Sulphate In Waters, Effluents And Solids (2nd Edition) 1988

Methods For The Examination Of Waters And Associated Materials

Her Majesty's Stationery Office

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Methods For The Examination Of Waters And Associated Materials

This booklet contains seven methods only two of which are almost unchanged from the first edition. The principle of a third method is also unchanged. For information on applications see the Introduction.

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About This Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods and notes being issued when necessary.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users—the senior technical staff to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has 9 Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage Works Control Methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee.

The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R PITTWELL
Secretary and Chairman

11 August 1988

Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field Operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use. Lone working, whether in the laboratory or field, should be discouraged.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete check-list, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', issued by the Royal Society of Chemistry, London: 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Service Monograph 6, HMSO, London.

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Introduction

0.1 Sulphate is ubiquitous and its estimation in many types of water and solids is frequently required. An appropriate method should be selected from the table below in accordance with the type of sample, expected sulphate concentration and probable interferences. This booklet contains methods using different types of apparatus.

Three tentative methods from the first edition (1979) have been withdrawn. The indirect EDTA titrimetric and indirect barium-AAS procedures have been found to give some unreliable results. The manual aminoperimidine colorimetric method has been superseded by the more reliable automated version. In addition, two other methods were considered but rejected as being not sufficiently reliable. These were the automated chloranilate colorimetric procedure and the manual barium sulphate turbidimetric method.

The recommended usage is as follows:

Method	Sample Types	Range mg/L SO_4^{2-}	Major Interferences	Use
A. Barium Sulphate Gravimetric	All types of water and solid samples which have been brought into solution	10–5,000	Chromate, phosphate, nitrate, iron and calcium, see Section A3	Reference method of analysis
B. Thorin Titrimetric	All types of water	30–200	Some anions and highly coloured samples, see Section B3	Rapid control analysis
C. ICPS	Raw, potable and saline waters	0.1–1,000	Sulphide, sulphite and calcium, see Section C3	Routine analysis
D. Automated Aminoperimidine Colorimetric	Raw, potable and waste waters	5–200 or 5–500	Sulphite, sulphide, phosphate, tin, arsenic and free chlorine, see Section D3	Routine analysis
E. Flow-injection Turbidimetric (Automated Discrete Analysers may also be used)	Raw and potable waters	10–200	Carbonate, bicarbonate and chloride, see Section E3	Routine analysis
F. Ion chromatographic	Raw, potable and saline waters	0.1–100	Substances which chromatograph with sulphate, see Section F4	Routine analysis
G. Automated Methylthymol Blue Colorimetric	Raw, potable, waste and saline waters	2–100	Coloured or highly turbid samples, see Section G3	Routine analysis

0.2 Through these methods, sulphate is always expressed as sulphate ion SO_4^{2-}.

0.3 The efficiency of the ion exchange media used in some of the following methods for a given reaction is dependent on the resin and on the operating conditions, such as bed volume and contact time used. Mention is made of the resin used in obtaining the test data. This in no way endorses this material as superior to other similar materials. Any equivalent resin may be substituted, provided it has a similar performance to the resin cited. Similarly, the instruments used in obtaining test data for methods C and F are mentioned; again, any equivalent

instruments are suitable and no endorsement is intended. The test data will not necessarily be as quoted, if changes are made.

0.4 The colorimetric (D and G) and turbidimetric (E) methods in this booklet can be adapted for use on discrete analysers (1).

Reference

(1) *Discrete and Air Segmented Automated Methods of Analysis including Robots. An Essay Review. 2nd Edn. 1988.* HMSO, in this series.

A Sulphate in Waters, Effluents and Some Solids, by Barium Sulphate Gravimetry

A1 Performance Characteristics of the Method

(For further information on the determination of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series.)

A1.1	Substance determined:	Sulphate ion
A1.2	Type of sample:	All types of water including sea water and most industrial effluents
A1.3	Basis of method:	A gravimetric method in which sulphate is precipitated as barium sulphate $BaSO_4$
A1.4	Range of application:	10–5,000 mg/L
A1.5	Standard deviation (a) (on synthetic solutions of sodium sulphate):	Sulphate concn mg/L SO_4^{2-} / Sample aliquot mL / Total SD mg/L SO_4^{2-} 50 / 200 / 3.3 1,500 / 20 / 21.5 5,000 / 10 / 29.4 (All with 9 degrees of freedom)
A1.6	Limit of detection (a):	10 mg/L SO_4^{2-} (With 9 degrees of freedom)
A1.7	Gravimetric factor:	$\frac{SO_4^{2-}}{BaSO_4} = 0.4115$
A1.8	Solubility of $BaSO_4$:	2.4 mg/L at 20°C
A1.9	Bias (a):	None detected
A1.10	Interferences:	Chromate, nitrate, iron, phosphate and calcium may interfere; for details see Section A3
A1.11	Time required for analysis (a):	For a batch of 10 samples Operator time—about 4 h Total analytical time—about 20 h

(a) The data quoted were obtained at Imperial Chemical Industries Limited, Mond Division, Research Department. Similar data were obtained at other laboratories.

A2 Principle

A2.1 The method as described is a gravimetric procedure suitable for sulphate determination in all types of water including sea water and industrial effluents. It should be directly applicable to most raw and potable waters and sea water with little risk of significant interference (see Section A3).

A2.2 The test portion of sample is neutralised, if necessary, and sufficient hydrochloric acid then added to make the solution about 0.05 M. The solution is boiled and any material remaining, after boiling, is filtered off.

A2.3 The filtered solution is boiled, an excess of hot barium chloride solution is slowly added and heating is continued for 2 hours on a boiling water-bath to allow the

barium sulphate precipitate to recrystallise, thereby reducing errors due to co-precipitation. Stand overnight; the precipitate is then filtered on a tared crucible (porosity 4), washed free from chloride and the crucible is dried at 105°C and reweighed when cool. The increase in weight of the crucible is due to $BaSO_4$.

A3 Interferences

Barium sulphate exhibits a marked tendency to carry down other salts (co-precipitation). This effect is reduced in this method by the slow addition of hot barium chloride solution and careful digestion of the precipitate. Of the constituents which may be present in waters and effluents, chromate, nitrate, phosphate, iron and calcium interfere although limited concentrations of these can be tolerated. Pre-concentration of the sample, by boiling down, should be avoided but provided the amount of any of these impurities present in the volume of test sample taken for the determination does not exceed the value quoted below, then no significant interference is likely.

Chromate (as CrO_4^{2-}) 10 mg	Nitrate (as NO_3^-) 1,000 mg
Phosphate (as $POSO_4^{3-}$) 10 mg	Calcium (as Ca^{2+}) 2,000 mg
Iron (as Fe^{3-}) 50 mg	

Sulphide and sulphite may interfere in the sulphate determination but only if samples are unduly exposed to air and oxidation to sulphate occurs. This effect may be minimised by observing the precautions detailed for sample collection and preservation (Section A7). The interference from sulphide and sulphite is overcome whilst boiling the sample with acid, removing hydrogen sulphide and sulphur dioxide respectively, before barium chloride is added to precipitate sulphate. For high concentrations of sulphides and/or sulphites, the reverse acidification procedure given in A8.2a can be used.

The solubility of barium sulphate in water is 2.4 mg/L at 20°C and increases in the presence of mineral acids because of the formation of the bisulphate ion (solubility in 0.1 M hydrochloric acid is 10 mg/L). The solubility is reduced in the presence of a moderate excess of barium ions and under these conditions is negligible in 0.05 M hydrochloric acid. The use of this acid concentration reduces interferences due to chromate, carbonate and phosphate and yields a precipitate of large crystals which is therefore more easily filtered.

A4 Hazards

Barium chloride is a schedule 1 poison and should be handled with care. Eye protection should be worn and fumehoods used when handling ammonium hydroxide (d_{20} 0.88) (as in Section A5.4). Should any ammonia solution get into the eye, wash thoroughly at once and obtain medical attention immediately stating that the injury is due to strong ammonia.

A5 Reagents

Use analytical grade reagents and distilled or deionised water throughout.

A5.1 50% V/V Hydrochloric acid

Dilute 500±10 mL of hydrochloric acid (d_{20}1.18) with water to 1 litre.

A5.2 10% m/V Barium chloride dihydrate

Weigh out 100±1 g of barium chloride dihydrate and dissolve by warming in about 850 mL of water, cool and dilute with water to 1 litre. (This reagent is toxic, see Section A4).

A5.3 0.1% m/V Methyl orange indicator

Weigh out 0.10±0.01 g of methyl orange and dissolve by warming in about 60 ml of water, cool and dilute with water to 100 mL.

A5.4 Ammonium hydroxide (d_{20}0.88)

A5.5 Silver nitrate/nitric acid solution

Dissolve 8.5±0.1 g of silver nitrate in 500 mL of water containing 0.5 mL of nitric acid (d_{20}1.42).

A5.6 Sodium carbonate anhydrous (required only if insoluble matter is to be analysed).

Precise preparation of the above solutions is not required. Shelf life of these reagents is greater than one year except for A5.3, which is usable for up to two months. The sodium carbonate must be anhydrous; if in doubt heat at 150–200°C for 15 minutes prior to use.

A6 Apparatus

A6.1 Sintered glass or silica crucibles, capacity of about 30 mL, porosity 4.

A6.2 Buchner flask, equipped with safety guard for vacuum filtration and adaptor for sintered crucibles.

A6.3 Analytical balance capable of weighing to 0.0002 g or better.

A7 Sample Collection and Preservation

Samples may be collected in glass or polyethylene bottles and should be analysed within 6 hours of collection or stored at 4°C for not more than 2 days. 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 minimize the risk of air oxidation of samples containing sulphide or sulphite, sample bottles should be filled to exclude air.

If significant insoluble matter is present homogenize sample before taking the portions for analysis (see Step 8.3 and Section 9).

A8 Analytical Procedure

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
A8.1	Measure into a 600 mL beaker, a volume of sample (V mL), of between 10 and 400 mL, with a maximum sulphate content of 50 mg (note a). If necessary make the volume up to 400 mL with water. Proceed to step A8.2 unless the sample contains high concentrations of sulphides and/or sulphites, in which case proceed with step A8.2a.	(a) Alternatively, weigh out a portion and dilute to 400 ml in a 600 mL beaker.
A8.2	Add 2 drops of methyl orange indicator and neutralize the sample with 50% V/V hydrochloric acid or ammonium hydroxide, as appropriate (note b). To the neutral solution add 4.0±0.2 mL of 50% V/V hydrochloric acid. Heat the solution to boiling for 5 minutes. If the solution is clear, proceed directly to step A8.4 (note c).	(b) The indicator changes from red (acid) to orange (alkaline). (c) The solution should now be about 0.05 M in hydrochloric acid.
A8.2a	If the sample contains high concentrations of sulphides and/or sulphites, put about 50 mL of water in a 600 mL beaker and bring to the boil in a fumehood, add 2 mL of 50% V/V hydrochloric acid and 2 drops of methyl orange indicator. Slowly stir in the sample (V mL). If the indicator changes colour, stop the addition of sample and add 2 mL more hydrochloric acid. Resume the addition of sample. Continue until all of the sample has been added, maintaining acid conditions all of the time. Cool the liquid in the beaker, neutralize with ammonium hydroxide, add 4.0±0.2 mL of 50% V/V hydrochloric acid and bring to the boil. If the solution is clear, proceed directly to step A8.4 (note c).	

Step	Procedure	Notes
A8.3	If insoluble matter is present, filter the solution through a fine porosity ashless filter paper. Wash with a small amount of hot water, collect filtrate and washings in a 600 mL beaker. Keep filter paper for Section A9.	
A8.4	Boil the solution from step A8.2, or the filtrate from step A8.3, and add dropwise while stirring 10.0±0.5 mL of hot 10% m/V barium chloride. Heat on a boiling water bath for 2 hours, set aside to cool and allow to stand overnight (notes d and e).	(d) The slow addition of hot barium chloride reduces co-precipitation. (e) Heating (not boiling) for 2 hours aids coagulation of the precipitate and renders it more crystalline, reducing co-precipitation.
A8.5	Prepare a clean and dry (105±2°C) sintered glass crucible (A6.1) (note f). Weigh it accurately to ±0.0002 g. Let the weight be m_2 (note g).	(f) A sintered silica crucible may be used. (g) Barium sulphate can be dissolved from crucibles by soaking overnight in a solution containing about 5 g of EDTA and about 25 mL of monoethanolamine per litre. Crucibles must be well washed with water under suction before re-use. After drying, cool in a desiccator before weighing.
A8.6	Fit the crucible with a suitable adaptor to a Buchner flask. Filter the sample solution through the crucible using gentle suction and transfer the whole of the precipitate to the crucible using warm water to rinse the beaker. Ensure that any precipitate adhering to the sides and bottom of the beaker is dislodged by means of a rubber-tipped glass rod. Using a little water, transfer all the dislodged precipitate and rinsings to the crucible.	
A8.7	Wash the precipitate with warm water until free from chloride and ensure that the rim on the underside of the crucible is also washed free from chloride. To test whether the precipitate has been washed free from chloride, collect a few ml of filtrate in a beaker containing dilute silver nitrate/ nitric acid solution. The precipitate is chloride-free when the filtrate gives no turbidity or opalescence.	
A8.8	Dry the crucible at 105±2°C until constant in weight (±0.0002 g, about 1 hour) (note h). Cool in a desiccator and weigh. Repeat this procedure until 2 successive weights differ by not more than 0.0002 g. Record this weight as m_1 (note i).	(h) If a sintered silica crucible is used, dry at 500°C±10°C. (i) To expedite drying of the chloride-free precipitate, it may be washed (using gentle suction) with three 5 mL portions of industrial methylated spirits and the crucible then dried.
A8.9	**Blank Test** Repeat the above steps substituting 400 mL of water for the sample. Let the weight of the blank crucible from step A8.5 be m_{2b} and step A8.8 be m_{1b}. The blank value, m_3, is given by $m_3 = m_{1b} - m_{2b}$.	
A8.10	**Calculation** Calculate the weight of barium sulphate (M) in mg precipitated from V ml of sample: $M = (m_1 - m_2 - m_3) \times 1{,}000$ where m_1, m_2 and m_3 are expressed in grams. (See steps A8.8, A8.5 and A8.9)	
A8.11	Sulphate in mg/L SO_4^{2-} is given by $\frac{M}{V} \times 411.5$	

A9 Insoluble Sulphate Procedure

Recovery and determination of sulphate present in the insoluble material filtered off at step A8.3.

The presence of insoluble sulphate in the material obtained at step A8.3 of the procedure is unlikely in most samples. If this is suspected, however, proceed as follows:

Place the paper and insoluble material from step A8.3 in a platinum crucible, partially cover with the lid and heat over a low non-luminous flame to burn off the paper (alternatively use a muffle furnace brought up to 500°C from cold). Calcium and/or barium sulphate which will be the most likely insoluble sulphates present, do not lose sulphur trioxide on heating until a temperature of about 1400°C is reached. However, they can be reduced to sulphide if ignited with carbon (of the filter paper) in the absence of air. Mix the ignited residue with 4.0±0.1 g anhydrous sodium carbonate and fuse the mixture, maintaining in the fused state for 15 minutes. Extract the cooled melt from the crucible with water and filter the solution to remove any barium and/or calcium carbonate and wash the residue with a few ml of water. Neutralize the solution with 10% V/V hydrochloric acid in a beaker. Acidify the solution to 0.05 M in hydrochloric acid. If silica was originally present in the insoluble material fusion will render it soluble and acidification using dilute acid should not re-precipitate it. However, if sufficient silica is present to cause re-precipitation it may be removed by evaporating the acid filtrate to dryness on a water-bath to dehydrate the silica; a little concentrated hydrochloric acid is added, followed by hot water. The silica is filtered off and the sulphate is determined in 0.05 M hydrochloric acid solution as described commencing at step A8.5. The sulphate found will be additional to the quantity found in the acid-soluble portion of the sample. For additional information see specialized texts.(1–2)

A10 References

(1) *W F Hillebrand, G E F Lundell, H A Bright and J I Hoffman, Applied Inorganic Analysis (2nd Edition)* Chapman and Hall Ltd London, Wiley, New York, 1953.

(2) A I Vogel, *A Text-Book of Quantitative Inorganic Analysis (3rd Edition)* Longmans, London, 1966.

B Sulphate In Waters And Effluents By Direct Barium Titrimetry Tentative Method

B1 Performance Characteristics of the Method

(For further information on the determination of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series.)

B1.1	Substance determined:	Sulphate ion
B1.2	Type of sample:	Raw, potable, waste and saline waters.
B1.3	Basis of method:	Sulphate ions are titrated with barium chloride using a suitable indicator.
B1.4	Range of application:	30–200 mg/L, without the use of dilution or smaller aliquots, using the 0.005 M barium chloride titrant.
B1.5	Standard deviation (a) (total and within batch, on synthetic solutions of sodium sulphate):	Sulphate concentration mg/L SO_4^{2-} / Standard deviation mg/L SO_4^{2-} 50 / 0.45 (All with 10 degrees of freedom)
B1.6	Limit of detection:	(b) 30 mg/L sulphate as SO_4^{2-}
B1.7	Sensitivity:	1 mL of 0.005 M barium chloride is equivalent to 24 mg/L sulphate as SO_4^{2-}
B1.8	Interference:	Several common anions cause interference including phosphate, fluoride, chromate, sulphide and various oxy-acids of sulphur. Strongly coloured waters may interfere. See Section B9.
B1.9	Time required for analysis:	5 minutes for 1 sample using a prepared column, using 2 columns, 10 samples in 30 mins.

(a) These data were obtained by North West Water Authority.

After removing interfering cations by a preliminary ion-exchange stage, the sulphate ions are titrated with barium chloride using carboxyarsenazo ('Thorin') as indicator (for the full name see Section B5.8).

B2 Principle

Since the titration is critical in respect of pH, a buffer solution is employed in which pyridine is the active ingredient. This solution also contains acetone to keep the coloured barium complex in solution.

The indicator also contains bromocresol purple. This serves both as an acid-base indicator and as a colour screen for the carboxyarsenazo.

B3 Field of Application and Interferences

B3.1 The method is applicable to almost all types of waters. Particulate matter should be settled or removed by filtration prior to the ion-exchange stage.

B3.2 In the case of waters containing sparingly soluble sulphates in suspension, for example calcium sulphate, care will be necessary since an increase in dilution could increase the concentration of sulphate ions. A local decision may be necessary to assess the relative importance of the suspended matter.

B3.3 Some anions interfere, usually causing positive bias, although limited concentrations can be tolerated. Such anions include phosphates, fluoride, chromate, sulphide and various other oxy-acids of sulphur.

If the following concentrations are exceeded then steps are needed either to remove interferences or to apply corrections. See Section B9.

Fluoride	5 mg/L
Chromate	5 mg/L
Sulphide	5 mg/L
Other sulphur oxy-acids	1 mg/L (as S)
Phosphates	0.5 mg/L (as P) after dilution.

B4 Hazards

Carboxyarsenazo indicator and barium chloride are toxic substances and should be handled with care. Barium chloride is a schedule 1 poison.

Eye protection should be worn when dealing with ammonia solution (d_{20} 0.88) (see Section A4).

Strong solutions of perchloric acid are strong oxidizing agents and can cause spontaneous fires if spilled on some readily combustible materials. Never allow such solutions to come into contact with wood, paper and similar materials. Dilute all spills and wipe up immediately; thoroughly rinse out any swabs used for such cleaning. Store stock bottles in a fireproof place in metal trays.

B5 Reagents

The reagents employed in the solvent-buffer solution are all hazardous and should be handled with care.

B5.1 Analytical reagent grade chemicals and distilled or de-ionized water should be used throughout.

B5.2 Approximately 1.0 M Ammonium hydroxide (HAZARD, SEE SECTION A4)

Dilute 60±5 mL ammonia solution (d_{20} 0.88) with water to 1,000±10 mL. The solution is stable for at least one month.

B5.2.1 In laboratories where the use of ammonia is undesirable, it can be replaced by **tetra-n-butylammonium hydroxide** of equivalent strength.

B5.3 Approximately 0.1 M Ammonium hydroxide

Dilute 50±5 mL of Solution B5.2 with water to 500±5 mL. The solution is stable for at least one week.

B5.4 Approximately 1.0 M Hydrochloric acid

Carefully add 176±2 mL of hydrochloric acid (d_{20} 1.18) to 1,000±100 mL of water, cool, transfer to a 2-litre calibrated flask and dilute with water to the mark. Store in a glass bottle. The solution is stable for at least 6 months.

B5.5 Solvent buffer solution (HAZARD, SEE SECTION B4)

To 2.5 litres of acetone in a suitable bottle add 25±1 mL of pyridine and 1.0±0.1 mL of 60% m/V perchloric acid. Allow to stand for 24 hours before use. This solution must be stored with care in fireproof storage. It is stable for at least one month if securely stoppered. 2.5 litres are sufficient for about 50 determinations.

B5.6 Standard sulphate solutions

B5.6.1 Solution A: 1 mL contains 1 mg SO_4^{2-}

Dissolve 1.814±0.001 g potassium sulphate (dried for one hour at 110±5°C) in about 500 mL of water, transfer quantitatively to a 1-litre calibrated flask. Dilute with water to the mark, stopper and mix thoroughly. This solution is stable for at least one year.

B5.6.2 Solution B: 1 mL contains 0.1 mg SO_4^{2-}

Pipette 50.0±0.1 mL of solution A into a 500 mL calibrated flask, dilute with water to the mark, stopper and mix thoroughly. This solution is stable for at least one month.

B5.7 0.005 M Barium chloride (HAZARD, SEE SECTION B4)

Dissolve 1.221±0.001 g barium chloride dihydrate in about 500 mL of water, transfer quantitatively to a 1-litre calibrated flask, dilute with water to the mark, stopper and mix thoroughly. This solution is stable for at least one month.

B5.7.1 Standardization of the 0.005 M barium chloride solution

Pipette 20.0±0.1 mL of standard sulphate solution B into a 250 mL conical flask. Carry out steps B8.4 and B8.5. Record the titre T_1 (T_1 is used directly in the final calculation).

B5.8 Indicator Solution (HAZARD, SEE SECTION B4. THIS SOLUTION IS TOXIC)

Dissolve 0.06±0.01 g carboxyarsenazo (disodium 2- (2-arsenophenylazo)-7-(2-carboxyphenylazo)-1, 8-dihydroxynaphthalene-3, 6-disulphonic acid)* in about 50 mL of water. Add 0.05±0.01 g of bromocresol purple dissolved in 2±0.5 mL of acetone. Make up to 100±2 mL with water. This solution is stable for at least one week.

* Also known as Thorin.

B5.9 A strongly acidic cation exchange resin in the hydrogen form (BSS mesh size 10–50 is preferred); Amberlite IR120H is suitable.

B5.10 Standard phosphate solution 1 mL contains 200 μg P

Dissolve 0.879±0.001 g of potassium dihydrogen phosphate in about 500 ml of water, transfer quantitatively to a 1-litre calibrated flask, add 1.0±0.2 mL of chloroform, dilute with water to the mark, stopper and mix thoroughly. The solution should be stored at 4°C and is stable for at least one month.

B5.11 pH paper to indicate pH 5.5.

B6 Apparatus

B6.1 10 mL Burette reading to 0.1 mL.

B6.2 10 mL Microburette reading to preferably 0.02 mL.

B6.3 Burette type ion-exchange column

To a 100 mL burette, fitted with a small glass wool plug positioned just above the tap, add 30±5 mL of resin (see Section B6.5) and insert another glass wool plug above the resin column.

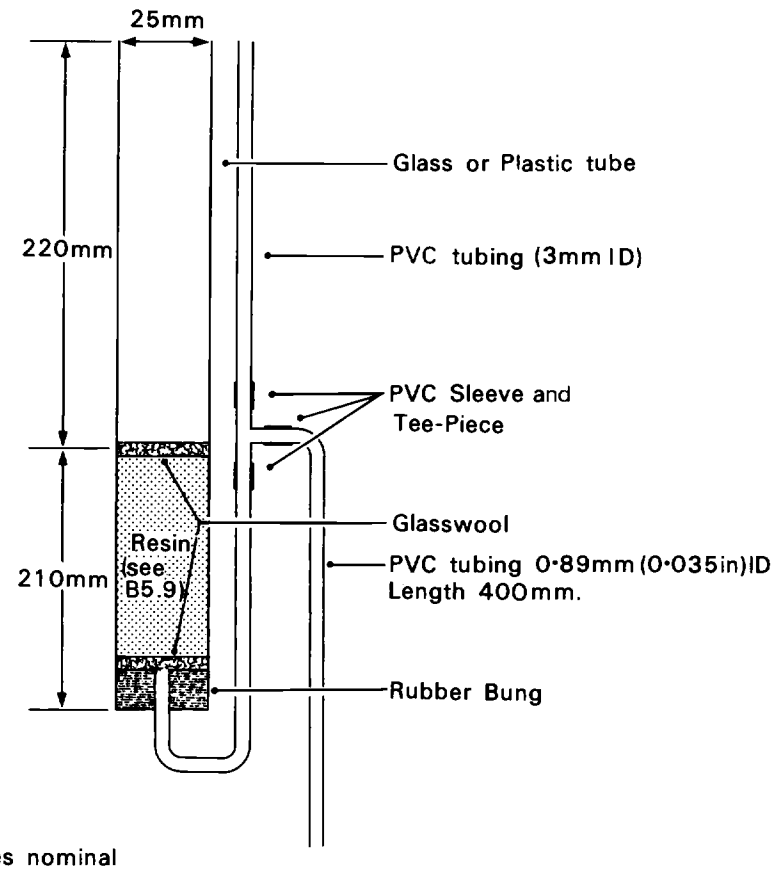
B6.4 Automatic ion-exchange column

This type of column may be used if desired. It may be constructed and prepared as indicated in figure B1, using a 100 mL burette or 15 mm diameter glass tube. The column should contain the same amount of resin as described in Section B6.3.

B6.5 Preparation and regeneration of ion-exchange resin

B6.5.1 Place a volume of fresh resin in a beaker and add 4–5 volumes of water. Swirl vigorously, allow to settle and then decant the liquid. Repeat the operation 4 times, and, for either column design, transfer 30±5 mL of resin to the column with water. Ensure that all air bubbles are removed.

Figure B1 A typical "automatic" ion exchange column



Not to scale, sizes nominal

B6.5.2 Pass a volume of 1.0 M hydrochloric acid solution through the column, equal to 3 times the resin volume.

B6.5.3 Wash the resin with water until the pH of the water rises above pH 5.5 (test with pH paper). A volume of water equal to about twice the volume of the acid used in step B6.5.2 will be required. When using the burette (B6.3), do not allow the liquid surface to fall below the resin level.

B6.5.4 The resin should have an exchange capacity of about 2 milliequivalents per ml of wet resin, hence the burette column will have a capacity of 60 milliequivalents. The column should be regenerated before 50% exhaustion using 1.0 M hydrochloric acid as in B6.5.2. As an example, 50–60 determinations of average strength can be dealt with and since this number is also equivalent to 2.5 litre of solvent buffer, renewal of the stock of the buffer solution (B5.5) represents a convenient stage to regenerate the column.

B7 Sample Collection and Preservation

B7.1 Samples may be collected in glass or polyethylene bottles and should be analysed within 6 hours of collection or stored at 4°C for not more than 2 days. Samples low in organic matter may be kept for longer periods, but tests should be carried out to ensure that samples are sufficiently stable.

B7.2 To minimize the risk of air oxidation of samples containing sulphide or sulphite, sample bottles should be filled to exclude air.

B7.3 Samples containing suspended matter should be filtered through a well washed glass fibre filter capable of retaining particles of over about 1 μm size before analysis, or clarified by either centrifuging or dissolution with 1.0 M hydrochloric acid before ion-exchange.

B7.4 If the sample pH-value is outside the range 6–8, note the volume and then adjust the pH-value to fall within this range using a small amount of hydrochloric acid

or sodium hydroxide solution. If the volume change is not negligible, record the new volume and correct the final results proportionally (step B8.7 note g).

B8 Analytical Procedure — **READ SECTION B4 ON HAZARDS BEFORE STARTING THIS PROCEDURE**

Step	Procedure	Notes
B8.1	Run the water level just below the top plug level in the burette column (note a).	(a) This is already adjusted with the 'automatic column'.
B8.2	Pour in 40±2 mL of sample (note b).	(b) For very high sulphate levels, the sample should be diluted appropriately. See note d.
B8.3	Allow the sample to run through the column at a rate of 10±2 mL per minute and discard the first 15±1 mL of eluate. Collect the remainder and pipette 20±0.1 mL into a 250 mL conical flask (notes c and d).	(c) Wash the column thoroughly with water between each sample. (d) For concentrations of sulphate greater than 200 mg/L, a smaller aliquot of the eluate can be taken and the volume adjusted with water to 20.0±0.1 mL. This ensures that the buffer concentration remains constant.
B8.4	Add 0.05±0.01 mL of carboxyarsenazo indicator solution (B5.8) and, using a burette (B6.1), neutralize with 1.0 M or 0.1 M ammonium hydroxide solution to a purple end point (note e).	(e) The stronger ammonia solution should be used for highly saline waters.
B8.5	Add 50±2 mL of solvent buffer followed by 0.25±0.02 mL of carboxyarsenazo indicator (B5.8). Then using a microburette (B6.2) titrate with standard barium chloride solution to a permanent grey colour which remains after 5 secs swirling. Note the titre T_2 ml (note f).	(f) There is a small indicator blank hence amounts of indicator should be accurately controlled, and be the same for all samples.
B8.6	Blank Test Repeat steps B8.3, B8.4 and B8.5 using 20.0±0.1 mL water in place of the sample. Note the titre T_3 mL (note f).	
	Calculation (note g).	(g) Be sure that the standardization titration used is that for the barium solution used to titrate the sample and blanks. Be sure that the calculation formula used is that for the correct barium solution. If the sample pH-value had to be corrected (Section B7.4) and the volume change was significant, correct the sulphate concentration found by multiplying by the ratio: pH-corrected sample volume / original sample volume
B8.7	Using 0.005 M barium chloride, the concentration of sulphate in sample is: $\frac{100(T_2 - T_3)}{(T_1 - T_3)}$ mg/L SO_4^{2-} or if an aliquot (V) mL was taken at step B8.3 (note d): $\frac{2{,}000(T_2 - T_3)}{V(T_1 - T_3)}$ mg/L SO_4^{2-}	

B9 Special Procedures

B9.1 Compensation for phosphate interference

The method as detailed provides results of sufficient accuracy for concentrations up to 0.5 mg/L as P, after making allowance for any dilution of the sample or aliquot. Correction can be made for higher concentrations of phosphate using the procedure detailed below.

B9.1.1 Set out 5 sets of five 50 mL calibrated flasks (25 flasks in all). Prepare 5 series of flasks each series containing 0.0, 0.5, 1.0, 2.5 and 5.0 mL of standard phosphate solution, respectively. From each of these 5 series prepare 5 sets of flasks each with constant phosphate content, but varying sulphate content, containing, for instance, 1.0, 2.0, 3.0, 4.0 and 5.0 mL of standard sulphate solution A or B dependent on the expected sample concentration range. Dilute each flask with water to the mark.

B9.1.2 Carry out steps B8.1 to B8.5.

B9.1.3 From the results of the titration, evaluate the increase in titre volumes over and above the titre with no phosphate present.

B9.1.4 For each sulphate concentration, plot a curve of phosphate concentration against increase in titration. An example is shown in figure B2.

B9.1.5 Determine the orthophosphate concentration in the sample (see ref 1).

B9.1.6 For each level of phosphate found in a sample, interpolate the increase in titre volume due to the interference effect and subtract from the sample titre. The effect will be found to be non-linear over the lower range of concentrations but is practically linear above 10 mg/L as P.

B9.2 Chromate

Chromate may be reduced by dropwise addition of tin II chloride solution to a simmering sample prior to the analysis. Use a slight excess of tin II chloride and then cool the sample before proceeding. No specific strength of tin II chloride solution is stipulated, the strength should match the chromium level so that the resultant volume change is negligible. If phosphate is present, it is precipitated during the reduction.

B9.3 Sulphite

This will quickly become oxidized to sulphate. The sulphite concentration should be determined separately (see ref 2) and then another portion of the sample oxidized with excess hydrogen peroxide and the resultant total sulphate concentration measured, the actual sulphate concentration being obtained by difference. A blank analysis should be made on each new batch of hydrogen peroxide.

B9.4 Other sulphur oxy-acids

These can be dealt with in a similar way to sulphite provided they can be determined separately in the sample.

B9.5 Colour

Very strongly coloured effluent may cause interference with the indicator end-point. In this case, the sample should be shaken with decolorizing carbon and the solution, after filtering, applied to the column.

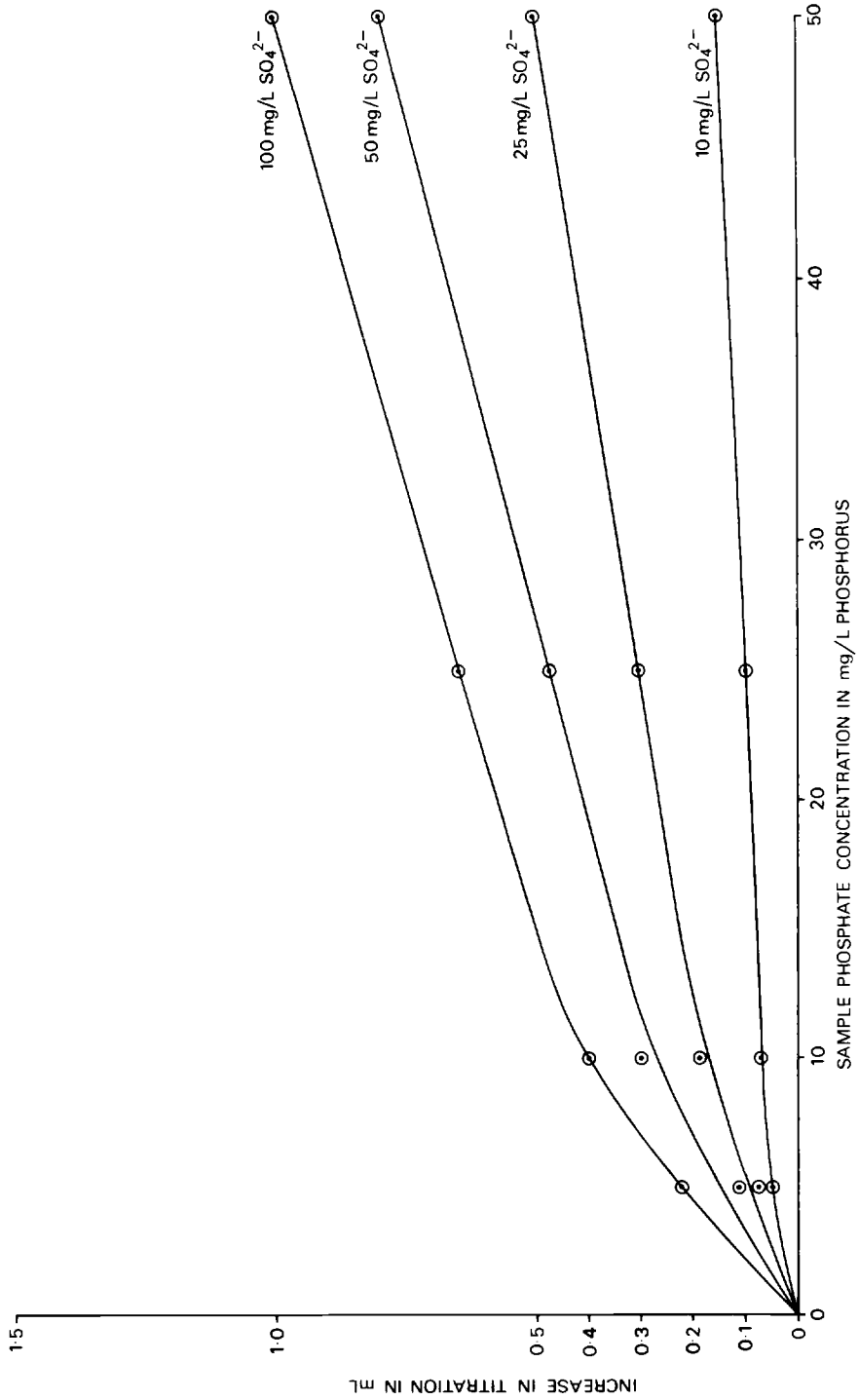
It has been found that most decolorizing carbons contain some sulphate and a blank is therefore essential.

B10 References

(1) *Phosphorus in Waters 1980.* HMSO in this series.

(2) *Determination of Sulphite, Sulphur Dioxide, Thiosulphate and Thiocyanate, with Notes on the Determination of Total Sulphur and Other Sulphur Compounds 1985.* HMSO in this series.

Figure B2 A typical set of phosphate correction curves



C Sulphate In Waters By Inductively Coupled Plasma Emission Spectrometry

C1 Performance Characteristics of the Method

C1.1	Substance determined:	Total sulphur.
C1.2	Type of sample:	Raw, potable (1) and saline waters (2).
C1.3	Basis of method:	Monitoring sulphur emission at 180.73 nm using inductively-coupled plasma emission spectrometry (ICP-OES). (See Ref 1).
C1.4	Range of application:	0.5–2,000 mg/L but greater sensitivity can be achieved by preconcentration on an activated alumina column with flow injection (3)
C1.5	Calibration curve:	Linear to at least 2,000 mg/L SO_4^{2-}.

C1.6 Standard deviation:

	Sulphate concentration mg/L SO_4^{2-}	Total standard deviation mg/L SO_4^{2-}
(a)	21.6 (With 13 degrees of freedom)	0.22
(b)	1,460 (With 12 degrees of freedom)	60

C1.7	Limit of detection (a):	Typically 0.5 mg/L SO_4^{2-} but see Ref 3.
C1.8	Interferences:	A weak spectral calcium line at virtually the same wavelength. Any other sulphur species, especially sulphide.
C1.9	Time required for analysis:	Following calibration of the instrument, approximately 1 minute per sample.

(a) These data were obtained by the Hydrogeology Research Group, British Geological Survey, Wallingford.
(b) These data were obtained by the Fluid Processes Research Group, British Geological Survey, Keyworth.

C2 Principle

The total sulphur content of the samples is determined by monitoring the emission intensity of the 180.73 nm sulphur line by inductively coupled plasma optical emission spectrometry during multi-element analysis. See (4).

C3 Interferences

C3.1 A weak calcium line at 180.734 nm partially overlaps the sulphur line such that 1,000 mg/L Ca^{2+} typically produces an apparent sulphate signal of 25 mg/L SO_4^{2-}, but this response is instrument dependent.

C3.2 Since the method is based on the detection of sulphur, any sulphur-containing species present in the sample will cause positive interference. In particular, sulphides, can produce greatly enhanced and erroneous signals through the generation of H_2S during nebulisation. Sulphides and sulphites are often removable prior to analysis.

C4 Hazards

The manufacturer's safety instructions for the operation of the ICP spectrometer should be followed. Eye protection must be worn as a precaution against the intense UV radiation emitted by the ICP. High voltages are lethal; large condensers may hold considerable electrical charge. Equipment should be switched off and grounded before maintenance.

C5 Reagents

Use analytical grade reagents and distilled or deionized water throughout.

C5.1 Sulphate stock solution (1 mL contains 10 mg sulphate)

Dissolve 18.144±0.001 g of potassium sulphate, dried for 1 h at 110±5°C, in about 500 ml of water and transfer quantitatively to a 1 L calibrated flask. Dilute to the mark with water, stopper and mix thoroughly. This solution is stable for at least one year.

C5.2 1% V/V nitric acid

Dilute 10 ml of nitric acid (d_{20} 1.41) to 1 litre with deionized water.

C5.3 Sulphate working standards

Prepare at least 5 standard solutions in the required concentration range by diluting the stock sulphate solution (C5.1) with 1% V/V nitric acid (C5.2).

C5.4 Calcium stock solution (1,000 mg/L calcium)

Dissolve 2.50±0.01 g of oven dried Specpure calcium carbonate in 200 ml of water in a beaker by the careful addition of 11.6 mL of nitric acid (d_{20} 1.41) and dilute to 1 litre with water. The final solution is 1% V/V with respect to nitric acid.

C5.5 Calcium working standards

Prepare 5 standard solutions in the range 50–500 mg/L calcium by diluting the stock calcium solution (C5.4) with 1% V/V nitric acid (C5.2).

C6 Apparatus

An ICP-OES instrument fitted with a vacuum or nitrogen purged spectrometer and having the optical path between the ICP and the entrance slit purged with a suitable gas.

C7 Sample Collection and Preservation

Samples may be collected in glass or polyethylene bottles and should be analysed within 6 hours of collection or stored at 4°C for not more than 2 days. Samples low in organic matter may be kept for longer periods, but tests should be carried out to ensure that samples are sufficiently stable.

C8 Sample Pretreatment

They should be filtered through a 0.45 μm pore sized membrane on collection and acidified to 1% V/V with nitric acid. If the presence of sulphides or sulphites is suspected, the acidified sample should be purged with nitrogen until all hydrogen sulphide or sulphur dioxide is removed (5).

C9 Analytical Procedure

READ SECTION C4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
C9.1	Set up the ICP-OES system according to the manufacturer's instructions to monitor the 180.73 nm sulphur line.	
C9.2	Perform a calibration routine using the sulphate standard solutions prepared in Section C5.3 (note a).	(a) Actual routine will depend on the manufacturer's software.

Step	Procedure	Notes
C9.3	Aspirate the calcium standard solutions prepared in Section C5.5 and record the emission intensities at 180.73 nm and at a suitable calcium wavelength. Calculate the equation for the response at the 180.73 nm sulphur line against the measured calcium concentration and insert this equation into the appropriate software (note a).	(If the equipment is not readily capable of doing this, see the section on overlapping line interference in ref 6, which gives the basic equations relating concentrations to line intensity and information on how to handle them).
C9.4	Aspirate the samples (C8) and record the sulphur emission intensity via the operating software (notes b and c).	(b) Use a solution of 1% V/V nitric acid (see Section C5.2) as the working blank. (c) Aspiration is necessary to remove all volatile sulphur compounds including hydrogen sulphide.

C10 Sources of Error

The chief source of error is the presence of sulphur compounds other than sulphate. The method is actually a method for total sulphur but with variation in response dependent on the volatility of the sulphur compound. It is necessary to ensure the removal of other sulphur compounds prior to analysis, or to use another method. Volatile sulphur compounds and compounds such as sulphides and sulphites decomposed by acids are relatively easy to remove but a few compounds such as some of the thionates are difficult and some such as thiosulphate may require more effort than is worthwhile to remove them.

C11 References

(1) D L Miles and J M Cook, *Anal Chim Acta* **141**, 207 1982.

(2) I B Brenner, H Eldad, S Erlich and N Dalman, *Anal Chim Acta* **166**, 51 1984.

(3) A G Cox, C W McLeod, D L Miles and J M Cook, *J Anal Atom Spect* **2**, 553 1987.

(4) *Inductively Coupled Plasma Spectrometry 1989*, HMSO, in this series.

(5) K Lewin, J N Walsh and D L Miles *J Anal Atom Spect* **2**, 249 1987.

(6) *Emission Spectrophotometric Multi element Methods of Analysis for Waters, Sediments etc 1980*, HMSO, in this series.

D Sulphate In Waters And Effluents By A Continuous Flow Indirect Spectrophometric Method Using 2-Aminoperimidine

D1 Performance Characteristics of the Method

D1.1	Substance determined:	Sulphate ion.
D1.2	Type of sample:	Raw, potable and waste waters.
D1.3	Basis of method:	Sulphate is precipitated with 2-aminoperimidine and the excess reagent is determined colorimetrically.
D1.4	Range of application:	i. 5–200 mg/L (a)(b). ii. 5–500 mg/L (b).
D1.5	Calibration curve:	Approximately linear.

D1.6 Standard deviations:

Sample type	Sulphate conc (mg/L)	Standard deviation (mg/L)		Degrees freedom
		Within batch	Total	
i. 5–200 mg/L				
Distilled water	—	0.8	—	5 (a)
Standard sulphate	70		2.9	9 (b)
Standard sulphate	112.3		0.9	9 (a)
Standard sulphate	150		4.3	9 (b)
Borehole water	24.0		0.8	9 (a)
River water	73.4		1.3	8 (a)
	56	2.2	—	9 (b)
Potable water	25.4		1.6	8 (a)
	85		3.8	9 (b)
Sewage effluent	60	2.1	—	9 (b)
ii. 5–500 mg/L				
Distilled water	—	—	1.4	— (b)
Standard sulphate	40	—	3.3	10 (b)
Standard sulphate	400	—	7.1	10 (b)
Standard sulphate	500	—	11.8	— (b)

D1.7	Limit of detection (a);	4.6–6.2 mg/L sulphate.
D1.8	Sensitivity:	No data available.
D1.9	Bias (a):	i. Standard 183 mg/L No significant bias detected. ii. River water 75 mg/L (mean) sulphate −2.4%

D1.10 Interferences:	No significant interferences from other commonly occurring constituents of raw and potable waters at levels usually encountered (see Section D3).
D1.11 Time for analysis:	(a). Approximately 25 samples/hr. (b). Up to 60 samples/hr.

(a) Data obtained at Anglian Water, Regional Standards Laboratory, Cambridge.
(b) Data obtained at Thames Water, New River Head Laboratory, London and Yorkshire Water.

D2 Principle

Sulphate reacts with 2-aminoperimidine to form a precipitate and the excess reagent is extracted by dialysis into a recipient stream. This excess reagent reacts with nitrous acid and alkali to form a red dye which is determined colorimetrically at 525 nm (1).

D3 Interferences

The effect of some possible constituents of raw, potable and waste waters are listed in Table D1. Most interference effects were found at the lower sulphate level and were due to sulphide, sulphite, phosphate and tin. These substances were present at levels above those usually found in raw and potable waters.

D4 Hazards

Whilst no untoward effects have been reported from the use of 2-aminoperimidine, it is recommended that skin contact should be avoided and any splashes washed off immediately.

Eye protection should be worn and a fume cupboard used when handling concentrated hydrochloric acid.

D5 Reagents

Distilled or deionised water should be used for the preparation of reagents and standards. Analytical reagent grade chemicals should be used whenever possible. Filtration of reagent solutions after preparation is unnecessary because in-line filters are incorporated in the manifold, but solutions should be shaken thoroughly when first made up to ensure that they are not supersaturated with air. With proper storage, reagents are stable for at least a year, unless otherwise stated.

D5.1 0.5% (V/V) Hydrochloric acid

Carefully add 2.5±0.2 mL of concentrated hydrochloric acid (d_{20} 1.18) to about 450 mL water in a 500 mL graduated flask. Make up to the mark with water and then add 5 drops of 30% (m/V) Brij-35 detergent solution. Store in a glass bottle.

D5.2 0.2% (m/V) 2-aminoperimidine hydrochloride solution

Dissolve 2.0±0.1 g of 2-aminoperimidine hydrochloride in water in a one litre graduated flask. Add 5.0±0.1 g of 30% (m/V) Brij-35 detergent solution and make up to the mark with water. Stored in an amber glass bottle, this solution is stable for at least one week.

D5.3 0.5% (m/V) Sodium nitrite solution

Dissolve 2.5±0.1 g of sodium nitrite in 500±5 ml of water. Stored in an amber glass bottle, this solution is stable for at least one month.

D5.4 15% (V/V) Ethanolamine solution

Thoroughly mix 75±2 mL of ethanolamine with about 100 mL of water in a 500 mL graduated flask. Make up the mark with water and store in a glass bottle. This reagent is stable for at least 6 months.

D5.5 15% (m/V) EDTA + 20% (V/V) Ethanolamine

Dissolve 15.0±0.2 g of EDTA and 20±2 mL of ethanolamine in 100±5 mL of water.

D5.6 Stock sulphate solution (1 mL contains 1 mg sulphate)

Dissolve 1.814±0.001 g of potassium sulphate freshly dried for 1 h at 110±5°C) in approximately 800 mL of water in a one litre calibrated flask. Make up to the mark with water and store in a glass or polyethylene bottle in the dark. This solution is stable for at least one year.

D5.7 Calibration standards

Working standards (20–200 mg/L SO_4^{2-}) may be prepared by adding, to a series of 250 mL graduated flasks, 5, 10, 20, 30, 40 and 50 mL of stock sulphate solution (D5.6). Make up to the mark with water. Stored in a glass bottle in the dark, these are stable for at least 6 months.

D6 Apparatus

The manifold used to obtain some of the performance data, and for which the reagents listed above are intended, is shown in Figure D1 (for an alternative manifold see Section D10 and Figure D4).

Most of the apparatus is common to all air-segmented continuous flow auto analysis systems (2) but some additional items are needed.

D6.1 In-line filters, consisting of a filter and weight assembly, with extra-fine porosity filter discs are fitted to the reagent bottle end of each line, except for the hydrochloric acid line on the donor side of the dialyser.

D6.2 Plating trap

It has been found beneficial to provide rapid mixing after the introduction of ethanolamine into the stream to prevent the relatively viscous ethanolamine from lying on the bottom of the tubes and forming a red coating on them.

Details of the trap are shown on Figure D2; an alternative design is shown in Figure D3.

D7 Sample Collection and Preservation

Samples may be collected in glass or polyethylene bottles and should be analysed within 6 hours of collection or stored at 4°C for not more than 2 days. 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 risk of air oxidation of samples containing sulphide or sulphite, sample bottles should be filled to exclude air.

D8 Sample Pretreatment

Samples containing large amounts of suspended matter should be filtered. If the suspended matter is suspected of containing insoluble sulphate it should be analysed separately. Method A of this booklet contains a procedure for analysing insoluble sulphates.

D9 Analytical Procedure

Step	Procedure	Notes
D9.1	Set up the manifold as in Fig D1 (notes a, b and c).	(a) An alternative manifold (Fig D4) giving higher throughput with reduced precision is available, see Section D10. (b) For further information see another booklet in this series (2). (c) This method may suffer from an unstable baseline. To minimise this effect the bubble spacing, reagent addition points and bubble phasing are adjusted so that roller lift-off occurs when a liquid segment is opposite each injection point.

Step	Procedure	Notes
D9.2	Switch on the colorimeter and leave at least half an hour to stabilise (note d).	(d) This method is somewhat sensitive to changes in temperature at the dialyser. If a dust cover is fitted onto the manifold it should be removed to prevent heat build-up.
D9.3	Start the pump, and place the reagent tubes in their respective reagent bottles (notes e, f, g).	(e) The wash water should be changed before each day's use. (f) Ensure there is sufficient of each reagent to complete the run. (g) Ensure no bubble is trapped in the flow cell (squeeze pull through line for a few seconds and release).
D9.4	When a satisfactory baseline has been obtained for 15 minutes adjust the recorder and colorimeter zeros to 10% of full scale (note h).	(h) This allows for any negative drift that may occur.
D9.5	Put the top concentration standard in a sample cup on the sampler turntable and sample one or 2 times. When there is a response at the recorder, adjust the gain control of the colorimeter to 90% of full scale (note i).	(i) This allows for any positive drift that may occur.
	Analysis of Samples	
D9.6	Arrange the standards, blanks and samples on the turntable in the following order, and start the sampler (notes j–n). Blank, Working standards in descending order of concentration, Blank, Samples, including a control standard. (Not more than 10 samples in any one group.) Blank. Repeat the sequence blank, samples, blank until all the samples have been analysed. Working standards in ascending order of concentration. Blank. If incomplete separation of the peaks is observed, or air bubble spikes affect a peak, the affected samples should be re-analysed.	(j) Suggested order; for other possible orders see reference 2. (k) Each bottle of standard should be shaken and the neck rinsed by pouring some solution to waste before filling the sample cup. (l) Each sample cup should be rinsed with the sample it is to contain. (m) The samples and standards can be loaded on the turntable during the initial setting up period. (n) The laboratory temperature should be kept as constant as is practical in order to avoid undue drift. The analyser should not be in direct sunlight, or a draught.
D9.7	When the response of the last blank has been recorded, the recorder may be turned off.	

Step	Procedure	Notes
D9.8	Transfer the reagent lines to a beaker of distilled water and allow to pump through for 10 minutes. The aminoperimidine line and the hydrochloric acid on the donor side of the dialyser should be placed in 15% EDTA + 20% ethanolamine soln, until manifold tubes are free of precipitate (note o). If the plating trap is heavily coloured, place the ethanolamine line in 50% HCl for a few minutes. Then pump water through the system for 10 mins.	(o) The treatment with the EDTA soln should remove all the precipitate from the second mixing coil and dialyser, whilst the acid wash removes staining from the plating trap and final mixing coil. The latter treatment may only be required after prolonged operation.
D9.9	Turn off the pump and colorimeter	
D9.10	Check pump tubes for wear and replace with new flow rated tubes if necessary (note p).	(p) New tubes should be run in for 2 hours before use to avoid drift.
D9.11	Measure the peak heights of the flat tops of standard and sample peaks, with reference to a baseline drawn between successive blank samples.	
	Calculation of Results	
D9.12	Plot a calibration curve of peak heights against concentration of the calibration standard solutions (note q).	(q) If sensitivity has changed significantly during the run, procedures suggested (2) can be used to obtain calibration curves.
D9.13	Convert the peak heights of the samples into concentrations from the calibration curve (note r).	(r) The peak heights of the samples should, if necessary, be corrected for any sensitivity changes.

D10 Alternative Manifold and Reagents

Some data (3) were obtained using the manifold shown in Figure D4, which incorporates the plating trap design depicted in Figure D3. This system uses a sodium acetate/acetic acid buffer solution (pH 4.1), 5% (m/v) sodium nitrite solution, 5% (v/v ethanolamine and 0.5% (v/v) Nonidet P40 as wetting agent.

The use of buffer solution has been found unnecessary for most waters, but, if required it may be prepared as follows:

Add 40±1 g of anhydrous sodium acetate to approximately 800 ml of distilled water. Mix in 120±2 mL of glacial acetic acid and stir until the solid has dissolved. After addition of 5 ml of Nonidet P40 surfactant, make up to one litre with distilled water.

The recommended sampling ratio is 60 samples per hour, with a sample to wash ratio of 2:1. Pumping volume ratios are given on the right of figure 3. For up to 200 mg/L of sulphate expected in the sample, the sampler is connected at B and dilution water at A; for higher concentrations up to 500 mg/L, connect the sampler at A and the dilution water at B.

D11 References

(1) A W Archer, *Analyst*, **100**, 755, (1975).

(2) *Air Segmented Continuous Flow Automatic Analysis in the Laboratory (1979).* Methods for the Examination of Waters and Associated Materials. HMSO, London. See also p8 reference.

(3) M Stockley & R J Vincent, *'Sulphate Analysis Using 2-aminoperimidine'*. Paper presented at a meeting of the Institute of Water Engineers and Scientists (Scientific Section) on 'The Work of the Standing Committee of Analysts', October 1979.

Table D1 The effect of other substances upon the automated 2-aminoperimidine method (b)

Substance	Concentration mg/L	*Effect upon the determination of:	
		400 mg/L SO_4^{2-} mg/L	40 mg/L SO_4^{2-} mg/L
Chloride	2,000	− 9	−10
Fluoride	10	− 3	− 2
Bromide	10	+ 2	+ 7
Iodide	10	+ 2	+ 7
Bicarbonate	2,000 (HCO_3^-)	+10	+ 5
Carbonate	1,000 (CO_3^{2-})	−14	−10
Nitrate	125 (N)	+ 2	− 5
Nitrite	10 (N)	− 1	− 5
Ammonia	100 (N)	− 1	+ 1
Phosphate	125 (PO_4^{3-})	+ 2	+ 2
Silicate	125 (SiO_2)	− 4	+ 2
Sulphide	10	+10	+14
Sulphite	10	−12	−12
Thiosulphate	14	−12	− 9
Cyanide	10	− 5	+ 4
Free Chlorine	50	−22	−17
Hexametaphosphate	0.025% ($NaPO_3$)	+13	+32
Manoxol OT	10	−12	+ 9
Calcium	1,000	− 4	− 2
Magnesium	200	− 9	− 7
Manganese	10	+ 1	− 2
Copper	10	+ 1	0
Zinc	10	+ 1	+ 6
Cadmium	10	+ 4	− 7
Chromium (VI)	10	+14	− 2
Nickel	10	+ 7	− 3
Molybdenum	10	+12	− 3
Tin	10	− 9	−45
Arsenic	10	− 9	−45
Selenium	10	+ 9	−11
Aluminium	10	+ 9	− 5
Iron	10	+ 9	− 3
Antimony	10	− 1	− 7
Lead	10	+ 7	−11

*If other substances did not interfere, the results expected (95% confidence level) assuming no interference would be:

±14 mg/L for 400 mg/L SO_4^{2-}, and

±7 mg/L for 40 mg/L SO_4^{2-}

(b) Data obtained by Thames Water/Yorkshire Water (3).

Figure D1 Flow diagram for sulphate analysis

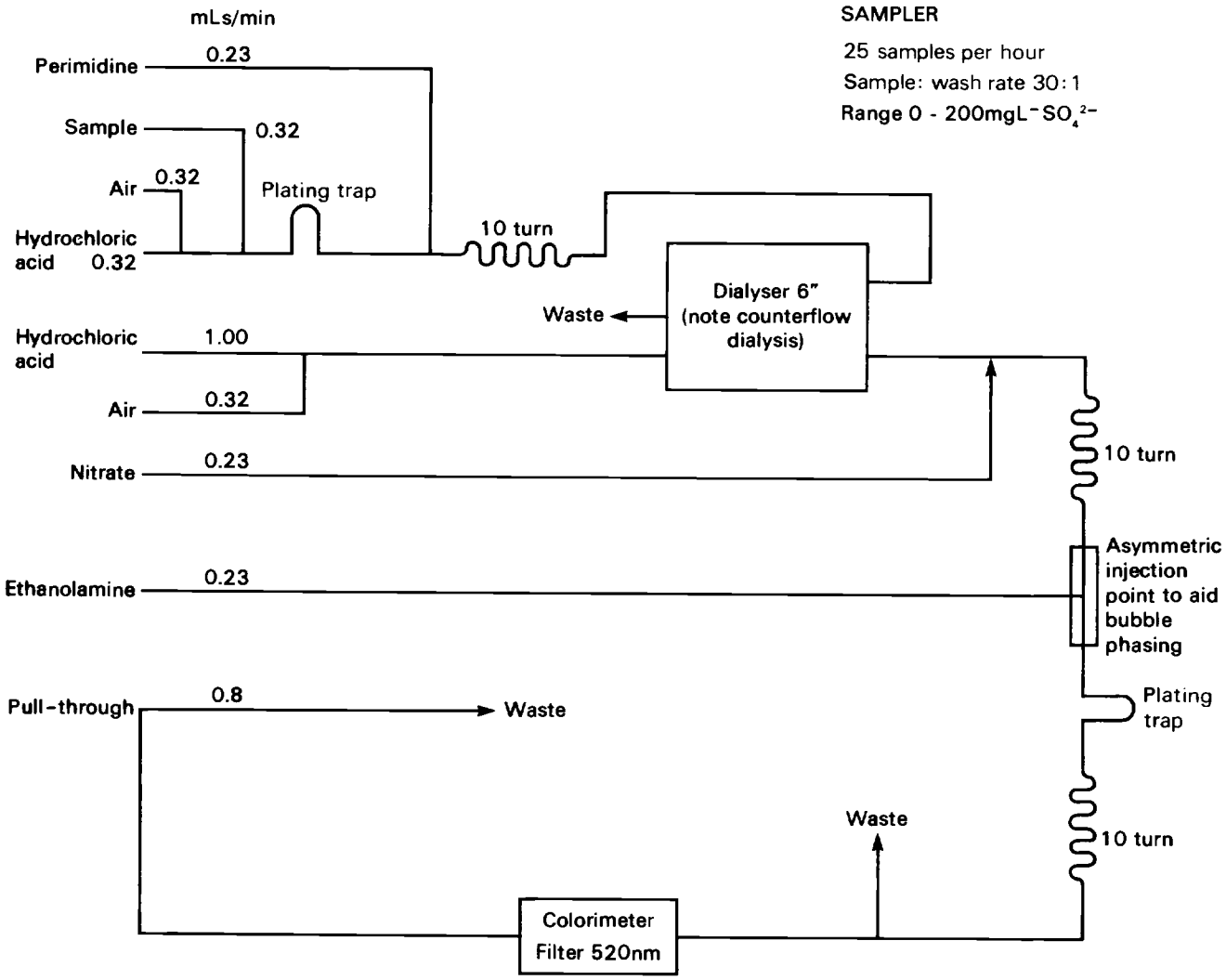


Figure D2 Detail of plating trap

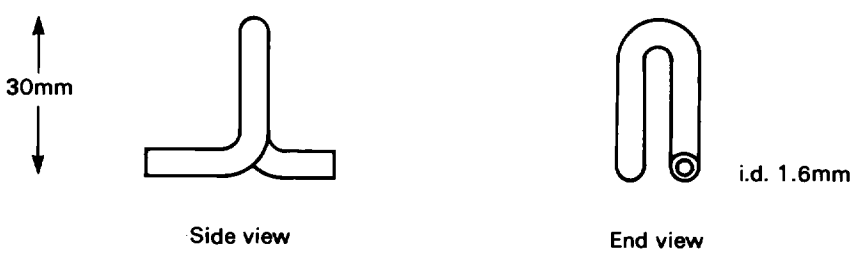
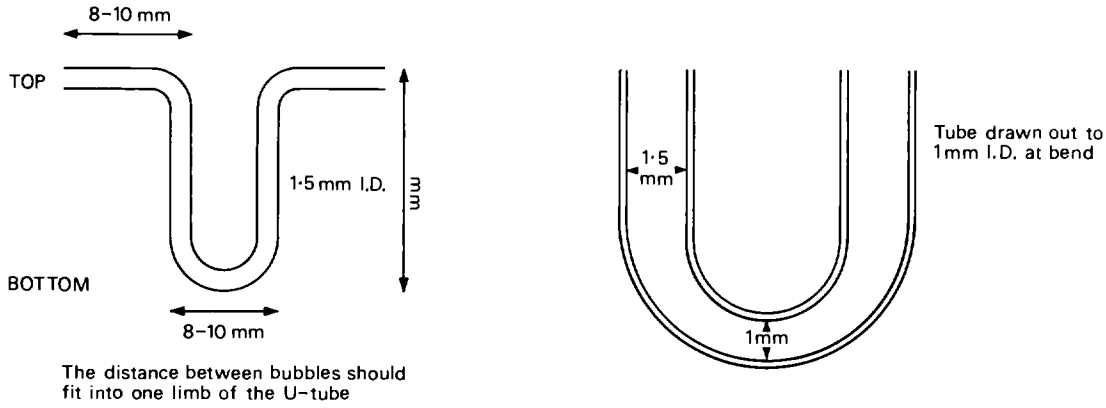
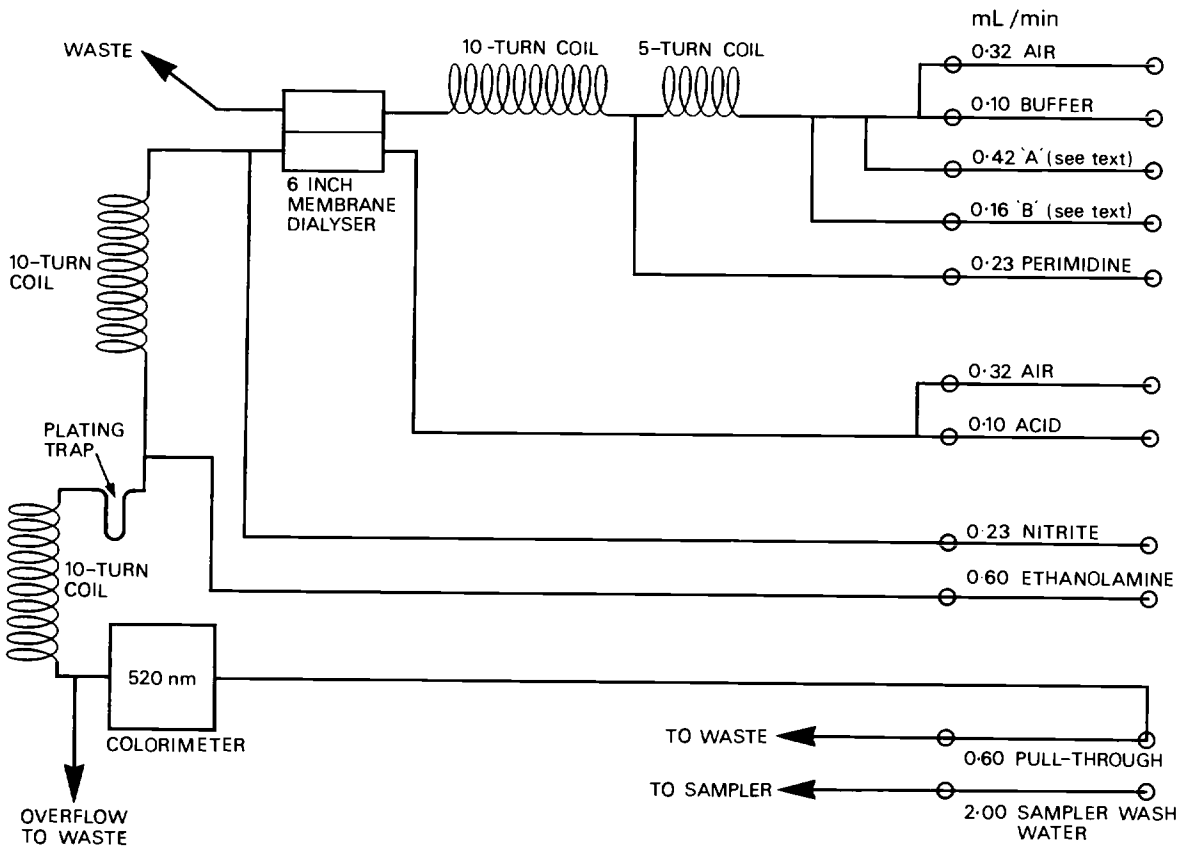


Figure D3 Detail of plating trap (alternative)



Although recommended in the reference, inclusion is not essential

Figure D4 Flow diagram for the automated determination of sulphate in water



E Sulphate In Waters By Flow Injection Analysis Using A Turbidimetric Method

E1 Performance Characteristics of the Method

(Tests have shown that the performance characteristics of this method are highly instrument dependent. Typical data are given for one instrument. Users should determine the performance characteristics of their own instrument before putting the method into routine use.)

Discrete Analysers may also be used See E11. Unautomated Turbidimetric Sulphate analyses have been shown to be exceedingly variable in both accuracy and precision.

E1.1	Substance determined:	Sulphate ion.
E1.2	Type of sample:	Raw and potable waters.
E1.3	Basis of method:	Sulphate ion reacts with barium chloride in acid solution to form a suspension of barium sulphate and the turbidity is measured at 540 nm.
E1.4	Range of application: (b)	10–200 mg/L sulphate. Instrument dependent, see E1.7 below and Section E9.
E1.5	Calibration curve:	Non linear.
E1.6	Standard deviations: (a)	

	Sulphate conc (mg/L)	Total std dev (mg/L)
Potable water	18.9 (5 degrees of freedom)	0.37
River water	104.3 (7 degrees of freedom)	1.15

E1.7	Limit of detection (b):	Instrument dependent below 10 mg/L sulphate. Users should determine the limit of detection (to a relative accuracy of 10%) and, if needed, the limit of reliable detectability, using their own instrument. It is suggested that if concentrations of below 5 mg/L need to be determined, either a larger sample injection or sample preconcentration be used depending on the instrument design. (See Section E9).
E1.8	Sensitivity: (a)	200 mg/L gives an absorbance of approximately 0.24 AU.
E1.9	Bias:	No data.
E1.10	Interferences: (a)	Main interfering substances are bicarbonate and carbonate (alkalinity), and chloride (see Section E3).
E1.11	Time for analysis (a)	Once the manifold has been fitted (5 mins) and flushed through with reagents (3 mins) samples can be analysed at a rate of approx 70 per hour.

(a) Data obtained by Anglian Water, Regional Standards Laboratory, Cambridge.
(b) Data obtained by Anglian Water, Regional Standards Laboratory, Cambridge and Thames Water, New River Head Laboratory.

E2 Principle

Sulphate reacts with barium chloride to form a suspension of barium sulphate which is stabilised by gelatin and thymol: hydrochloric acid is present to prevent the precipitation of barium carbonate, phosphate and sulphite. The turbidity is measured colorimetrically at 540 nm.

E3 Interferences

The effects of some commonly occurring constituents of raw and potable waters are listed in Table E1. The main interfering substances at zero sulphate level, bicarbonate, and carbonate (alkalinity) and chloride, were all present at levels not usually found in raw and potable waters. The interferences, apart from that of carbonate, are probably due to physical rather than chemical effects; viscosity and refractive index differences between sample and carrier can cause mixing boundaries. These matrix effects can be lessened, if necessary, by using a carrier of similar composition to the sample.

Although interference effects are more marked at the higher sulphate levels they are generally only a small proportion of the actual sulphate concentration and, again, are found at levels of interfering substances not usually found in raw and potable waters. The alkalinity interference is probably due to consumption of the acid in the reagent.

Highly coloured or turbid samples are also a potential source of error.

E4 Hazards

Barium chloride is a Schedule 1 poison and should be handled with care. Eye protection should be worn and a fume cupboard used when handling.

E5 Reagents

Distilled or deionised water should be used for preparing reagents and standards. Analytical Grade reagents should be used where possible although SLR grade barium chloride and thymol, and technical grade gelatin powder have been satisfactorily used.

E5.1 Hydrochloric acid (d_{20} 1.18)

E5.1.1 Hydrochloric acid 0.01 M.

Carefully add 0.09 ± 0.02 mL of concentrated acid (E5.1) to approximately 800 mL of water; make up to one litre with water.

E5.2 Barium chloride reagent

This should be prepared strictly in accordance with the published procedure (1) because the degree of suspension of barium sulphate is controlled by several factors and can depend on the mode of preparation of the reagent.

Dissolve 0.20 ± 0.02 g of thymol crystals in approximately 500 mL of 0.01 M HCl with stirring, at a temperature of 80 ± 10°C. Cool the resulting solution to 40 ± 5°C and then add the remaining 500 mL of acid (total one litre). Slowly add 4.0 ± 0.1 g of powdered gelatine. Once it has dissolved add 20.0 ± 0.1 g barium chloride dihydrate and continue stirring until all has dissolved. Filter the resulting solution through GF/C filter paper under slight vacuum.

This reagent is usually stable for up to 3 months, but discard if the sensitivity starts to deteriorate.

E5.3 Sulphate stock solution (1 mL contains 1 mg SO_4^{2-})

See Section B5.6.1 alternatively:

Dissolve 1.479 ± 0.001 g of anhydrous sodium sulphate (dried for 3 hrs at 105°C) in 500 ml of water and dilute to one litre. Store this solution in amber glass bottle and keep cool. This solution is stable for several months.

E6 Apparatus

Many of the items of equipment needed for this method are commonly available in most laboratories. The manifold used to provide the performance data is shown schematically in Fig E1.

The apparatus for this method consists basically of the following:

Multi-channel peristaltic pump (as used for air-segmented flow analysis), preferably pulse free

Sample injection valve

Analytical cartridge (manifold) including reaction coil

Spectrophotometer with flowcell

Recorder or computer integrator

Other equipment required includes:

Syringes, 2 or 5 ml disposable

Reagent and carrier stream filters (in container type)

Reagent storage bottles (polyethylene or glass in which reagent may be degassed)

Sample filters (optional) 0.45 μm pore size, to fit syringes

E7 Sample Collection and Preservation

Samples may be collected in glass or polyethylene bottles and should be analysed within 6 hours of collection or stored at 4°C for not more than 2 days. 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 minimize the risk of air oxidation of samples containing sulphide or sulphite, sample bottles should be filled to exclude air.

E8 Analytical Procedure

For highly saline waters use standards made up in a similar but sulphate free water, see Section F12.4 before starting

Step	Procedure	Notes
	Starting Operation	
E8.1	Set up manifold as in figure E1 (notes 1a—1d).	(a) Follow the manufacturer's instructions for the correct assembly of joints and 3-way connectors.
		(1b) Tightness of the nipples on the sample loop is critical—too slack and leaks occur, too tight and the tube becomes constricted. Since the nipples are tightened while in the valve, care should be taken when re-fitting sample loops.
		(1c) A new manifold should be tested for leaks with distilled water before use, paying particular attention to the hand-tightened junctions.
		(1d) Ensure that the on-line filters are clean, with no coating of dried reagent; renew if necessary.
E8.2	Switch on the spectrophotometer and the recorder or integrator (note 2a).	(2a) For low sulphate levels an integrator may be incapable of accurate measurement; in such cases manual measurement of peak heights is necessary.
E8.3	Where necessary (note 3a) degas carrier water and reagents by bubbling helium through each for about 10 mins (notes 3b, c, d).	(3a) Although degassing is not essential for ambient temperature methods, it can be beneficial by reducing the risk of bubble formation at pressure reduction points such as on the suction side of the pump.

Step	Procedure	Notes
		(3b) Long, disposable, glass Pasteur pipettes have been found to be suitable.
		(3c) 'Balloon gas' grade helium has been found to be of adequate purity.
		(3d) Vacuum (5) or ultrasonics can also be used for degassing.
E8.4	Place carrier and reagent tubes in the appropriate bottles (note 4a) and start the pump. When the system is full of liquid check that there are no bubbles in junctions, carrier/reagent lines, coils and cell (note 4b).	(4a) 500 ml brown glass or one litre polythene bottles are suitable, having a top which allows insertion of a filter unit; they also serve as storage containers.
		(4b) Bubbles in junctions can usually be removed by gentle tapping with a spatula; those in carrier/reagent lines and reaction coils can be removed by flicking with a finger. Bubbles in the flow cell, which are the most usual, can be removed by taking the cell out of the spectrophotometer, holding it in an appropriate orientation and temporarily stopping the liquid flow by pinching the tubing between finger and thumb and then suddenly releasing it. If none of these methods work a slug of air can be loaded into the sample loop and injected into the system.
E8.5	Once solutions are flowing normally through the system and any bubbles have been removed check that the recorder/integrator baseline is steady with no excessive pulsing (note 5a) or intermittent 'spiking' (note 5b). Set an appropriate sensitivity.	(5a) Usually a sign of a bubble in the flow cell.
		(5b) This is usually caused by bubbles passing rapidly through the flow cell.
	Analysis of Samples	
E8.6	**Manual Injection**	
	Load the injection syringe (notes 6a, b, c) with sample as follows: take up approximately 4 mL of sample, flush to waste through the filter, then remove the filter. Take up air into the syringe, fit the filter to the syringe and holding vertical with the filter downwards, expel the air through the filter; remove filter and repeat. Take up a further 4 mL of sample into the syringe, fit the filter, invert, and with filter uppermost, expel air bubbles by depressing the plunger until the sample flows out smoothly (notes 6d, 6e).	(6a) 5 ml, plastic, disposable syringes have been found suitable even after several hundred injections; lubrication with silicone oil is occasionally necessary.
		(6b) This operation may be carried out while the previously injected sample is in the system.
		(6c) Any previous sample remaining in the syringe/filter unit should be removed as follows: take off filter unit and discharge sample from syringe, then take up air into the syringe, refit the filter unit and, keeping it downards, expel the air through it; remove filter unit and repeat.
		(6d) Sample filters should be renewed as necessary when discharging of the syringe becomes difficult.
		(6e) If plenty of sample is available, see notes 7c and 7d.

Step	Procedure	Notes
E8.7	Load the sample loop of the injection valve as follows: with the valve in the 'load' position securely fit the syringe and filter unit containing the sample into the injection valve, flush the loop with 2 ml (approx) of sample stop and then flush with a further 1 mL (approx) (notes 7a, b, c, d).	(7a) This procedure, and that in step 8, has been found to result in negligible carry-over between samples. (7b) If bubbles are introduced by this operation the following procedure has been found effective in removing any persistent bubbles from the valve/loop: gradually increase and then decrease the pressure on the plunger during the initial 2 mL flush, stop, and then slowly flush with the final 1 mL. (7c) If an ample volume of sample is available these volumes may be increased, to ensure no carry-over between samples, by using a 10 ml syringe; large volumes would be needed for step 8.6 however. (7d) If duplicate or triple injections of each sample are required a larger (10 ml) syringe could be used, with larger volumes in step 8.6.
E8.8	Inject the sample into the system by turning the valve to the 'inject' position with a fast, smooth action immediately after step 8.7 (note 8a).	(8a) This ensures minimum perturbation of flow; perfection of the action comes with experience.
E8.9	Repeat step 8.6 with a second syringe.	
E8.10	When the sample peak returns to baseline (note 10a) return the injection valve to the 'load' position with a quick and smooth action, and remove the syringe and filter unit.	(10a) Or before if necessary and it has been established that no perturbation affects the measurement of the peak in question or even the following peak, particularly when an integrator is used.
E8.11	Repeat steps 8.6 to 8.9 for each sample. Inject samples in the order (note 11a): calibration standards (in ascending order and including a distilled water blank) (note 11b), samples (including control standards), then calibration standards (in descending order) (note 11c).	(11a) Suggested order only. (11b) Seven calibration standards including blanks, have been found adequate to define the calibration curve. (11c) Precipitation may occur in the manifold. Check regularly and, if it does, wash out thoroughly.
E8.12	**Automatic Injection** Follow the manufacturer's instructions (note 12a) and load the sampler with standards and samples interspersed with appropriate controls (note 11c).	(12a) Samples with high turbidity or suspended solids should be filtered prior to loading into the sample presentation unit.
E8.13	When the last sample has passed through the system the spectrophotometer can be switched off (note 13a).	(13a) If an integrator is used for response measurement, a print out of results should be obtained before it and the spectrophotometer are switched off.
E8.14	Remove reagent lines from their bottles, rinse with distilled water and then invert (note 14a) the filter unit until air is drawn through before placing it in distilled water. Continue pumping until reagents have been flushed from the system. Flush out the sample loop on the injection valve with distilled water.	(14a) Inversion of each filter unit may be accomplished by inserting it in the top of a 13 mm id test tube supported in a suitable rack.

Step	Procedure	Notes
	Calculation of Results	
E8.15	Plot a calibration curve of measurement unit response (note 15a) against concentration of the calibration standard solutions (note 15b).	(15a) Usually peak height but if an integrator is used peak area can be measured. However, for very small peaks it can be difficult for some integrators to determine the start and end of peaks, resulting in area measurement variability. Peak height is usually a better parameter to measure in such circumstances. (15b) If sensitivity has changed significantly during the run, procedures suggested for segmented flow analysis (6) can be used to obtain calibration curves.
E8.16	If necessary, correct measurement unit responses for blank.	
E8.17	If necessary, the measurement unit responses of the samples should be corrected for any sensitivity changes. Then convert the measurement unit responses of the samples into concentrations from the calibration curve.	

E9 Change in concentration range of method

Lower or higher concentrations of sulphate may be determined by varying the sample loop volume; up to 150 μl (0.8 mm id, 30 cm length) has been satisfactorily used for low sulphate concentrations (2.5 mg/L) but no detailed performance data are available. The analyst should verify the performance of any modified system.

E10 Alternative wavelengths

Wavelengths varying between 410 and 480 mm have been used by other workers (1–4) but no detailed performance data are available and the analyst should verify the performance of any method using a wavelength other than 540 mm.

E11 Use of Discrete Analysers

This method has been successfully adapted for use with discrete analysers.

The method may be instrument dependent, especially at low sulphate concentrations (less than 10 mg/L sulphate). For convenience calibration may be divided into a high range (100–1,000 mg/L sulphate) and a low range (0–150 mg/L of sulphate). Turbidity is measured by absorbance or by turbidimetry at 520 nm. The reagents are as above. For information on discrete analysers see Ref 11.

Range 100–1,000 mg/L SO_4^{2-}

Sulphate conc mg/L SO_4^{2-}	Bias %		Precision % RSD	
	(a)	(b)	(a)	(b)
100	3.35	4.90	2.95	3.50
900	−0.49	−1.62	2.02	1.11
163, River water		—	5.07	

Range 0–150 mg/L SO_4^{2-} (b)

Sulphate conc mg/L SO_4^{2-}	Bias %		Precision % RSD
15	−3.55		3.16
135	5.69		0.56
		Limit of Detection	2 mg/L SO_4^{2-}

Range 0–100 mg/L SO_4^{2-} (a)

Sulphate conc mg/L SO_4^{2-}	Bias %		Precision % RSD
10	−3.46		5.30
90	−2.53		4.21
53, Tap water	—		4.37
		Limit of Detection	1.6 mg/L SO_4^{2-}

The limit of detection was taken as 4.652 × Std dev of deionised water blanks.

(a) Southern Water, Chatham Laboratory
(b) Welsh Water, Caernarvon Laboratory

E12 Analytical Quality Control

It is essential, especially at both the low and high ends of the concentration range to include control standards in among the samples at steps E8.11 or E8.12. These controls will also warn of incipient precipitation (E8.11 note 11c). Routine analytical quality control procedures must be observed (Refs 7, 8, 9 and 10).

E13 References

(1) J F van Staden, *Fresenius Z Anal Chem,* **312** 438 (1982).

(2) F J Krug, E Zagatto, B F Reis, O Bahia, A Jacintho and S S Jorgensen. *Anal Chim Acta,* **145**, 179 (1983).

(3) F J Krug, H Bergain Filho, E A G Zagatto and S S Jorgensen, *Analyst,* **102,** 503 (1977).

(4) S Baban, D Beetlestone, D Betteridge and P Sweet, *Anal Chim Acta,* **114,** 319 (1980).

(5) J Ruzicka and E H Hansen, *'Flow Injection Analysis'* pub: John Wiley & Sons (1981). ISBN 0-471-081912-2.

(6) *'Air Segmented Continuous Flow Automatic Analysis in the Laboratory' (1979).* Methods for the Examination of Waters and Associated Materials. London HSMO.

(7) *General Principles of Sampling and Accuracy of Results 1980.* HMSO in this series.

(8) Davy D J, and Hunt D T E, *WRC Technical Report TR174,* Medmenham 1982.

(9) Cheeseman R V and Wilson A L, *WRC Technical Report TR66,* Medmenham 1978, or its revision now in preparation.

(10) British Standards 5700 to 5703 inclusive and 5750.

(11) *Discrete and Air Segmented Automated Methods of Analysis, including Robots, An Essay Review, 2nd Edn, 1988.* HMSO, in this series.

Table E1 *Sulphate—Interference Data* (a)

Other substance (expressed in terms of substance in brackets)	Compound used as other substance	Conc of other substance (mg/L)	Effect (mg SO_4^{2-}/L of other substance at a sulphate conc (mg SO_4^{2-}/L) of:	
			0	180
Chloride (Cl)	NaCl	2,500	−4.1	−5.3
Carbonate (CO_3^{2-})	Na_2CO_3	1,000(1)	65.3	92.1
		300(2)	0.7	6.2
		150(3)	0.6	2.3
Bicarbonate (HCO_3^-)	$NaHCO_3$	1,000(4)	2.1	23.4
Orthophosphate (P)	Na_2HPO_4	100	−0.2	3.6
		10	−0.7	0.3
Silica (SiO_2)	$Na_2SiO_3.5H_2O$	100	0.3	−2.4
Nitrite (N)	$NaNO_2$	10	−0.3	−0.6
Nitrate (N)	$NaNO_3$	100	−0.7	10.5
Ammonia (N)	NH_4Cl	50	−0.5	−1.0
Calcium (Ca)	$CaCl_2.6H_2O$	1,000	−3.5	−4.0
Magnesium (Mg)	$MgCl_2.6H_2O$	100	0.1	−5.5
Iron III (Fe)	$FeCl_3.6H_2O$	10	1.4	−2.2
Chromium VI (Cr)	K_2CrO_4	5	0.1	6.1
Cyanide (CN)	KCN	10	0.2	2.3
Thiocyanate (SCN)	KSCN	20	−0.5	0.8
Fluoride (F)	NaF	10	−0.3	0.7
Bromide (Br)	KBr	10	0.3	2.3
Iodide (I)	NaI	10	0.1	0.4
Sulphide (S)	$Na_2S.9H_2O$	20	0.1	1.8
Thiosulphate ($S_2O_3^{2-}$)	$Na_2S_2O_3.5H_2O$	10	0.4	8.2

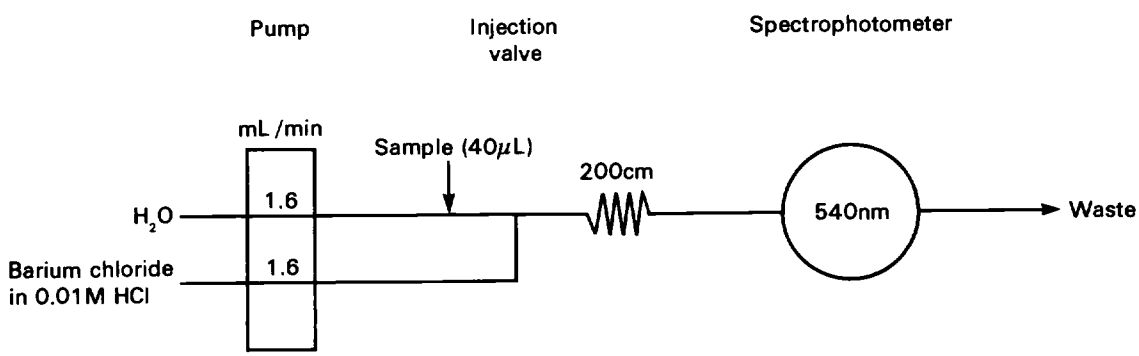
(a) Data obtained at Anglian Water, Regional Standards Laboratory, Cambridge.

If other substances did not interfere the effect would be expected (95% confidence) to lie between:

± 0.8 mg/L SO_4^{2-} at a sulphate conc of 0 mg/L SO_4^{2-}
± 0.8 mg/L SO_4^{2-} at a sulphate conc of 180 mg/L SO_4^{2-}

(1) equivalent to 1,670 mg/L $CaCO_3$
(2) equivalent to 500 mg/L $CaCO_3$
(3) equivalent to 250 mg/L $CaCO_3$
(4) equivalent to 820 mg/L $CaCO_3$

Figure E1 Manifold for sulphate in waters (manual injection)



F Sulphate In Waters By Ion Chromatography

F1 Introduction

The number of published methods for sulphate analysis by liquid chromatography is large, indicating how many options there are available. An analyst may choose a method on historical grounds or on the particular features of available equipment. Two instruments, configured in different ways are capable of producing *equally* valid results. There is no single 'correct' way of performing the analysis. Therefore no single definitive method is given, but a guidance of the minimum performance to be achieved, with some examples of working methods. The separation, detection and quantification is achieved by employing liquid chromatography commonly referred to as 'ion chromatography'. The same well established principles and equipment for liquid chromatography apply to this technique.

F2 Performance Characteristics of the Method

F2.1	Substance determined:	Sulphate ion
F2.2	Type of sample:	Raw, potable and waste waters. Saline waters following dilution (see Section F4).
F2.3	Basis of the method:	Chromatography of ions with detection by electro-conductivity.
F2.4	Range of Application:	0.1–100 mg/L SO_4^{2-}
F2.5	Calibration curve:	May deviate slightly from linearity.

F2.6 Standard deviations (a) and (c):

Sulphate concn. mg/L SO_4^{2-}	No of replicates	SD mg/L
0.72	340	.03
0.94	482	.03
3.60	122	0.11
10.00	10	0.053

F2.7	Limit of detection	0.1 mg/L SO_4^{2-} or better, depending on the system and conditions used.
F2.7	Bias (a) & (b).	None detected.
F2.9	Interferences:	Organic compounds which co-elute with sulphate, and relatively higher levels of other ions such as Cl^- in sea water (see Sections F4 and F12.4).
F2.10	Time required for analysis:	Depends on chromatographic column. Sample run time typically 2–10 mins.

Data supplied by:

(a) BP, Sunbury-on-Thames.
(b) Canada Centre for Inland Waters.
(c) British Gas.

F3 Principles

Sulphate is separated from other anions in a chromatograph by means of sample interaction between the stationary and mobile phases. A low capacity ion exchanger serves

as the stationary phase packed in a column separator (column). The mobile phase is a solution of an alkali metal salt of a weak mono- or di-basic acid. Conductivity detection is used for sulphate. A 'suppressor' may be used in combination with the conductivity detector in order to decrease the conductivity of the mobile phase. Hydrogen ion replaces the alkali metal of the mobile phase and changes sulphate in the sample to sulphuric acid. References covering ion chromatography and a comprehensive text in this series on 'The Chromatography of Ions' in preparation are listed in Section F13.

F4 Interferences

Compounds such a maleate, succinate, tartrate and selenates, if present in sufficient concentrations, may interfere with the determination of sulphate (see F12.3). Insufficient separation (cross sensitivity) may occur in cases where relatively large concentrations of other ions are present. In general a 500 to 1,000 fold excess of Cl^- or NO_3^- will result in loss of separation or overload the column; for sea water it will be necessary to dilute the sample to reduce these effects, see also Section F12.4.

Solid material and organic compounds (such as mineral oils, detergents and humic acids) shorten the life of the column. They should therefore be removed prior to analysis (section F9).

F5 Hazards

Eye protection and gloves should be worn, and fume hoods used when handling sulphuric acid (d_{20} 1.84).

F6 Reagents

Reagents of recognised analytical grade must be used. High purity water is essential, it must have an electrical conductivity of less than 0.1 μS/cm and be free from colloidal, organic (eg, removal by reverse osmosis) and particulate matter (<0.2 μm).

F6.1 Mobile phase preparation

The choice of mobile phase depends on the stationary phase material in the separator column and whether a suppressor is used. Consult the column manufacturer's manual for the exact composition.

Typical examples are:

Sodium hydrogen carbonate/sodium carbonate.
Potassium hydrogen phthalate.

In order to eliminate problems due to air bubbles in the system, it may be necessary to degas the mobile phase using He sparging, or vacuum. To avoid the growth of algae, the solution must be stored in the dark and renewed every 2 to 3 days.

F6.2 Mobile phase concentrate

Prepare a solution one hundred times the composition of the mobile phase (if possible). This may be used to prepare the mobile phase or to add to the samples to match their matrix to the mobile phase (see Section F9).

F6.3 Regenerant (0.0125 M)

For chemically suppressed chromatography using either a hollow fibre or membrane suppressor.

Dilute 2.8 ± 0.1 mL sulphuric acid (d_{20} 1.84) to 4 litres.

F6.4 Sulphate stock solution (1 mL contains 1 mg SO_4^{2-}).

See Section D5.6, alternatively, dissolve 1.479 ± 0.001 g of anhydrous sodium sulphate (dried for 3 hrs at 105°C) in 500 ml water and dilute to 1 litre. Store this solution in an amber glass bottle and keep cool. This solution is stable for several months.

F6.5 Working standards

Use the stock solution to prepare at least 5 standard solutions to cover the expected working range. Prepare fresh solutions for each day of measurement.

For saline waters, match the standard solutions to the matrix of the sample with sulphate-less artificial seawater, see Section F12.4.

F7. Apparatus

F7.1 Equipment

The chromatographic system (see figure F11) must be capable of detecting sulphate in the appropriate concentration range and separating it from the other constituents in the sample. It will normally have the following components:

7.1.1 Mobile phase reservoir typically of 4 litres capacity, preferably sited above the pump to provide a gravity feed.

7.1.2 Liquid chromatography pump operated at 1 to 3 mL/min.

7.1.3 Sample introduction loop (20 to 200 μL)—typically 50 μL.

7.1.4 Suitable guard and separator columns for the required performance (see F7.3).

7.1.5 Suppressor (if required) of hollow fibre or membrane material operated at a constant flow of 3 to 4 mL/min.

7.1.6 Recording device and/or data processor.

F7.2 Maintenance of equipment

Carry out regular maintenance of the equipment (eg change pump seals regularly) as outlined in the manufacturers instructions. Develop a routine cleaning schedule for the tubing, valves etc to prevent the build up of algae in the system. It is important however to ensure that these procedures do not lead to column contamination.

F7.3 Quality requirements for separator column

The stationary phase packed in the separator column is the critical part of the chromatographic technique. Its separation performance is determined by several factors such as the column material and the nature and concentration of the mobile phase. Use only such columns which, after introducing a standard solution containing NO_3^- and SO_4^{2-} at 10 mg/L (equivalent to 500 ng of each component using a 50 μl loop), will allow baseline resolution of these components (figure F2). The peak resolution should not be lower than R = 1.3 (see equation F1 and figure F3).

$$R = 2\,\frac{(t_2 - t_1)}{W_2 + W_1} \quad \text{equation F1}$$

where

R = peak resolution
t_1 = retention time of the 1st peak
t_2 = retention time of the 2nd peak
W_1 = peak width of 1st peak
W_2 = peak width of 2nd peak

F7.4 Column maintenance.

The most important factor in this method is the performance of the guard and separator columns. Once it has been established that the column meets the quality requirements (F7.3), then the system should be maintained at this standard. To achieve this, monitor performance characteristics of the columns such as operating pressure and peak resolution, and take corrective measures once a change is detected.

F8 Sampling and sample storage

Samples may be collected in glass or polyethylene bottles and should be analysed within 6 hours of collection or stored at 4°C for not more than 2 days. Samples low in organic matter may be kept for longer periods, but tests should be carried out to ensure that samples are sufficiently stable.

F9 Sample pre-treatment

Ensure that highly contaminated samples are not injected directly onto the column without establishing the nature of the matrix. If the sample contains soluble organic compounds such as humic acids, the use of a pre column containing the same resin material as the separating column or a cartridge of C18 packing is recommended for their removal.

In order to avoid precipitation reactions on the column and to eliminate chromatographic baseline disturbance, it may be advantageous to add one part of concentrate (F6.2) to a hundred parts of the sample. Dilution effects are eliminated by the same treatment of the calibrating solutions. It may be necessary to dilute the sample with water and mobile phase concentrate. After the addition of concentrate, filter the sample through a membrane filter (pore size 0.45 μm) to remove the particulate matter.

F10 Operating Protocol

Only guidelines for operation are given in this text as the details are dependent on the configuration and components of the chromatographic system and the operating conditions employed. Working examples are given in section F11.

F10.1 Start up procedure.

Start the chromatograph in accordance with the instrument manufacturer's instructions. Determine performance characteristics of the system (see F7.5) to ensure that the chromatographic system will perform to the required minimum standard for the chosen analytical range.

Allow the system to equilibrate for 30 minutes and then check that the baseline is stable (drift of less than 1%/min).

F10.2 Peak identification.

Introduce a standard solution of sulphate (and other components of interest) into the chromatograph by means of a loop valve and identify the peaks by their retention time from the point of injection. Retention times may vary slightly with concentration and matrix in the sample. Such problems may be overcome by the use of relative retention times.

If there is doubt, reanalyse one sample with added extra sulphate and note which peak is increased.

F10.3 Calibration.

Chromatographically analyse the standard and blank solutions prepared according to section F6.5. Plot a graph of peak height or area against concentration or calculate using a polynomial regression. A smooth line should result which is either straight or slightly curved.

F10.4 Sample analysis.

After establishing the calibration curve, the pretreated sample (F9) can be analysed.

If the ionic concentration of the sample exceeds the analytical range, dilute the sample. Do not record values below the lowest calibration standard. In such an event it may become necessary, if possible, to establish a new calibration curve for a lower concentration range.

After each sample series, or at most after 10 to 20 measurements, two standard solutions of different concentrations in the lower and upper part of the working range should be measured in order to check the validity of the calibration curve. If need be, perform a new calibration. For accurate work, follow the quality control procedures outlined in Section H of this booklet.

F11 Working examples

The following figures (F4–F6) illustrate the type of chromatogram which can be obtained from working systems. In general, sulphate tends to be the last major component on the chart.

F12 Notes

F12. Concentrator columns can be used for trace level work. Monitor the performance of the column (F7.4) to check for deterioration.

F12.2 For isocratic separations, sulphate tends to be the last component on the chromatogram. It is possible to change the operating conditions to speed up the analysis if sulphate is the only ion of interest. This can be achieved through use of a stronger mobile phase, higher flow rate or shorter column eg guard column.

F12.3 The presence of organic compounds which co-elute with sulphate can be determined using a UV detector in series with the conductivity detector.

F12.4 Mention has been made in Section F4 that samples high in chloride or nitrate may give problems due to column overload. Analysts must determine the degree of dilution required for their samples, keeping a portion of sample in reserve during the initial analyses if overloading is expected. Standards should be made up in a similar matrix to real samples and Section F6.5 suggests the use of synthetic sea water (omitting the sulphate) for making up such standards. Such standards would then need diluting to the same degree as the samples being analysed. The concentration of sea water varies somewhat with locality, though usually of fairly constant inter-ionic ratios. Analysts should adjust the strength of their synthetic sea water accordingly. There are various published recipes for synthetic sea water. A suitable approximate sulphate-less synthetic sea water is obtained by dissolving the following amounts of salts in water and making up to 1 litre ± 20 ml: sodium chloride 23.5 ± 0.1 g, potassium chloride 0.75 ± 0.05 g, magnesium chloride hexahydrate (blot dry) 9.0 ± 0.1 g, calcium chloride dihydrate 1.5 ± 0.1 g. Use to make up the required special sodium sulphate standards. If other brines differ markedly in composition from this, analyse them approximately and make up a suitable solution in similar manner. After addition of the sodium sulphate, the recipe above approximates to sea water, but lacks traces of bromide and carbonate.

F13 References

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The Determination of Anions and Cations, Transition Metals and Other Complex Ions, and Organic Acids and Bases in Water by Chromatography 1989, in preparation in this series.

Figure F1 Schematic diagram of ion chromatograph

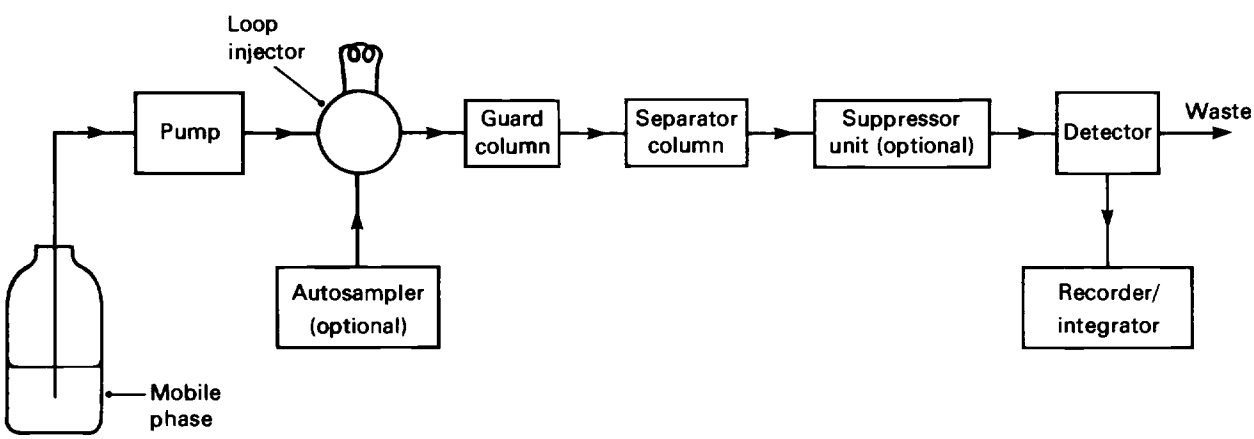
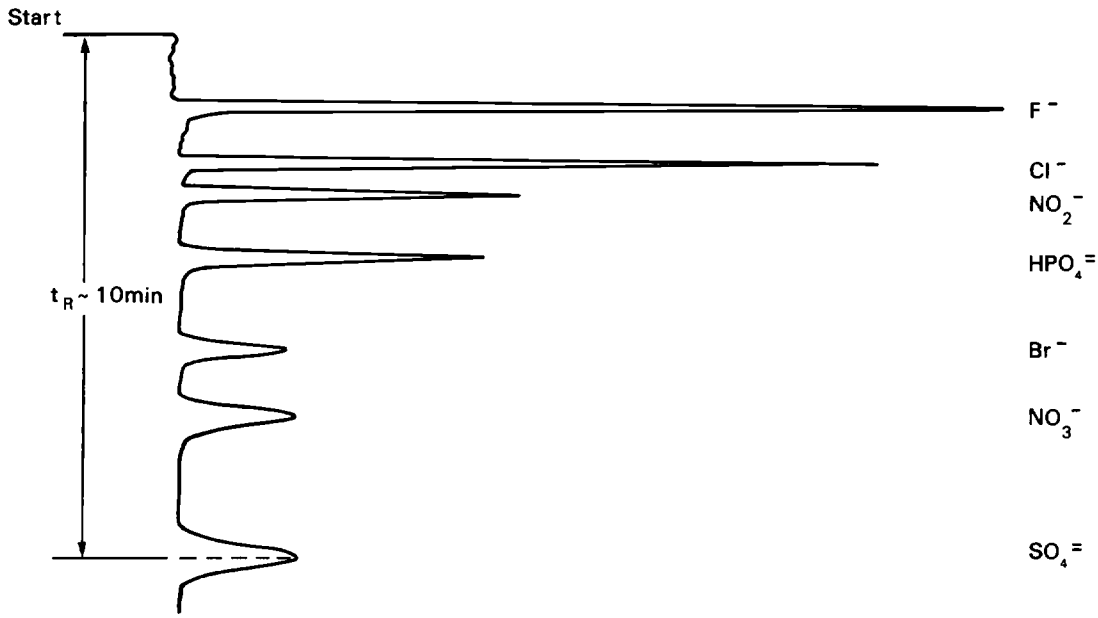


Figure F2 Chromatogram of a mixed anion standard

1 mg/L - standard; sample volume 50µl



Elution sequences and retention times may vary, depending on the type of column and the composition of the mobile phase

Figure F3 Idealized representation of the chromatographic separation

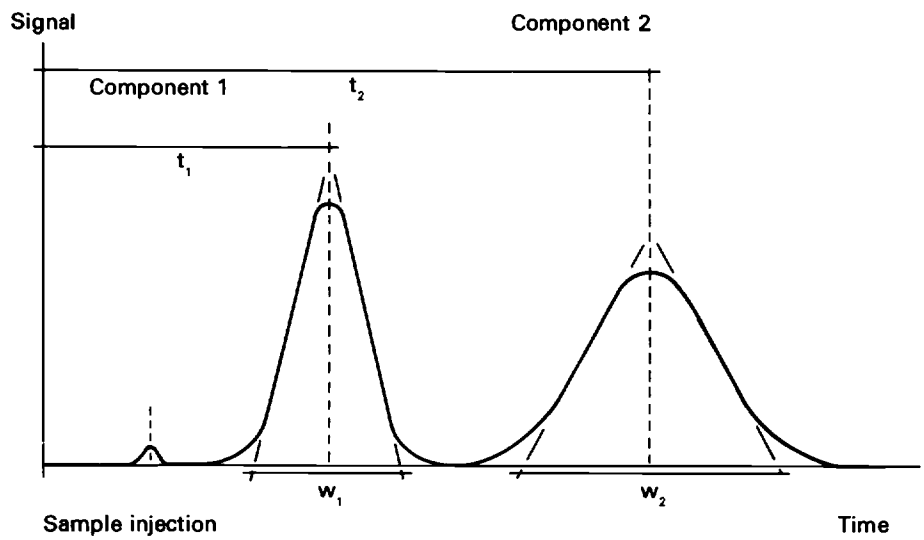
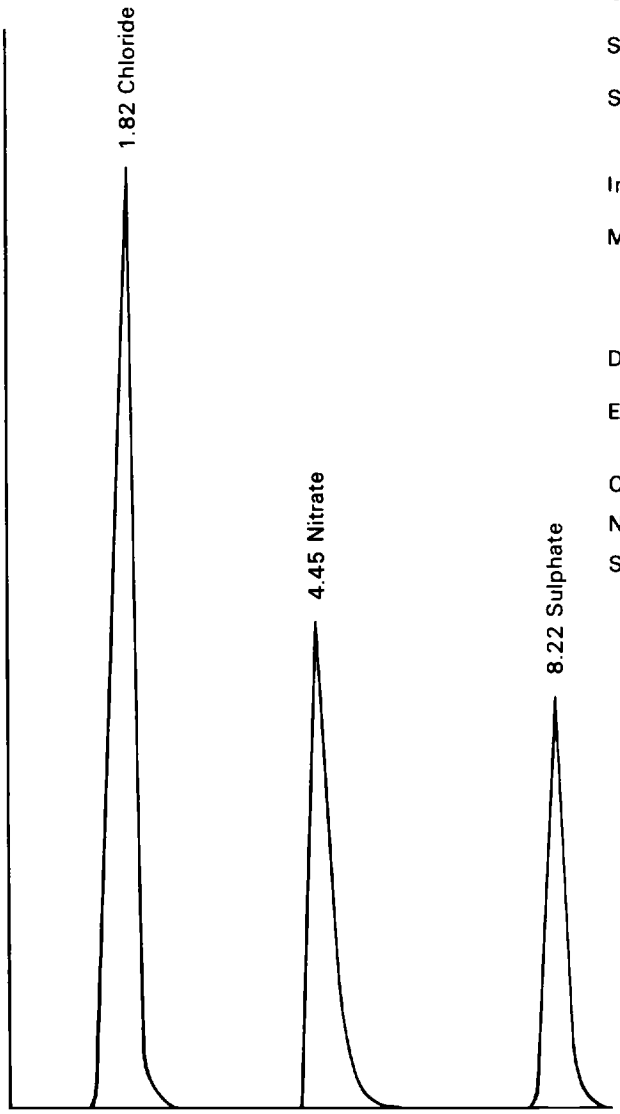


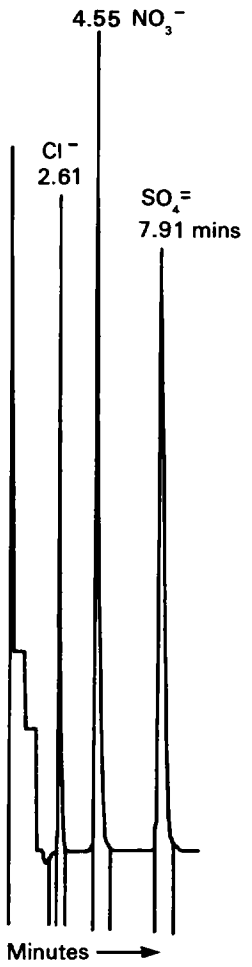
Figure 4a Working example of $SO_4^=$ by ion chromatography with a suppressor column



Guard column:	AG4A - Dionex	
Separator column:	AS4A - Dionex	
Suppressor:	Membrane 3.5mL/min (H_2SO_4 regenerant)	
Injector loop:	50μL	
Mobile phase:	Na_2CO_3 2.0mM $NaHCO_3$ 0.75mM 2.0mL/min	
Detector:	Conductivity	
Element	Concentration (mg/L)	Full scale (μS)
Cl^-	20	300
NO_3^-	20	300
$SO_4^=$	50	300

Supplied by Southern Water, Kent Division

Figure F4b Working example of $SO_4^=$ by ion chromatography with a suppressor column

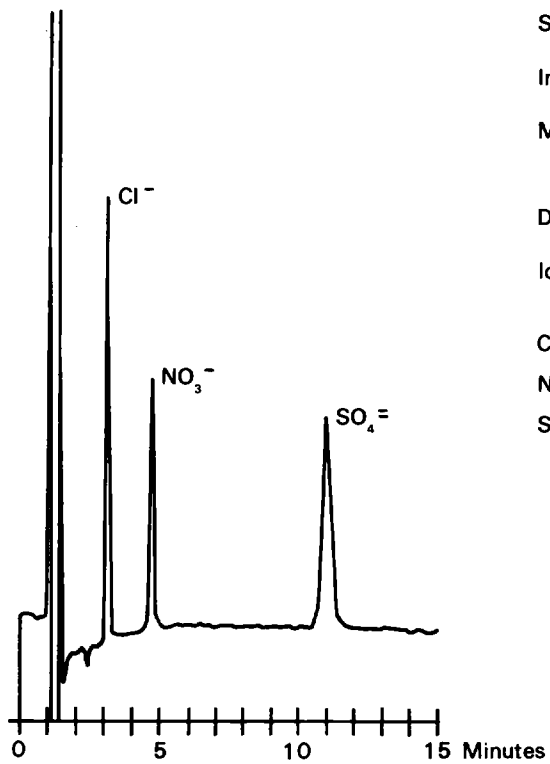


Guard column:	AG4A - Dionex
Separator column:	AS4A - Dionex
Suppressor:	Membrane 3.5mL/min (H_2SO_4 regenerant)
Injector loop:	50μL
Mobile phase:	Na_2CO_3 2.0mM $NaHCO_3$ 0.75mM 2.0mL/min
Detector:	Conductivity

Element	Concentration (mg/L)	Full scale (μS)
Cl^-	20	100
NO_3^-	4.1	10
$SO_4^=$	24	30

Data supplied by Institute of Terrestrial Ecology

Figure F5 Working example of $SO_4^=$ by ion chromatography (not suppressed)



Separator column:	3021C – Vydac (25 x 4cm)
Injector loop:	100μL
Mobile phase:	Potassium hydrogen phthalate 2.0mM at pH 4.74 in 1% methanol 3.0mL/min
Detector:	Conductivity

Ion	Concentration (mg/L)
Cl^-	1.7
NO_3^-	2.6
$SO_4^=$	3.1

Data supplied by Institute of Terrestrial Ecology

Figure F6 Working examples of $SO_4^=$ by ion chromatography

Figure F6a

Vydac 3001C405

Eluent 1.5mM phthalic acid ph 8.9

Cl^-	1mg/L
NO_2^-	1.5mg/L
Br^-	3mg/L
NO_3^-	2.5mg/L
$PO_4^{\equiv}$	3mg/L
$SO_4^=$	3mg/L

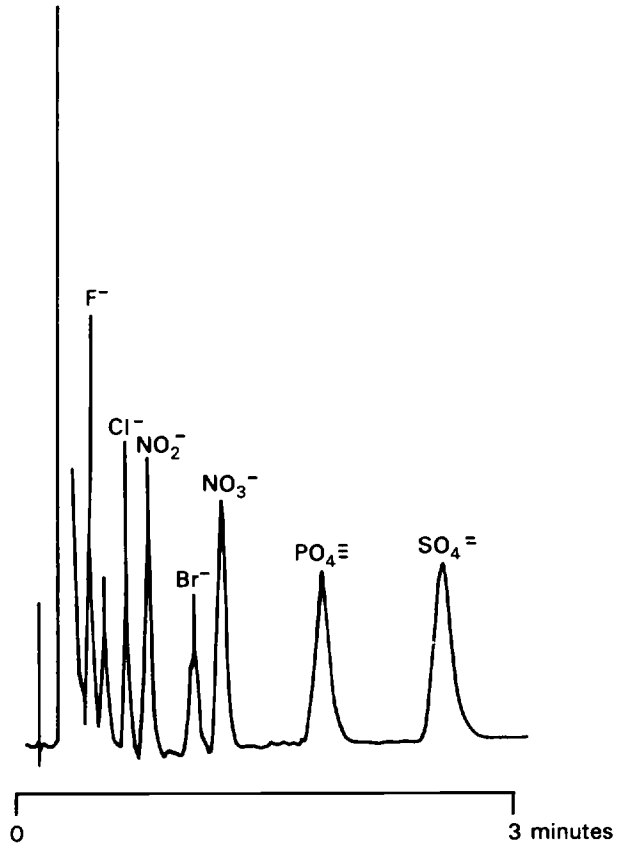


Figure F6b

Waters 1C Pak A

Eluent 1mM phthalic acid ph 7.0

Flow rate 1.2mL/min

Sample volume 10μL

Cl^-	100mg/L
NO_2^-	100mg/L
NO_2^-	100mg/L
Br^-	100mg/L
$SO_4^=$	100mg/L

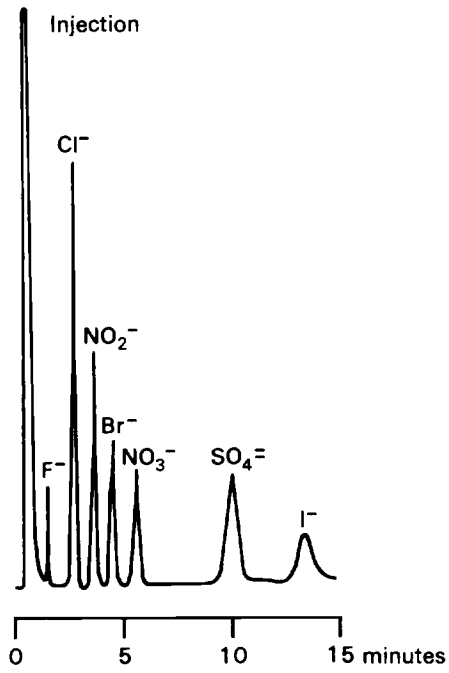
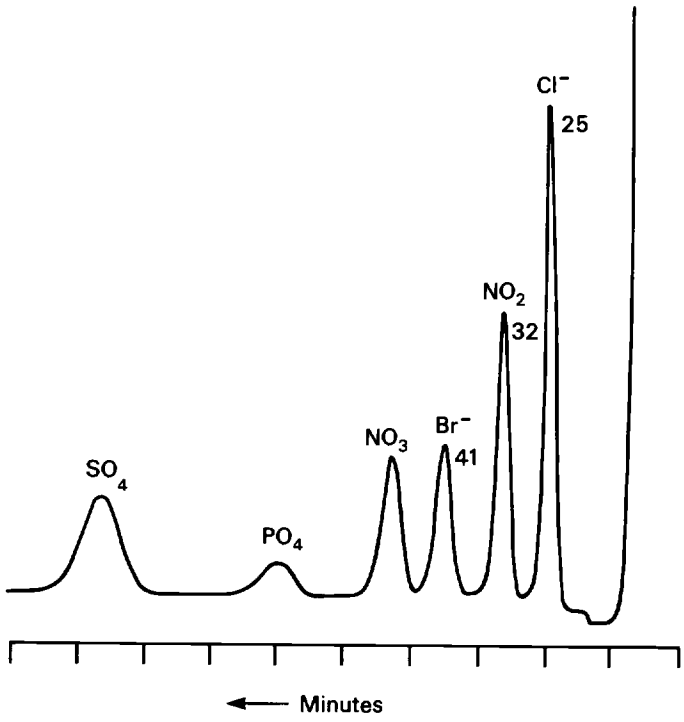


Figure F6c



Columns – anion sep + anion guard
Waters 1C Pak A
Waters ICL 1 chromatograph

Eluent borate/gluconate

Flow rate 1.2mL/min

5mg/mL each anion

Eluent concentrate
Water 875mL
Sodium gluconate 16g
Boric acid 18g
Sodium tetraborate (10 H_2O) 25g
Glycerin 125mL

Eluent
Concentrate 20mL
Acetonitrate 120mL
Water 860mL

G Sulphate in Waters by Air-Segmented Continuous Flow Colorimetry using Methylthymol Blue (TENTATIVE).

G1 Performance Characteristics of the Method

(For further information on the determination of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series).

G1.1	Substance determined:	Sulphate ion
G1.2	Type of sample:	Raw, potable, waste and saline waters provided that they are not highly turbid or coloured.
G1.3	Basis of method:	The sulphate is reacted with barium chloride to form barium sulphate. Excess barium reacts with methylthymol blue at high pH and the uncomplexed dye, which is a measure of the sulphate concentration, is measured colorimetrically at 460 nm
G1.4	Range of application:	2–100 mg/1 SO_4^{2-}
G1.5	Calibration curve:	Linear (see Section G10).
G1.6	Standard deviation(a) (on potable waters)	Sulphate concentration mg/L SO_4^{2-} / Total standard deviation mg/L SO_4^{2-} 8 / 0.63 64 / 1.25 98 / 1.64 (All with 8 degrees of freedom)
G1.7	Limit of detection(a):	1.8 mg/L SO_4^{2-}
G1.8	Sensitivity(a):	100 mg/L gives an absorbance of approximately 0.3 AU
G1.9	Bias(b):	Results may be biased high at low levels of sulphate
G1.10	Interferences:	Cations interfere by complexing with methylthymol blue. These ions are removed by passage through an ion exchange column.
G1.11	Time required for analysis	The automated system described is capable of operating at up to 30 determinations per hour. Set-up time and wash-through time may amount to 90 minutes and 30 minutes respectively.

(a) Southern Water, Kent Division.
(b) Canada Centre for Inland Waters.

G2 Principle

The sample containing sulphate is reacted with excess barium chloride at pH 2.5–3.0 to form barium sulphate. Residual barium reacts with methylthymol blue at pH 12.5–13.0 to form a blue chelate. The uncomplexed methylthymol blue, grey in colour, which is a measure of the sulphate concentrations is measured colorimetrically at 460 nm (1).

G3 Interferences

Cations, such as calcium, aluminium and iron, interfere by complexing with methylthymol blue. These ions are removed by passing the sample through an ion-exchange column. Some anions, such as sulphite, phosphate and sulphide, may cause a positive interference if present in large amounts. However, these ions are not normally present in concentrations great enough to produce a significant effect. Highly coloured or turbid samples are also a potential source of error.

G4 Hazards

Barium chloride is a Schedule 1 poison and should be handled with care. Eye protection should be worn and fumehoods used when handling ammonium hydroxide (d_{20} 0.88) and hydrochloic acid (d_{20} 1.18). Industrial methylated spirits is highly flammable and should be handled accordingly.

G5 Reagents

Use analytical grade reagents unless otherwise specified. Distilled or deionised water is suitable for blank determiniations and for preparing reagent and standard solutions.

G5.1 Barium chloride solution

Dissolve 1.66±0.01 g of barium chloride dihydrate in 500 ml of water and dilute to 1 litre with water. Store in a polythene bottle. This reagent is stable for at least one month.

G5.2 Hydrochloric acid (d_{20} 1.18)

G5.2.1 Hydrochloric acid 2M

Carefully add 172±1 ml of hydrochloric acid (d_{20} 1.18) to 800 ml of water. Cool and dilute to 1 litre with water.

G5.3 Sodium hydroxide solution

Dissolve 7.2±0.05 g of sodium hydroxide in 500 ml of water. Cool, dilute to 1 litre with water and store in a polyethylene bottle. This solution is stable for at least one month.

G5.4 Ammonium hydroxide (d_{20} 0.88)

G5.5 Ammonium chloride

G5.6 Buffer solution pH 10.1

Dissolve 6.75±0.01 g of ammonium chloride in 500 ml of water. Add 57±1 ml of ammonium hydroxide (d_{20} 0.88) and dilute to 1 litre with water. Adjust the pH value to 10.1±0.1 and store in a polyethylene bottle. This solution is stable for at least one month.

G5.7 EDTA wash solution

Dissolve 40.0±0.1 g of tetrasodium ethylenediamine tetra-acetate in 500 ml of pH 10.1 buffer solution. Dilute to 1 litre with pH 10.1 buffer solution and store in a polyethylene bottle. This solution is stable for at least one month.

G5.8 Industrial methylated spirits

G5.9 Brij-35 solution 30% m/V (or other suitable wetting agent)

Dissolve, with warming 30±1 g of Brij-35 in 100 ml of water. Store in a glass bottle. This solution is stable for at least 3 months.

G5.10 Methylthymol blue—barium chloride reagent

Each batch of methylthymol blue (laboratory reagent) must be tested to determine the optimum weight required to obtain a linear calibration, since the purity of the dye varies from batch to batch (see Section G.10).

Dissolve the optimum weight, w, found in G.10 in 50 ml of water. Add 25±0.1 ml of barium chloride solution (G5.1), 4.00±0.05 ml of 1 M hydrochloric acid (G5.2.2) and 3 ml of Brij-35 wetting agent (G5.9). Make up to 100 ml with water and then dilute to 500 ml with industrial methylated spirits. Filter through a 0.45 μm membrane prior to use. Store in a glass bottle. This reagent should be prepared fresh daily.

G5.11 Cation exchange resin

Amberlite IR 120 (Na), standard grade, 14–52 mesh or equivalent.* Stir the resin with 2M hydrochloric acid (G5.2.1). Decant the acid and repeat the process. Wash the resin at least 3 times with water.

G5.12 Standard sulphate solution A 1 ml contains 1 mg SO_4^{2-}.

See Section D5.6 or alternatively, dissolve 1.479 ± 0.001 g of anhydrous sodium sulphate in 500 ml of water and dilute to 1 litre with water. Store in an amber glass bottle. This solution is stable for at least one month.

G5.12a It may be necessary to prepare a few extra standard samples below 25 mg/L SO_4^{2-} for use in optimizing the barium-MTB reagent. If so, aliquot dilution is the best method. Pipette 25 ml of solution G5.12 into a 250 ml calibrated flask and make up to the mark and mix well. Used as instructed in Table G1, this solution (G5.12a) gives standards of one tenth the strength listed in the table (1 to 10 mg/L SO_4^{2-}).

G6 Apparatus

G6.1 Apparatus for this continuous flow method consists basically of the following:

Sample presentation unit (sampler)
Multichannel peristaltic pump
Analytical cartridge (manifold) including pump tubes, mixing coils and ion-exchange column
Colorimeter, incorporating a flow cell
Recorder

Consult the essay review (2) on continuous flow analysis for further information.

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*Bio-rex 70, 20–50 mesh and Dowex 50W-X8, 20–50 mesh, have both been found satisfactory.

Wetting agent B has been found suitable.

G6.2 The design of the manifold is as in Fig (G1).

G6.3 An interference filter giving a maximum transmission at 460 nm is used with a flow cell of 10 or 15 mm path length.

G6.4 Ion exchange column

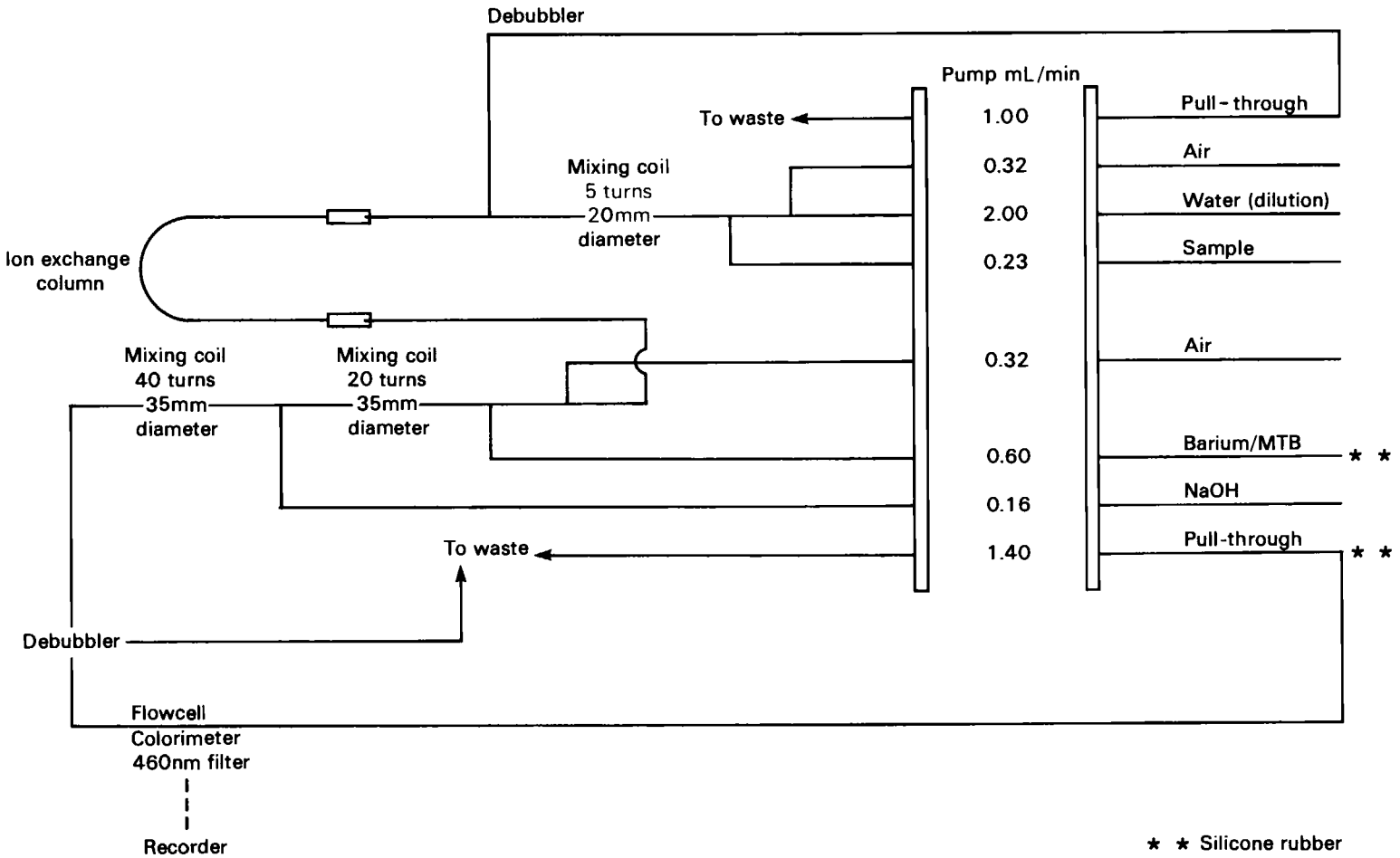
This consists of a length of U-shaped glass tubing (200 mm total length, 2 mm id, 3.6 mm od) filled with commercial ion-exchange resin (G5.11) excluding any air. The ends of the tube are covered with nylon gauze or lightly plugged with glass wool to prevent the resin escaping. Care should be taken not to use excess glass wool in order to prevent high back pressure.

The column may be conveniently filled by attaching a 50 ml plastic syringe to one end of the U-tube, with the plug or gauze in place. The open end of the tube is immersed into a slurry of fresh resin and the column filled by slowly withdrawing the syringe plunger. The open end is removed from the slurry and plugged, ensuring that no air enters the column. The syringe is removed and the column fitted to the manifold with plastic sleeving or nipples. The resin should be replaced each day rather than be regenerated in situ (See G12).

G7 Sampling and Sample Storage

Samples may be collected in glass or polyethylene bottles and should be analysed within 6 hours of collection or stored at 4°C for not more than 2 days. Samples low in organic matter may be kept for longer periods, but tests should be carried out to ensure that samples are sufficiently stable.

Figure G1 Manifold for sulphate in waters



Step	Procedure	Notes
G8.1	Following manufacturer's general operating instructions, connect the system as shown in Fig G1 (note a)	(a) See the Essay Review (2) on Continuous Flow Analysis, in this series.
G8.2	With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents. Ensure that there is sufficient of each reagent to avoid 'topping up" during one batch of analysis. Start the pump and switch on the detection and measurement units (note b).	(b) To avoid entraining air in the column it may be necessary to pump solutions for 15 minutes first. Then stop the pump, remove and re-pack the column, reconnect it and start the pump again.
G8.3	Allow the system to equilibrate for at least 1 hour and during this period check that the bubble pattern and hydraulic behaviour is satisfactory. If not, eliminate difficulties before proceeding to step G8.4.	
	Initial Sensitivity Setting	
G8.4	When an acceptably smooth baseline trace is given at the measurement unit, adjust the baseline response to about 5 per cent of full scale (note c) with the zero control and then transfer the sample probe into a C_m standard solution, where C_m is the greatest concentration that the calibration is intended to cover.	(c) An elevated setting of the baseline allows for any negative drift that may occur.
G8.5	When there is a positive stable response at the measurement unit due to the colour produced from the C_m standard solution (note d), adjust this response with the scale expansion control to read between 90 and 95 per cent of full scale (notes e and f).	(d) The sample probe need remain in the C_m solution only for sufficient time to give a steady reading. (e) A setting 5 to 10 per cent below full scale allows for any increase in sensitivity that may occur. (f) This may be directly possible on some measurement units but others may require range expansion facilities.
G8.6	Remove any traces of standard solution from the outside of the probe. Then return the sample probe to rest in the wash position.	
	Analysis of Samples	
G8.7	Load the sample turntable in the following order (notes g and h).	(g) The turntable can be loaded during the initial stabilisation period (steps G8.2 to G8.5).

Position No on turntable	Solution
1–5	Calibration standards in ascending order (see Section G9)
6–7	Blank water
8–17	Samples (note i)
18	Calibration standard (note j)

(h) Other loading patterns may be used. See reference 2.

(i) A control standard should occupy one of the sample positions as a check of system control.

(j) The standard which occupies position No 4 to check calibration.

Step	Procedure		Notes
	19–20	Blank water	
	21–30	Samples (note i)	
	31	Calibration standard (note j)	
	32–33	Blank water	
	34–38	Calibration standards in ascending order	
	Repeat the sequence 6–38 until all the samples have been processed.		
G8.8	When a steady baseline is obtained on the measurement unit, re-adjust it to about 5 per cent of full scale if necessary and start sampling unit.		
G8.9	When cross contamination occurs between 2 samples (visible on the recorder trace as incomplete separation of consecutive sample responses), re-analyse both samples separated by a blank solution.		
G8.10	When all of the system responses due to the processed solutions have appeared on the measurement unit and a final baseline has been obtained, this unit can be switched off.		
	Calculation of Results		
G8.11	Provided the blank-corrected responses of the calibration standard analysed at the end of each group and those at the end of the turnable are all acceptably close to their respective initial blank-corrected calibration responses, plot a calibration curve of measurement unit response (y-axis) against concentration (x-axis) of standard solutions. If not, refer to reference 2 for suggested procedures to obtain calibration curves.		
G8.12	First correct the measurement unit responses of the samples for any baseline and sensitivity changes, then using the calibration curve, convert the measurement unit responses due to the samples into concentrations of sulphate in the samples. The results are expressed as mg/L SO_4^{2-}.		
	Shut-down Procedure		
G8.13	Transfer the MTB and sodium hydroxide lines to water and continue pumping for 5 minutes. Then transfer these 2 reagent lines to the EDTA wash solution and continue pumping for at least 10 minutes. Replace the lines in water and continue pumping for at least 15 minutes. Finally, switch off pump, detection and measurement units.		

G9 Preparation of Calibration Curve

G9.1 As indicated in G8.6, at least five calibration standards should be run at the beginning of, and at intervals in, each batch of samples. Add, from a burette, volumes of the stock standard solution (G5.12) to a series of 100 mL of volumetric flasks, as shown in Table G1 below:

Table G1

Volume of stock solution G5.12, mL	mg/L SO_4^{2-}
1.0	10
2.5	25
5.0	50
7.5	75
10.0	100

G9.2 Make up to the mark and mix well. These solutions should be prepared fresh daily.

G9.3 Continue as given in Procedure, steps G8.6 to G8.9.

G10 Optimization of the Barium-MTB Reagent

G10.1 In order to obtain a linear calibration it is necessary to optimize the barium-MTB reagent. This procedure must be carried out for each batch of MTB since the purity is variable. Linearization of the calibration curve is accomplished by adjusting the barium-to-MTB molar ratio (3).

G10.2 Prepare a solution of MTB by dissolving 0.5193 ± 0.0002 g of methylthymol blue in 50 mL of water. Dilute to 100 ml in a volumetric flask.

G10.3 Pipette 5.00 ± 0.05 mL of barium chloride solution (G5.1) into each of five 100 mL volumetric flasks. Add volumes of the MTB solution (G10.2) to the flasks, as shown in Table G2. Add 0.80 ± 0.01 mL of 1 M hydrochloric acid (G5.2.2) and sufficient water to bring the volume to 20 mL. Add 0.60 ± 0.01 mL of Brij-35 solution (G5.9) and dilute to 100 mL with industrial methylated spirits (G5.8).

Table G2

Flask	Volume of MTB, mL	$[Ba^{2+}]/[MTB]$
1	4	1.25
2	5	1.00
3	6	0.83
4	7	0.72
5	8	0.63

G10.4 Run a set of calibration standards for each barium-MTB reagent ratio mixture in Table G2 through the experimental procedure (G8). Since most curvature occurs at low sulphate levels, it is useful to include some extra standards in the calibration, below 25 mg/L SO_4^{2-}; see Section G5.12a and G9.1.

G10.5 From the calibration curves obtained, select the optimum barium-to-MTB molar ratio (R) for the particular batch of dye. Calculate the weight of dye, w, required for routine preparation of solution G5.10 from:

$$w = \frac{0.1298}{R}$$

This weight corresponds to the particular batch of MTB and it can be used each time the barium-MTB reagent is prepared from that batch. For each new batch of MTB, the optimisation must be repeated to establish the optimum barium-to-MTB ratio.

G11 Changes in Concentration Range of the Method

Lower concentration ranges may be accommodated by changing the sample dilution, or by eliminating the dilution completely and passing the sample directly into the ion-exchange column. The calibration curves should remain linear as long as the barium-MTB reagent is prepared using the optimum weight calculated from the results of the linearity study. The analyst should verify the performance of the modified system.

G12 Sources of Error

G12.1 Continous flow analysis removes procedural errors associated with manual techniques and providing that the apparatus is properly maintained the main sources of error are likely to be those detailed below.

G12.2 Interfering substances (see Section G3)

Interfering cations are removed by the ion-exchange column. However, care should be exercised to ensure that the column does not become exhausted during a long analysis run. If unusually high concentrations of anions such as phosphate, sulphite or sulphide are present either recovery experiments should be carried out or the results should be checked by another method in this series. Change columns well before the limiting capacity indicated by such preliminary tests. Care should be taken when analysing highly coloured or turbid samples.

G12.3 Drifting Calibration Curve

A well maintained system should exhibit little drift of either calibration standard response or baseline. The presence of blanks and drift standards in an analytical run provide a means of checking the calibration. Small amounts of drift can be corrected by means of these standards, but large drifts should be investigated further.

G12.4 Inter-sample Carryover

The sample to wash ratio of the sampling device should be optimised with due regard to the required performance, at the introduction of the method to a laboratory*. However, where carryover is still a problem, mainly when a very high concentration is followed by a low concentration, the 2 samples concerned must be re-run separated by a water blank.

G13 References

(1) Lazrus A L Hill K C and Lodge J P *Automation in Analytical Chemistry*, Technicion Symposia 1965, Mediad, (1966) pp 291–293.

(2) *Air Segmented Continuous Flow Automatic Analysis in the Laboratory (1979).* Methods for the Examination of Waters and Associated Materials London HMSO. (See also E13 ref 11).

(3) Colovos G, Panesar M R and Parry E P *Analytical Chemistry* **48**, (12), 1963–6, (1976)

*Performance data quoted was obtained using a 1:1 sample to wash ratio.

H Analytical Quality Control Procedures

H1 Routine Control

Once a method has been selected for routine use, a system of analytical quality control should be adopted in order to validate the analysis. At least one control standard should be analysed with each batch of samples and the result plotted on a control chart. Corrective action should be taken if one value falls outside of the action limit (at ± 3s) or 2 values exceed the warning limit (at ± 2s). As more data is acquired, the standard deviation, s, should be updated and the control chart limits recalculated. See Miller and Miller (1984) for further details of analytical quality control.

H2 Estimation of the Accuracy of Analytical Results using these Methods

H2.1 Introduction

Not all the methods given in this booklet have been thoroughly investigated in more than 5 laboratories, others need adaptation to local equipment. Before general use, the accuracy achievable should be known. It would be of great value if any laboratory using or considering the use of any of these methods would estimate the accuracy of its own analytical results and report the findings to the Secretary of the Department of the Environment's Standing Committee of Analysts.

The precision achieved and the effects of any interfering substances that may be present in samples are of particular interest. Information on these aspects would be useful, but the value of such information would be greatly enhanced if it were obtained to a common plan so that such information can be compared and valid conclusions drawn. Accordingly, suggestions for a suitable experimental design and analysis of results are given in the following sections and it is suggested that laboratories follow this design whenever possible. The design has been chosen to be as simple as possible; more complex designs are possible and would give more information.

H2.2 Basis of Suggested Tests

The limit of detection is governed by the within-batch variability of blank determinations. The precision of analytical results may depend on the concentration of determinand in the sample analysed and on the type of sample, eg worse precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of at least 2 portions of each of the following solutions on each of n days, where n is at least 5 and preferably up to 10.

Solution No	Description
1	Blank
2	Another blank
3	Standard solution low concentration
4	Standard solution high concentration
5	Typical sample
6	Same sample spiked with a known amount of sulphate (y mg/L SO_4^{2-})

It is essential that these solutions be treated exactly as if they were samples and the appropriate specified procedure be rigidly followed. These solutions should be analysed in random order in each batch of analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method and should be treated exactly as routine samples. The same batch of water should be used on each day to prepare all 4 solutions. For solutions 5 and 6 a total of 5 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5. The results of the analyses of solutions 5 and 6 will provide a check of the effect of sample type on precision. Any deviation of the recovery of spiked sulphate from 100% may give an indication of the presence of interfering substances.

Note that the Blank water should be as appropriate for the method being evaluated.

H2.3 Evaluation of Results

The raw experimental results may be sent direct to the Department of the Environment for evaluation together with the results obtained from the standards used to establish the calibration curve in each batch of analyses. However, for those laboratories wishing to make the calculations themselves, the details are given below.

H2.3.1 Convert all results to concentrations as described in the method. Deduct the first of the 2 blank values (solution 1) from each of the other solution values.

H2.3.2 Calculate the mean concentration of the n results for each solution.

H2.3.3 Calculate the standard deviation, s, of the n results for each solution from:

$$s = \sqrt{\frac{\Sigma(\bar{x}_i - \bar{x})^2}{n-1}}$$

where x_i = the result from the ith batch

$\bar{x}$ = the mean value of x_i.

H2.3.4 Calculate the within-batch standard deviations, s_w, of the blank from:

$$S_w = \sqrt{\frac{(\bar{x}_{ii} - \bar{x}_{2i})^2}{2n}}$$

where x_{ii} = the 1st blank result (solution 1) from the ith batch.
x_{2i} = the 2nd blank result (solution 2) from the ith batch.

H2.3.5 Calculate the mean percentage recovery, R of the spiked sulphate in solution 6 from:

$$R = \frac{(\bar{x}_6 - \bar{x}_5)}{y} \times 100$$

where $\bar{x}_5$ = the mean value of the results of solution 5.
$\bar{x}_6$ = the mean value of the results for solution 6.
y = the added concentration of sulphate used in the spiked sample.

H2.3.6 Summarise the results as in the following table:

Solution	No of results n	Mean Sulphate Concentration	Standard Deviation	Mean Recovery %
2 Blank				—
3 Standard, low				—
4 Standard, high				—
5 Sample.....				—
6 Solution 5 + spike				8

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step 3.4 is entered for the blank solution 2 and the standard deviations from step 3.3 are entered for solutions 3 to 6.

H2.4 Evaluation of Interference Effects

If interference effects are suspected, analyse a series of standard samples with and without known amounts of interference, plus also real samples, spiked real samples and spiked real samples with interferent added. If interference removal is contemplated, this should be evaluated in the same way.

H3 Reference

Miller J C and Miller J N *'Statistics for Analytical Chemistry'* (1984) J Wiley

Department of the Environment

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A Address for Correspondence

However thoroughly a method may be tested there is always the possibility of a user encountering a hitherto unreported problem.

Correspondence about these methods should be addressed to:

The Secretary
The Standing Committee of Analysts
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