI) and organically bound chromium in sea water. They found that sea water in the sea of Japan contained about $9 \times 10^{-9} \text{ mol L}^{-1}$ dissolved chromium. This is shown to be divided as about 15% inorganic Cr(III), about 25% inorganic Cr(VI), and about 60% organically bound chromium. These workers studied the coprecipitation behaviours of chromium species with hydrated iron(III) and bismuth oxides.

The collection behaviour of chromium species was examined as follows. Sea water (400ml), spiked with $10^{-8} \text{ mol L}^{-1} \text{ Cr(III)}$, Cr(VI) and Cr(III) organic complexes labelled with ^{51}Cr , was adjusted to the desired pH with hydrochloric acid or sodium hydroxide. An appropriate amount of hydrated iron(III) or bismuth oxide was added; the oxide precipitates were prepared separately and washed thoroughly with distilled water before use [100]. After about 24h, the samples were filtered on $0.4 \mu\text{m}$ Nuclepore filters. The separated precipitates were dissolved with hydrochloric acid and the solutions thus obtained were used for γ -activity measurements. In the examination of solvent extraction, chromium was measured by using ^{51}Cr , while iron and bismuth were measured by electrothermal atomic absorption spectrometry. The decomposition of organic complexes and other procedures were also examined by electrothermal atomic absorption spectrometry.

The percentage collection of Cr(III) with hydrated iron(III) oxide may decrease

considerably in the neutral pH range when organic materials capable of combining with Cr(III), such as citric acid and certain amino acids, are added to the sea water [101]. Moreover, synthesized organic Cr(III) complexes are scarcely collected with hydrated iron(III) oxide over a wide pH range [101]. As it was not known what kind of organic matter acts as the major ligand for chromium in sea water Nakayama *et al.* [99] used EDTA and 8-quinolinol-5-sulphonic to examine the collection chromium species, because these ligands form quite stable water-soluble complexes with Cr(III) although they are not actually present in sea water. Both these Cr(III) chelates are stable in sea water at pH 8.1 and are hardly collected with either of the hydrated oxides. The organic chromium species were then decomposed to inorganic chromium(III) and chromium(VI) species by boiling with 1g ammonium persulphate per 400ml sea water and acidified to 0.1mol L⁻¹ of acid with hydrochloric acid. Iron and bismuth, which would interfere in atomic absorption spectrometry, were 99.9% removed by extraction from 2mol L⁻¹ hydrochloric acid solution with a *p*-xylene solution of 5% tri-iso-octylamine. Cr(III) remained almost quantitatively in the aqueous phase in the concentration range 10⁻⁹–10⁻⁶mol L⁻¹ whether or not iron or bismuth was present. However, as about 95% of Cr(VI) was extracted by the same method, samples which may contain Cr(VI) should be treated with ascorbic acid before extraction so as to reduce Cr(VI) to Cr(III).

When the residue obtained by the evaporation of the aqueous phase after the extraction was dissolved in 0.1mol L⁻¹ nitric acid and the resulting solution was used for electrothermal atomic absorption spectrometry, a negative interference, which was seemingly due to residual organic matter, was observed. This interference was successfully removed by digesting the residue on a hot plate with 1ml of concentrated hydrochloric acid and 3ml of concentrated nitric acid. This process had the advantage that the interference of chloride in the atomic absorption spectroscopy was eliminated during the heating with nitric acid.

Boniforti *et al.* [102] compared several preconcentration methods in the determination of metals in sea water. A comparison was made of ammonium pyrrolidinedithiocarbamate-8-quinolinol complexation followed by extraction with methyl isobutyl ketone or Freon-113, coprecipitation with magnesium hydroxide or iron (II) hydroxide or chelating by batch treatment with Chelex-100 for the determination of chromium. Atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry were used for analysis. Interferences, recovery, precision, accuracy, and detection limits were compared. The Chelex-100 resin method was most suitable for the preconcentration of all determinands except chromium, whereas preconcentration of Cr(III) and Cr(V) was achieved only by coprecipitation with iron(II) hydroxide.

The preconcentration of phosphates in seawater is also discussed in section 15.1.8.

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Chapter 16

On-site measurement of anions

This chapter discusses available portable instrumentation that can be carried around by inspectors to carry out measurements for anions on rivers, reservoirs, effluents, etc.

Merck supply a range of test kits covering many different determinands (Table 16.1). Test strips and test kits, both visual and photometric are available and all are suitable for use in the field.

Merckoquant Test Strips

These consist of a reactive test zone firmly bonded to a plastic backing. The test zone is impregnated with reagents, buffers and other substances. The strips are used for rapid exploratory testing of substance concentrations as low as 1mg L^{-1} . To test a sample the test zone is immersed in the water sample for 1–2s and matched against a colour scale.

Aquamerck Test Kits

These consist of titrimetric and colorimetric test kits supplied in boxes or blister packs. The simplest titration tests contain a dropping bottle or precision dropping pipette. The number of drops of reagent required to change the colour of the indicator is a measure of the concentration of the substance being tested for. Aquamerck colorimetric tests incorporate a waterproof scale with precise directions, or alternatively a testing vessel consisting of a 10mm cell with coloured reference blocks to the right and left of it so that a colour comparison can be made.

Aquaquant Test Kits

The aquaquant system for rapid water analysis fully meets the stringent requirements relating to detection sensitivities, ease of use and economy. Each Aquaquant test kit consists of a plastic case containing a sliding colour comparator, which is of a moulded construction designed to hold

Table 16.1 Test kits supplied by Merck

Determination	Measuring range graduation mg L^{-1}	Merckoquant test strips	Aquamerck titrimetric test with dropping	Aquamerck colorimetric test in a blister pack	Aquamerck colorimetric test with colour scale	Aquan colorimetric test te

			<i>bottle or titrating pipette</i>			v
Carbonate	1–100		8048			
Chloride	25–2500/25		11132			
	2–800/2		11106			
	5–300					
	3–300					
	0.4–40					
Chromate	3–100	10012				
	0.005–0.1					
	0.1–1.6					
	0.1–10					
	0.025–2.5					
Nitrite	0.1–10					
	0.03–3					
Phosphate (vanadate- molybdate method)	2.2–29 (P_2O_5) 5.67 (Na_3PO_4)					
	1–40					
	1.5–100					
	0.25–25					
<i>Determination</i>	<i>Measuring</i>	<i>Merckoquant</i>	<i>Aquamerck</i>	<i>Aquamerck</i>	<i>Aquamerck</i>	<i>Aquan</i>
	<i>range</i>	<i>test strips</i>	<i>titrimetric</i>	<i>colorimetric</i>	<i>colorimetric</i>	<i>colorim.</i>
	<i>graduation</i>		<i>test with</i>	<i>test in a</i>	<i>test with</i>	<i>test</i>
	<i>mg L⁻¹</i>		<i>dropping</i>	<i>blister pack</i>	<i>colour scale</i>	<i>te</i>
			<i>bottle or</i>			<i>v</i>
			<i>titrating</i>			
			<i>pipette</i>			
(ammonium heptamolybdate method)	0.1–2.0			14661		
	1–10(P_2O_5)					1
	0.01–0.16					
	0.1–3.0					

	0.024–2.4		
Phosphate	1–10		1
silicate	(P ₂ O ₅) 0.3– 3(SiO ₂)		
Sulphate	200–1600	10019	
	25–300		
	25–300		
	10–600		
Sulphide (lead acetate paper)		9511	
Sulphite	10–500	10013	
2.5–200/2.5		11148	

Source: Own files

test solutions, reagents and accessories as a test is being performed. Short-tube and long-tube test kits are available. The different path lengths allow for lower and higher sensitivities.

Microquant Test Kits

There is often a need for a rapid colorimetric test in a medium sensitivity range roughly equivalent to that covered by the Aquamerck and Aquaquant short tube tests, but which will also permit coloured or turbid samples to be measured. The Microquant tests, which work with transmitted light, are eminently suitable for this type of analysis.

Spectroquant Analysis System

This comprises an SQ 115 digital photometer a TR 205 Thermoreactor for elevated temperature test, 100 and 148°C and the Spectroquant test kits. The SQ 115 photometer measures absorbance and concentration in the range 370–1000nm. The photometer is conveniently calibrated with calibration cells, which incorporate transparent coloured windows to simulate standard solutions of precisely defined concentrations. The inconvenience of calibrating against standard solutions and the unreliability of using calibration factors are thus avoided.

Merck also supply compact laboratories consisting of packs of reagent bottles and accessories. These include the determination of carbonate, nitrite and nitrate.

Palintest Rapid Test Kits

These are available in a visual test form (tablet count, colour match and turbidity tests) or as a spectrophotometric version using the Palintest Photometer 5000 (Table 16.2). Palintest also supply swimming pool and spa test kits for the determination of alkalinity

and calcium hardness (0–1000mg L⁻¹) chloride (0–5000mg L⁻¹), and sulphate (0–200mg L⁻¹), Comparator 2000 and photometer 5000 versions are available.

De Longe Cuvette and Pipette Tests

These are all based on the use of portable spectrophotometers, the LASA Aqua filter photometer for small numbers of water analyses, the LPIW filter photometer for water and sewage analysis and the top-of-the-range Cadas 100 with print-out of results for water and sewage analysis (Table 16.3). The latter instrument covers the spectral range 200–900nm among many others.

Table 16.2 Test kits available from Palintest

<i>Order code</i>	<i>Test</i>	<i>Range</i>	<i>Test method</i>
PS 440	Nitrate	0.2–1.0mg L ⁻¹ N	CM
		0.88–4.4mg L ⁻¹ NO ₃	CM
PS 445	Nitrite	0.05–0.5mg L ⁻¹ N	CM
		0.15–1.6mg L ⁻¹ NO ₂	CM
PS 450	Phosphate	0.80mg L ⁻¹ PO ₄	CM
CS 112	Total alkalinity	0–500mg L ⁻¹	TC
CS 113	Chloride	0–1000mg L ⁻¹	TC
CS 120	Nitrite	0–1500mg L ⁻¹	TC
CS 131	Phosphate limit	30–70mg L ⁻¹	CM
CS 132	Sulphate	0–3000mg L ⁻¹	TU
CS 123	Sulphite LR	0–50mg L ⁻¹	TC
CS 124	Sulphite HR	0–500mg L ⁻¹	TC
PM 179	Fluoride	0–1.5mg L ⁻¹	
PM 175	Molybdate HR	0–100mg ⁻¹ MoO ₄	
PM 163	Nitrate	0–1.0mg L ⁻¹ N	
PM 109	Nitrite	0–0.5-mg L ⁻¹ N	
PM 177	Phosphate	LR 0–4.0mg L ⁻¹	
PM 114	Phosphate	0–100mg L ⁻¹	
PM 154	Sulphate	0–200mg L ⁻¹	
PM 168	Sulphide	0–0.5mg L ⁻¹	

LR=low range, HR=high range

Source: Own files

Table 16.3 De Lange test kits

	<i>Measuring range mg L⁻¹</i>	<i>Method Aqua^a</i>	<i>LASA</i>	<i>LIPWa 100</i>	<i>CADAS^b temperature</i>	<i>Reaction</i>
LCK 311 chloride	1–70	Iron-III-thiocyanate	×	×	×	Ambient
LCK 313 chromium total	0.05–1.0	Diphenylcarbide	×	×	×	Ambient
and hexavalent	0.01–0.25	in analogy to DEVE 10		×	×	and 100° C
LCK 323 fluoride	0.1–1.5	Spadns	×	×	×	Ambient
LCK 315 cyanide	0.01–0.5	Barbituric pyridine in analogy to DIN 38 405 D 13	×	×	×	Ambient
LCK 339 nitrate	3–80	2, 6-Dimethyl phenol in analogy to DIN 38 405 D9	×	×	×	Ambient
LCK 341 nitrite	0.1–3.0 0.01–0.1	Sulphanilic acid/naphtylamine in analogy to DIN 38 405 D 10	×	×	×	Ambient
LCK 049 o- phosphate	5–100	Vanadate molybdate (VMR)	×	×	×	Ambient
LCK 349 total and 0-phosphate	0.1–5.0 0.01–0.5	Phosphomolybdic blue in analogy to DIN 38 405 D 10	×	×	×	Ambient and 100° C
LCK 153 sulphate <i>pipette tests</i>	10–150	Barium sulphate	×	×	×	Ambient
LCW 053 sulphide	0.05–1.0	Dimethyl-p- phenylenediamine in analogy DEV 07	—	×	×	Ambient
LCW 054 sulphite	0.1–5.0	Iodide/iodate	—	×	×	Ambient

Source: Own files

Chapter 17

On-line measurement of anions

On-line process analysers are used throughout the water industry in applications such as the monitoring of rainwater, water in distribution systems, potable water and effluent and sewage treatment processes. A wide range of instrumentation is available from various suppliers. Some instruments determine single parameters and some are multi-parameter instruments. It is convenient to discuss these under separate headings.

Industrial scale on-line instrumentation supplied by Kent Instrumentation Ltd. for the determination of anions (chloride, nitrate, phosphate, ammonia, fluoride and silica) in various types of water are reviewed in Table 17.1. All of these instruments are microcomputer-based and, with the exception of silica, have autocalibration built-in. Generally the sensitivities are adequate for the requirements of the water industry.

In addition Iskra produce an industrial-scale cyanide analyser (model MA 540). This is a sensitive instrument based on the flow electrode measuring cyanide at concentrations down to $1\mu\text{g L}^{-1}$ and, as such, might be of interest in the water industry for cyanide monitoring of effluents or reservoir water. PHOX also supply a digital ammonia monitoring module with auto-clearing.

Some multi-parameter instruments are reviewed in Table 17.2. The Kent System 19 has been specifically designed for use in the water industry. In these systems continuous single-point and multi-stream analytical instruments gather data for data logging or transmission by telemetry to a control station. Control features of this component are the model 7975 multi-parameter water quality monitor which can analyse up to six streams simultaneously and the 8080 series microprocessor. In abstraction from rivers, reservoirs or boreholes, the instrumentation and systems allow raw water to be monitored continuously before and during pumping to the water treatment plant.

Additionally, mobile or permanent water-quality monitoring stations can be supplied to check environmental conditions and either log the data locally or transmit it by telemetry to a central station. The data thus

Table 17.1 Single-parameter microprocessor-controlled on-line industrial anion and cation analysers from Kent Instrumentation Ltd.

Parameter	Samples type	Model No.	Ranges				Accuracy	Description
			Concn. $\mu\text{g L}^{-1}$	Flow	Temp. (°C)	Pressure (lb in ⁻²)		

Anions

Chloride	Boiler water treatment plants	Cabinet version 8024 Panel version 8034	0–100 0–200 0–1000 0–2000 0–5000	2.5– 750ml min ⁻¹	5–45	2–20	±5µg L ⁻¹ or ±5%	Solid-state chloride ion selective electrode and sulphate reference electrode for potentiometric determination of chloride
Nitrate	Potable water Surface waters	8026	0–1000 0–500 500– 1000	0.5L h ⁻¹	5–45	2–20	±5%	Liquid membrane nitrate ion selective electrode
Phosphate	Water quality monitor reservoirs	8086	0–	0.5L	5–55	2–20	±5%	Liquid membrane nitrate ion selective electrode Spectrometric method. Up to 1000 µg L ⁻¹ silica results in positive error of ±2 µg L ⁻¹ phosphate error increasing at higher levels of silica
		Wall mounting	5000mg L ⁻¹	0.5L h ⁻¹	5–50	2–20	±5%	
		8063	0–20mg L ⁻¹	0.5L h ⁻¹	5–50	2–20	±5%	
		Panel mounting 8064	0–10mg L ⁻¹	0.51L h ⁻¹				
Fluoride	Potable water	8081	0.1– 1000mg L ⁻¹	0.5L h ⁻¹	5–55	2–20	±5%	Fluoride-lanthanum chloride ion selective electrode with
Silica	Power generation industry	Cabinet mounting 8061 Panel mounting 8062	0–50 0–200 0–500 0–1000 0–2000	6ml min ⁻¹	5–0	2–20	±2...g L ⁻¹ or ±2%	calomel reference electrode sodium hexametaphosphate sodium chloride reagents added suppress aluminium and iron Spectrophotometric ascorbic acid–H ₂ SO ₄ –ammonium citric acid. Reduction up to 5mg L ⁻¹ phosphate causes positive error of <2 µg L ⁻¹ silica 30mg L ⁻¹ phosphate results in positive error of 4 µg L ⁻¹

Source: Own files

Table 1 7.2 Multi-parameter industrial instrumentation

<i>Type of sample</i>	<i>Supplier</i>	<i>Model No</i>
Raw water ex rivers, boreholes and reservoirs	Kent Industrial Measurements	System 19 instrumentation package for determining nitrate, ammonia, chloride, silica, fluoride and phosphate
Potable water treatment	Kent Industrial Measurements	Nitrate fluoride, ammonia
Effluent and sewage treatment	Kent Industrial Measurements	nitrate
Distribution water, water towers, etc.	Kent Industrial Measurements	nitrate
Surface water, water treatment, potable water, sewage effluent, sea water	Skalar	SA9000 on-line process analyser, alkalinity, chloride, total cyanide, nitrate, nitrite, silica, sulphate, sulphide
Waste water treatment processes	Skalar	Series 8 1 00 process analyser, chloride, fluoride, nitrite, phosphate, bromide, nitrate, sulphate, silica

Source: Own files

gathered can be used for control intervention and the generation of reports on, for example, the effects of long-term abstraction.

Both before and during raw water treatment, the instruments and systems play an important role in helping to ensure the quality of the drinking water supply.

A wide range of standard discrete monitoring and control products are offered, many of which are also available in System 19 rack-mounting form for compact and economical installation.

These are ably complemented by other, more specialised equipment and systems for both analytical and water treatment applications, to meet the exacting requirements of the industry.

Kent Instruments and systems and water meters are widely used throughout the water distribution network in pipelines, water towers, reservoirs and so on.

In recent years a variety of microprocessor-based and computer-compatible add-on systems have been developed to provide hard data on leakage control, water distribution and other useful analyses.

The System 19 instrumentation and systems can be found in all areas monitoring the outfalls from industrial processes, in rivers and at the treatment plant itself.

From individual monitors to complete on-line systems, these analysers are deployed throughout many treatment processes to improve efficiency and ensure effective treatment as well as to protect the environment and ultimately the drinking water supply.

The Skalar SA 9000 on-line process analyser is available in two models—as a free-standing unit complete with its own storage section for reagents or as a unit which may be bench or wall mounted or built into an even more comprehensive control system. The main unit consists of the on-line analyser, in which the analysis of the process stream is fully automated. The analysis process is based on the automated addition of sample to reagents which form a coloured complex under controlled conditions. The complex is measured photometrically. The signal is fed into the microprocessor which offers the flexibility for the specific application. Sampling is carried out directly from the process stream.

For analysing the same process stream component from several sources, a multi-stream attachment can be supplied. For samples carrying suspended particles, a special continuous in-line filter system is available. Calibration valves allow the introduction of standards and blanks for automatic calibration. Some applications of the SA-9000 analyser are shown in Table 17.3.

The Dionex series 8100 process analyser employs ion chromatography, high performance liquid chromatography, or flow-injection techniques for the on-line determination of a variety of constituents in process streams. This is a modular instrument which can be modified should processing needs change (Fig. 17.1).

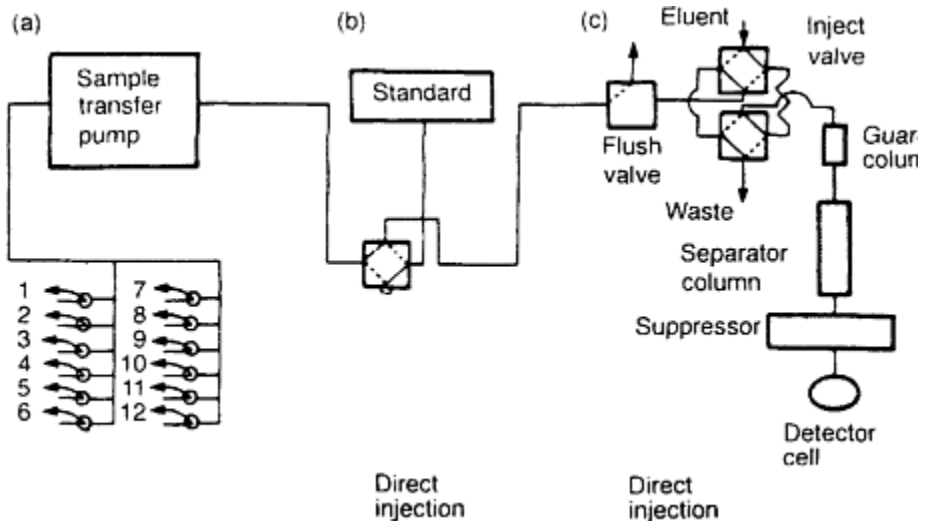


Fig. 17.1 Flowchart: Dionex series 8100 process analyser: (a) sample selection module—up to 18 sample points, continuous or sample on demand, non-metallic, NEMA 4 enclosure; (b) sample preparation module: dilution, reagent addition, standard preparation, preconcentration, matrix elimination; (c) chromatography hydraulics module: ion chromatography, high performance liquid chromatography, flow

injection analysis

Source: Own files

Table 17.3 Applications of Skalar SA-9000 on-line process analyser

<i>Process stream component</i>	<i>Surface water</i>	<i>Water treatment</i>	<i>Potable water</i>	<i>Boiler water</i>	<i>Cooling water</i>	<i>Condensate</i>	<i>Sewage effluent</i>	<i>Sea water</i>
Chloride	•		•		•	•	•	•
Chromium	•		•		•			
Cyanide (free)	•		•				•	
Cyanide (total)	•		•				•	
Fluoride	•							•
Nitrate	•		•				•	•
Nitrite	•		•				•	•
Phosphate	•		•	•			•	•
Silica	•			•	•	•		
Sulphate	•		•				•	
Sulphide							•	

Source: Own files

Chapter 18

Sample preservation prior to analysis

18.1 General discussion

Aqueous solution of some anions eg chloride and sulphate are quite stable (ie do not undergo decomposition) when stored up to one month at ambient temperatures. However, it is necessary to consider what happens if the sample also contains a further anion which upon storage decomposes to produce additional amounts of the anion of interest. For example, if a sample which is required to analyse for sulphate also contains sulphide, polysulphides, sulphite, thiosulphate, dithionate, polythionates then it is certain that the true initial sulphate content of the sample at the moment of sampling will not be obtained even if the sulphate analysis is carried out within 1h of the sample being taken. A similar situation would exist for a sample in which it is required to determine chloride but which also contains anions such as chlorite, chlorate and hypochlorite and possibly perchlorate.

In such circumstances the best that can be done is to analyse the sample by ion chromatography for the anions of interest and all other likely interfering anions within 1h of the sample being taken.

Williams [1] for example, has published an ion chromatographic method capable of resolving for different sulphur containing anions which can be detected by placing an ultraviolet and electrical conductivity detector in series after the elution column.

The retention times are as follows:

	<i>Retention time min. Detection</i>
Sulphide	2.4 UV 205nm
Sulphite	3.8 EC
Thiosulphate	12.6 UV 195nm
Sulphate	22.8 EC

Similarly, the following chlorine-containing anions could be determined in a single run:

	<i>Retention time min. Detection</i>
Chloride	4.6 UV 192nm
Chlorite	3.0 UV 195nm
Chlorate	15.2 UV 195nm
Perchlorate	19.6 EC

Dionex Corporation [2] have issued an ion chromatographic method capable of resolving the following phosphorus-containing anions in natural waters: phosphate, pyrophosphate, tripolyphosphate and tetrapolyphosphate with retention times, respectively, of 3, 7, 10 and 14min.

The advantage of this approach is that by analysing a sample at timed intervals after the sample was taken it is possible to gain information on any changes occurring in the composition of the sample, to observe particular anions decreasing in concentration and possibly to observe an increase in concentration in new anions produced by time-dependent reactions in the sample. By plotting observed concentrations versus time interval since sampling it may be possible to deduct the concentration of a particular anion at time zero, ie at the moment the sample was taken.

Very often such considerations as these do not apply and the analysis can be carried out within a few days of the sample being taken without interference effects occurring. This would apply in the case of nitrite, nitrate, chloride, fluoride, phosphate, sulphate, perchlorate, borofluoride, ferrocyanide, silicate and borate; also many metal-containing anions (molybdate, uranate, vanadate, titanate, tellurate, germanate and tungstate) and also many of the organic anions.

Anions which can change during sample storage by, for example, aerial oxidation by dissolved oxygen in the sample include iodide, bromide, bromate, iodate, polysulphide, sulphide, dithionate, polythionates, cyanate, thiocyanate, arsenite and possibly carbonate and bicarbonate. In general for the analysis of these anions the original paper should be referred to, and certainly, the interval between taking the sample and carrying out the analysis should be minimal. The original paper should also discuss the need or otherwise for a preserving agent to be present in the bottle at the moment of sampling. Unfortunately many published methods do not publish this detail and in some instances are thereby invalidated.

It is necessary to go to the leading workers in the field to obtain reliable recommendations regarding sample preservation. Thus, the US Environmental Protection Agency [3] has published a list of sampling preservation and holding times for several common anions, when sampled into scrupulously clean glass or polyethylene bottles.

<i>Analite</i>	<i>Preservation</i>	<i>Holding time</i>
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate	Cool to 4°C	48h
Nitrite	Cool to 4°C	48h
o-phosphate	Filter and cool to 4°C	48h
Sulphate	Cool to 4°C	28 days

Available information on the preservation of particular anions is reviewed below.

18.2 Chloride

No preservation is required. The sample can be held for up to 28 days after sampling. Sample bottles, made of glass or plastic must be halide free. In particular, high density polyethylene containers must not be employed as these are likely to contain traces of water extractable chloride ions. Low density polyethylene is suitable.

No preservative is needed for the chloride itself. If prevention of decomposition of other sample components is necessary, hydrochloric acid, chlorides and disinfectants containing halogens, mercury or silver must not be used for preservation of the sample.

18.3 Sulphate

Samples may be collected in glass or polyethylene bottles and should be analysed within 6h of collection according to one authority [4] and 28 days of collection according to another authority [3]. Samples under anaerobic conditions should not be stored at 4°C for more than 2 days [4]. Samples low in organic matter may be kept for longer periods, but tests should be carried out to ensure that samples are sufficiently stable. To eliminate the risk of air oxidation to sulphate of samples containing sulphide or sulphite, sample bottles should be filled to exclude air. A settled unfiltered sample may be taken for sulphate determination if desired. Alternatively, samples containing suspended matter should be filtered through a well washed glass fibre filter capable of retaining particles of over about 1µm size before analysis. If the sample is to be analysed by direct barium titrimetry, its pH should, before analysis, be adjusted to 6–8 by addition of dilute hydrochloric acid or sodium hydroxide.

18.4 Nitrite and nitrate

18.4.1 *Estuarine waters*

Biological instability of samples can be due to bacterial oxidation of ammonia to nitrite which can be further oxidised to nitrate and, also, denitrification whereby nitrate is reduced to nitrite and then to nitrogen gas. Both of these mechanisms will produce changes in the content of oxidised nitrogen or nitrite.

To overcome instability the samples are filtered on collection and stored frozen in polyethylene bottles. Before analysis, they are completely thawed out and mixed and, if the total analysis time is to exceed 1 day 1ml chloroform added per litre of sample. The samples should be stored at 4°C between analyses.

18.4.2 *Non saline waters*

In the case of anaerobic bacteria-free samples no pretreatment of the sample is needed other than an initial suitable dilution if the concentration is greater than 50mg L⁻¹ total

oxidised nitrogen or 1mg L^{-1} of nitrite.

In certain circumstances however, nitrite may undergo either reduction or oxidation with some rapidity in certain types of sample. It may also be formed either by reduction of nitrate or oxidation of ammonia. Stringent precautions are necessary when nitrite is to be determined, when nitrate is present in significant concentrations or when nitrate alone is to be determined in the presence of a significant concentration of nitrite.

Samples should be collected in glass bottles and must be analysed as soon as possible after collection. Tests should be carried out on each par-ticular sample type to determine the maximum acceptable delay between sampling and analysis. No reliable preservation method is known.

When the nitrite concentration is insignificant, samples may be collected in glass or hard polyethylene bottles and should be analysed as soon as possible. When delays in analysis are inevitable, storage at 4°C may improve stability. Allow the samples to warm to room temperature before analysis. Preservation may be affected by addition of sufficient preservative solution (1% phenyl mercuric acetate in 20:80 v/v methanol:water) to give an overall concentration of 0.1% v/v. Tests have shown that the nitrate concentration of raw and potable water is thus stabilised for at least four weeks. However, tests should be carried out to verify the stability of other types of sample.

If the samples are to be analysed using ultraviolet spectroscopy [21], this form of preservation may be unacceptable because of the interference arising. However, addition of exactly equivalent amounts of preservation solution to all standards and samples will allow correction of the interference, although with an increase in the limit of detection.

Table 18.1 Results of stability tests for total oxidised nitrogen

Results in mg N/L

Lab No.	Time T (hours)	Sample concn	Stability target	Change in sample concentration			
				after T/4		after T	
				Mean	(Max 95% confidence limit)	Mean	(Max 95% confidence limit)
2	30	1.9	0.10	0.010	0.098	-0.053	-0.074
3	24	1.75	0.088	-0.013	-0.0998†	0.0 II	0.086
3	24	1.98	0.099	0.010	0.0408	-0.011	-0.094
6	24	4.82	0.24	-0.040	-0.064	-0.080	-0.102
7	48	8.4	0.42	-	-	-0.012	-0.126
8	48	5.2	0.26	0.013	0.064	-0.018	-0.057
8	48	1.1	0.055	0.037	0.062*	0.016	0.041
10 ^a	48	2.7	0.14	-0.015	-0.049	-0.035	-0.061

10 ^a	48	4.0	0.20	-0.019	-0.056	-0.021	-0.050
11	31	1.9	0.10	-0.003	-0.010	0.12*	0.175*
11	31	5.3	0.26	0.15	-0.32†	0.13	-0.30†

*exceeds target (either mean change or λ max poss change)

†exceeds target but inadequate power in test

^aLaboratory 10 performed the second analysis at time T/2.

Time T was chosen in each laboratory to be the maximum time between sampling and analysis which is routinely encountered

Source: Reproduced with permission from the Water Research Centre, UK [5]

A study has been reported [5] of stability tests of solutions containing nitrate and nitrite.

Briefly, the tests involved the analysis of a sample on three occasions—one as soon as possible after sampling and subsequently, after intervals chosen to represent the likely periods for which the sample may be transported and stored.

The tests of sample stability were designed with the objective of demonstrating that any change in determinand concentration between sampling and analysis should not be greater than a target maximum instability. These targets were set as half of the target for maximum possible bias in analytical results which had been agreed for each determinand. The results of these tests have been evaluated with respect to the following guidelines.

The maximum (95% confidence) instability, or change in determinand concentration, observed during the period of storage under consideration should not be greater than the stability target. In the case of total oxidised nitrogen and nitrite, this target is 0.025mg N L⁻¹ or 5% of the determinand concentration in the sample, whichever is the greater.

Table 18.2 Results of stability tests for nitrite nitrogen Results in mg N L⁻¹

Lab No.	Time T (hours)	Sample concn	Stability target	Change in sample concentration			
				after T/4		after T	
				Mean	(Max 95% confidence limit)	Mean	(Max 95% confidence limit)
2	30	0.06	0.025	-0.017	-0.025	-0.015	-0.021
3	24	0.00	0.025	0.00	0.00	0.0095	0.0106
3	24	0.025	0.025	0.00	0.00	0.0015	0.0043
6	24	0.022	0.025	0.002	0.006	0.005	0.013
6	24	0.047	0.025	0.002	0.003	0.003	0.003
8	48	0.013	0.025	-0.002	-0.002	0.0002	0.0007
8	48	0.08	0.025	0.0007	0.0015	-0.0025	-0.004

9	96	0.34	0.025	-0.0035	-0.010	-0.006	-0.012
9	96	0.08	0.025	-0.002	0.07†	0.0008	0.065†
10 ²	48	0.022	0.025	-0.0005	-0.001	-0.0005	-0.0013
10 ^a	48	0.112	0.025	0.0001	0.0026	-0.0027	-0.0046
11	31	0.014	0.025	-0.0005	-0.0034	0.002	0.006
11	31	0.015	0.025	0.004	0.009	0.023	0.028*

*exceeds target (either mean change or max poss change)

†exceeds target but inadequate power in test

^aLaboratory 10 performed the second analysis at time T/2

Time T was chosen in each laboratory to be the maximum time between sampling and analysis which is routinely encountered

Source: Reproduced with permission from the Water Research Centre, UK [5]

The results of the tests are shown in Tables 18.1 and 18.2. No precautions, other than refrigeration (employed by all laboratories except Laboratory 2) were taken to preserve the samples. The samples were analysed to establish the initial determinand concentration within 1h of being collected. Each laboratory then performed an analysis after times T/4 and T hours, where T was chosen as the maximum time between sampling and analysis in that laboratory. For some determinands, tests were performed on two samples in a given laboratory. All laboratories used sample containers of glass except Laboratory 6, which used polyethylene bottles.

Total oxidised nitrogen

From a possible 21 sample/storage time combinations there were five instances, involving four samples, of failure to demonstrate adequate stability. Of these, one was for a mean change in concentration; one was for maximum possible instability greater than the target (with adequate power); and the remaining three were instances where the power of the test was insufficient.

The indication is that, in most cases, samples are adequately preserved. The observed change in concentration observed for the unrefrigerated sample (Laboratory 2) did not exceed the target.

Nitrite

From a possible 26 sample/storage time combinations, there were three instances of failure to meet the target. Of these, two were almost certainly due to lack of power in the tests and the remaining one was marginal.

The evidence is that sample preservation for nitrite is satisfactory though the results for the unrefrigerated sample suggest that refrigeration is desirable.

18.5 Phosphate

There are two approaches to the preservation of samples for phosphate analysis.

18.5.1 Phosphate content in the range up to 0.4mg L^{-1}

Glassware for sampling should be cleaned and allowed to stand overnight filled with sulphuric acid (density 1.84g mL^{-1}), then rinsed several times with water and stored filled with water. On no account should the glassware be allowed to come into contact with detergents or alkaline liquids. This acid hardening treatment need only be repeated occasionally.

Phosphate is readily adsorbed on to a plastic surface (see section 18.4.2) and for this reason, good quality borosilicate glass containers are preferred. They should be conditioned as described above and stored in a dark cool place. The use of plastic containers for samples in the higher phosphate concentration range may be acceptable. Some losses may occur, but they may be small in relation to the phosphate present. Ideally, waters should be analysed as soon as possible after sampling as there is no generally satisfactory method of preservation. Refrigeration (but not freezing) is reasonably effective after short periods of storage, eg a few days.

Some samples may require filtering on site to ensure that changes are not occurring during transit and storage.

The determination of orthophosphate, pyrophosphates and poly-phosphates (ie condensed phosphates) and organophosphates has been discussed [6].

Interference effects in phosphomolybdenum blue methods for phosphate

There is little detailed information concerning the effect of interfering substances on the method. Generally, no important interference problems are likely with unpolluted saline and fresh waters; but the effect of interferences should be considered particularly in polluted samples and at very low phosphate levels. The most likely sources of interferences and implications are discussed below with references, and by Burton [7] who also highlights other problems associated with the analysis of phosphorus compounds.

Arsenic

Arsenic present as arsenate causes serious interference in the method. The extent of interference is time dependent because the colour of the arsenomolybdate develops slowly. However, as a guide 0.025mg L^{-1} As may give a response equivalent to about 0.015mg L^{-1} P (40ml sample volume).

Silicon

The method will tolerate 10mg L^{-1} of silicon present as silicate [8] but high silicon/phosphorus ratios in samples where the phosphate level is very low may cause significant errors.

Chromium

Cr(VI) is reported to interfere at 1mg L^{-1} level [9].

Oxidising agents

The action of oxidising agents in this method is complex. They may destroy the reducing

agent, or subsequently reoxidise the phospho-molybdenum blue.

Nitrite

A concentration of 1mg L^{-1} N (as nitrite) may be tolerated in the presence of 0.1mg L^{-1} phosphorus but the interference of nitrite is both complex and variable and appears to be related to exposure to the air.

Nitrate

Nitrate nitrogen may be tolerated up to 20g L^{-1} (as N) provided that the absorbance is measured within 2h of colour development.

Sulphide

Interference from sulphide is complex, variable, and, dependent on conditions, reacting with both antimonate and molybdate. Complete removal is advocated (by oxidation to sulphate or by aspiration with nitrogen) [10].

Removal of interferences

There is no single pretreatment that will systematically deal with all interference problems. There are, however, certain processes that will have a selective effect and the analyst must use his discretion in their application.

The effect of oxidising agents and arsenate may be overcome by treatment with an excess of metabisulphite/thiosulphate in acid solution [11]. The presence of sulphur dioxide has no influence on the final production of molybdenum blue, but the treatment can only be applied to determinations of inorganic phosphorus and total phosphorus, ie where hydrolysis is acceptable, as opposed to the determination of dissolved reactive phosphorus.

A slight excess of sulphamic acid [12,13] is effective in breaking down nitrite; 100mg of the acid will deal with a nitrite concentration of 10mg L^{-1} N in a 40ml aliquot of test solution.

A solvent extraction procedure [14] that is also effective in reducing certain interferences by virtue of the dilution effect is described in section 18.4.2.

18.5.2 Phosphate contents in oligotrophic waters in the range up to $25\mu\text{g L}^{-1}$

In this method the phospho-molybdenum blue complex is formed and the colour extracted into a small volume of n-hexanol [6]. Because of the extreme sensitivity of the method and of phosphate losses by adsorption on glass sampling bottles, the samples in this method are collected in iodised polyethylene bottles.

Low density polyethylene or nylon (babies feeding type) bottles are suitable but high density polyethylene or polypropylene bottles are not. The plastic bottles must be treated with iodine to prevent the adsorption of phosphorus which can lead to significant errors.

Iodisation procedure [15]

Remove any rubber washers from the bottle caps and place a small quantity of iodine (about 0.1g) in the bottle. Replace the cap and store at 60°C for long enough to ensure uniform absorption of iodine (usually 24h) during which time the bottle should be rotated

and more iodine added if necessary.

Place the bottles in a well ventilated fume cupboard and remove the screw caps. Expel iodine vapour by squeezing the bottle gently. Rinse the bottle with a little ethanol and drain.

Wash the bottle by repeated filling with water at daily intervals until the iodine content of the water is reduced to the extent that the absorbance of the water at 680nm is not greater than that of water stored in untreated bottles.

When not in use store the bottles in the dark filled with water.

Where the major requirement is to measure 'dissolved reactive phosphate' in samples containing less than $25\mu\text{g L}^{-1}$ P either:

- (a) filter the sample 'on site' through a glass fibre paper, pre-washed with about 500ml of water [15], into a plastic bottle and analyse within 3h of sampling; or if this is not possible—
- (b) filter the sample through a pre-washed glass fibre paper [15] within 3h of sampling into an iodised bottle and store in the dark at, or close to, 4°C

NOTE. If the filtration pressure is too high or if the sample is allowed to freeze, changes of dissolved phosphate concentration may result from biological cell rupture and the release of phosphate into the solution.

'On site' filtration may be mandatory depending upon which forms of phosphate are to be measured. In this respect it should be noted that the insoluble phosphate content of an unfiltered sample can increase due to the continuation of zooplankton activity to give deposits containing phosphate in the sample.

In addition to filtration discussed above it may be necessary to consider whether the special requirements of freshwaters with an oligotrophic nature indicate the need for digestion of low levels of 'total phosphorus'.

Rossin and Lester [16] evaluated some of the methods available for the preservation of condensed phosphates in samples of domestic waste waters, ie the prevention of the hydrolysis of condensed phosphate to orthophosphate. They showed that mercuric chloride at 40mg L^{-1} at normal pH is the most effective preservative examined for samples stored at 20°C for 6 days (Table 18.3). Samples should be filtered as soon as possible after they have been taken. Mercuric chloride at high pH was not a satisfactory preservative. Addition of sodium hydroxide to raise the pH increases phosphatase activity but lowers the rate of spontaneous hydrolysis and, on balance, is not a satisfactory treatment. Formaldehyde at elevated pH was less efficient than mercuric chloride at normal pH.

The samples treated with mercuric chloride at normal pH presented the smallest difference from the mean with a range between -0.07 and $+0.06$. When formaldehyde was used at high pH, the range was between -0.16 and 0.00 . The samples containing mercuric chloride at pH 10 showed a range between -0.15 and $+0.21$. A variation between -0.21 and $+0.35$ was found when pH was increased in the filtered samples. The use of formal-dehyde at normal pH resulted in a variation between -0.25 and $+0.34$.

Table 18.3 Concentration of orthophosphate in settled sewage samples, filtered and unfiltered, with different preservatives, analysed at different times

Sample		Orthophosphate as P mg L ⁻¹ after storage				
		0	1 day	3 days	6 days	Mean
Settled	unfiltered	5.26	5.96	6.33	6.63	–
Sewage	filtered	4.28	4.20	4.48	4.74	4.43
	D.M. ^a	–0.15	–0.23	+0.05	+0.31	
Settled	unfiltered	4.19	5.35	6.04	6.44	–
Sewage	filtered	4.19	4.03	4.14	4.59	4.24
pH 10	D.M. ^a	–0.05	–0.21	–0.10	+0.35	
Settled	unfiltered	4.89	4.77	5.34	5.85	–
Sewage	filtered	4.09	4.16	4.14	4.24	4.16
HgCl ₂	D.M. ^a	–0.07	0.00	–0.2	+0.06	
Settled	unfiltered	5.11	5.24	5.49	5.53	–
Sewage	filtered	3.56	3.54	3.76	3.90	3.69
HgCl ₂ +pH 10	D.M. ^a	–0.13	–0.15	+0.07	+0.21	
Settled	unfiltered	5.00	5.52	6.20	6.48	–
Sewage	filtered	4.15	4.16	4.54	4.74	4.40
Formaldehyde	D.M. ^a	–0.25	–0.24	+0.14	+0.34	
Settled	unfiltered	5.11	5.43	5.43	5.46	–
Sewage	filtered	3.84	4.09	4.04	4.00	4.00
Formaldehyde						
pH 10	D.M. ^a	–0.16	+0.09	+0.04	0.00	

^aD.M.=deviation from the mean concentration in filtered samples

Source: Reproduced with permission from Sulpher Ltd., Chiswick, UK [16]

18.6 Sulphide

Samples for sulphide determination must always be fixed immediately after sampling. Any sized bottle can be taken, but normally a 200ml bottle is convenient. As the stabilised sample is a glutinous suspension and the use of the whole sample is recommended, it is best to measure the volume of sample poured into the bottle. The bottle neck should be sufficiently wide to allow for adequate policing (not with rubber) if necessary. When stoppered, it should be airtight. If multiple determinations are made to

increase accuracy, the taking of several separate samples may be considered as an alternative to aliquotting. The fixing process is as follows [17].

Place the sample carefully, with a minimum of aeration, in a bottle until it is almost full. Add 2.0 ± 0.1 ml of 0.75M sodium carbonate, mix, and then add 2.0 ± 0.2 ml 0.5M zinc acetate per 100ml sample and mix again.

The whole sample is normally taken for analysis, but if volatile organic compounds are present, the sample can be centrifuged or filtered and the solid portion retained. If only part of the sample is taken for analysis special attention must be paid to thorough mixing before removing the portion to be analysed.

It has been found that the presence of a large amount of suspended matter (10mm on bottom of bottle) in the sample reduces the effectiveness of the preservatives. This was due to anaerobic bacterial action within the settled solid.

The stabilised sample is stable for up to 5 days.

18.7 Fluoride

No sample preservation is needed. Samples can be stored for up to 28d without risk of losses.

18.8 Cyanide

In a sample preservation procedure described by Csiki and Barnard [18] 600ml of a wastewater sample is transferred to a well-rinsed screwcap polyolefin bottle and stabilised by adding 5ml of 50% sodium hydroxide solution (this sample can be stored for several weeks without significant change in the total cyanide content). To remove sulphide, 600ml of the well-mixed sample is transferred to a 1L beaker containing a magnetic stirring bar. 0.2g of cadmium carbonate is added and the solution stirred for a few minutes. If a yellow precipitate forms, the cadmium carbonate addition collected is repeated until no yellow precipitate is observed. The solution is filtered promptly through paper and 500mL collected in a graduated cylinder.

18.9 Chromate and dichromate

Stollenwerk and Grove [19] investigated the effect on the concentration of hexavalent chromium of sample preservation techniques. Acidification of samples could reduce hexavalent chromium to the trivalent form. The rate of such reduction was increased by impurities such as nitric oxide present in nitric acid. Organic matter could also accelerate reduction of hexavalent chromium in acidified samples, and could also reduce the chromium even in unacidified samples. The best method for preserving hexavalent chromium involved filtration and cooling of the sample. Storing the sample at 4°C might preserve the concentration of hexavalent chromium for some time, depending on the reactivity of other constituents in the sample, but should not be relied on. Measurement of

total chromium is recommended as a method of checking on chromium reduction.

18.10 Selenate and selenite

Cheam and Agemian [20] studied the preservation and stability of inorganic selenium compounds at $\mu\text{g L}^{-1}$ levels in non saline water samples. They adopted the use of sulphuric acid as the preserving medium as this was found not to interfere with the hydride generation method they adopted for the determination of arsenite and arsenate. They found that the use of polyethylene sample containers and pH adjustment to 1.5 (with 0.2 vol.% sulphuric acid) provided optimal conditions for the preservation of samples for periods of up to 125 days. Storage at 4°C also preserves samples effectively over the same time span.

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