Sulphate in Waters, Effluents and Solids 1979

Methods for the Examination of Waters and Associated Materials

The booklet contains five methods. For information on application see the introduction.

Contents

London Her Majesty's Stationery Office

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 a properly equipped laboratory. 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 others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specification 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.

There are numerous handbooks on first aid and laboratory safety. One such publication is *Code of Practice for Chemical Laboratories* issued by the Royal Institute of Chemistry, London. Another such publication, which includes biological hazards, is *Safety in Biological Laboratories* (editors E Hartree and V Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London.

Where the committee have considered that a special or usual 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. 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 radiochemical 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.

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 checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of the 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. If in doubt, it is safer to assume that a hazard may exist and take reasonable precautions rather than to assume that no hazard exists until proved otherwise.

First published 1980

ISBN 0 11 751492 6

About this series

This booklet is one of a series intended to provide recommended methods for the determination of water quality. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has 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 individual methods, 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 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 user – the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst 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 one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine 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 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis
9.0 Radiochemical methods

The actual methods etc 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, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysis.

TA DICK
Chairman

LR PITTWELL
Secretary

20 July 1977

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 those given below in accordance with the type of sample, the expected sulphate concentration and probable interfering substances. This booklet contains methods using different types of apparatus. The recommended usage is as follows:

Method		Sample types	Range mg/l SO_4^{2-}	Major Interference	Use
A.	Barium Sulphate Gravimetric	All types of water, including sea-water and most industrial effluents. The method may also be used for many solid samples which have been brought into solution	50–5000	Chromate, phosphate, nitrate, iron and calcium may interfere, for details see Section A3	Referee analysis
B.	Indirect Titrimetric	All types of water	0–1400		Rapid control analysis especially of mixed batches of samples
C.	Direct Titrimetric	All types of water	0–200 0–20 (low range variant)		Single rapid control analysis or low range analysis
D.	Indirect Barium Atomic Absorption Spectrophotometry (using an acetylene–air flame)*	Most types of waters	5–175	Calcium over 200 mg/l	Rapid control analysis
E.	Indirect Colorimetric using 2-aminoperimidine	Most types of waters and most solids	20–120	Substances absorbing at 305 nm or alternatively absorbing at 525 nm	Rapid control analysis

* A nitrous oxide flame is not suitable

0.2 Throughout these methods, sulphate is never expressed as sulphur or as SO_3; it 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 instrument used in obtaining the test data in method D is mentioned; again, any equivalent instrument is suitable and no endorsement is intended. The test data will not necessarily be as quoted, if changes are made.

Method 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 (a):	50–5000 mg/l.
A1.5	Standard deviation (a) (on synthetic solutions of sodium sulphate):	Sulphate concentration mg/l SO_4^{2-} / Sample aliquot ml / Total standard deviation mg/l SO_4^{2-} 50 / 200 / 3·3 1500 / 20 / 21·5 5000 / 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 product:	$0{\cdot}87 \times 10^{-10}$ at 18°C (concentrations in moles/l).
A1.9	Bias (a):	None.
A1.10	Interferences:	Chromate, phosphate, nitrate, iron and calcium are among possible inorganic interferences if in excess of the tolerance levels quoted.
A1.11	Time required for analysis (a):	For a batch of 10 samples Operator time —about 4 hours Total analytical time—about 20 hours.

(a) The data quoted were obtained at Imperial Chemical Industries Limited, Mond Division, Research Department. Almost identical 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. The method should be directly applicable to most raw and potable waters and sea water with little risk of interference (see Section A3).

A2.2 The test portion of sample is neutralized and sufficient hydrochloric acid then added to make the solution about 0·05M. The solution is boiled and, if an unfiltered sample is originally taken for the test, any insoluble material remaining after boiling with acid is filtered off.

A2.3 The filtered solution is boiled, an excess of hot barium chloride solution is added and boiling is continued for at least 20 minutes to coagulate the barium sulphate precipitate and render it more crystalline. After allowing to stand overnight, the precipitate is filtered on a tared sintered glass crucible (porosity 4), the precipitate is 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

Of the constituents which may be present in waters and industrial effluents, chromate, phosphate, nitrate, iron and calcium interfere although limited concentrations of these can be tolerated. Provided the amount of any of these impurities present in the volume of test sample taken for the determination is not in excess of the values quoted below, then no interference is likely:

Chromate	(as CrO_4^{2-})	10 mg	Nitrate	(as NO_3^-)	1000 mg
Phosphate	(as PO_4^{3-})	10 mg	Calcium	(as Ca^{2+})	2000 mg
Iron	(as Fe^{3+})	50 mg			

Sulphide and sulphite could interfere in the sulphate determination but only if samples are unduly exposed to air and oxidation to sulphate occurs (see Section A7). Interference from sulphide and sulphite is overcome by boiling the sample with acid to remove hydrogen sulphide and sulphur dioxide respectively at the stage before barium chloride is added to precipitate sulphate. Alternatively, the reverse acidification procedure given in step A8.2a can be used.

A4 Hazards

Barium chloride is a toxic substance and should be handled with care. Eye protection should be worn and fumehoods used when handling ammonium hydroxide (d_{20} 0·88) (as in 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 deionized water throughout.

A5.1 **50% V/V Hydrochloric acid**

Dilute 500±10 ml of hydrochloric acid (d_{20} 1·48) with water to about 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 800 ml of water, cool and dilute with water to about 1 litre. (This reagent is toxic see Section A4.)

A5.3 **1 g/l Methyl orange indicator**

Weigh out 1±0·1 g of the indicator and dissolve by warming in about 500 ml of water, cool and dilute with water to about 1 litre.

A5.4 **Ammonium hydroxide** (d_{20} 0·88).

A5.5 **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 up to at least one month. 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 crucibles,** capacity of about 30 ml, porosity 4.

A6.2 **Buchner flask,** equipped with safety guard for vacuum filtration.

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 eliminate risk of air oxidation of samples containing sulphide or sulphite, sample bottles should be filled to exclude air. A settled unfiltered sample may be taken for the sulphate determination if desired.

A8 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
A8.1	Measure into a 400-ml beaker, a volume of sample (V ml), of between 10 and 200 ml, with a maximum sulphate content of 50 mg (note a). If necessary dilute the sample quantitatively prior to measuring out (note a). Unless the sample contains high concentrations of sulphites and/or sulphides, proceed with step A8.2. If the sample contains high concentrations of sulphites and/or sulphides, proceed with step A8.2a.	(a) The test may be carried out on a settled unfiltered sample if so desired.
A8.2	Add 2 drops of methyl orange indicator and neutralize the sample with 50% V/V hydrochloric acid or ammonium hydroxide. To the neutral solution add 2·0±0·2 ml of 50% V/V hydrochloric acid and adjust the volume to about 200 ml with water. Heat the solution to boiling point and boil for about 5 minutes. If the solution is clear, proceed directly to step A8.5 (note b).	(b) The solution should now be about 0·05M in hydrochloric acid.
A8.2a	If the sample contains high concentrations of sulphites and/or sulphides, put about 50 ml of water into a 400-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. Then resume the addition of sample. Rinse any residual solid into the boiling liquid with a few ml of water. Cool the liquid in the beaker, just neutralize with ammonium hydroxide, add 2·0±0·2 ml of 50% V/V hydrochloric acid and bring to the boil. If the solution is clear, proceed directly to step A8.5 (note b).	

Step	Experimental Procedure	Notes
A8.3	If insoluble matter is present, either filter the solution through a fine porosity ashless filter paper, wash with a small amount of hot water, collect the filtrate and washings in a 400-ml beaker, then proceed to step A8.5; or proceed directly to step A8.5, but also carry out step A8.4. If it is suspected that the insoluble material retained by the filter paper contains insoluble sulphate such as calcium sulphate (gypsum or anhydrite), carry out the procedure in Section A9 and add this extra sulphate to the soluble sulphate prior to calculating the total sample sulphate concentration.	
A8.4	If insoluble matter is left in the sample, take a second sample and carry out exactly the same procedure as is used for the first sample except that step 8.5 is omitted. This second sample gives the suspended solids correction weight (S mg), where $S=m_1''-m_2''$, m_1'' and m_2'' being the second sample weights in steps A8.6 and A8.9.	
A8.5	Boil the solution from step A8.2 or the filtrate derived from step A8.3 and add slowly $10{\cdot}0\pm0{\cdot}5$ ml of hot 10% m/V barium chloride. Continue to boil for at least 20 minutes, set aside to cool and allow to stand overnight (notes c and d).	(c) The slow addition of the hot barium chloride reduces the possibility of co-precipitation. (d) Boiling for 20 minutes aids coagulation of the precipitate and renders it more crystalline, again helping to reduce co-precipitation of other anions and cations.
A8.6	Prepare a clean and dry sintered glass crucible (A6.1) and weigh it accurately to $\pm0{\cdot}0002$ g (m_2) (note e).	(e) Barium sulphate can be dissolved from crucibles by soaking overnight in a solution containing about 5 g EDTA and about 25 ml monoethanolamine per litre. Crucibles must be well washed with water under suction before re-use.
A8.7	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 cold 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.	
A8.8	Wash the precipitate with cold 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 mls of filtrate in a beaker containing dilute silver nitrate/nitric acid solution. If no precipitate or turbidity forms, the precipitate is chloride-free.	
A8.9	Dry the crucible at 105 ± 2°C until constant in weight ($\pm0{\cdot}0002$ g) (about 1 hour), cool in a desiccator and weight. Repeat this procedure until two successive weights differ by not more than 0·0002 g. Record this weight (m_1) (note f).	(f) 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 at 105°C.

Step	Experimental Procedure	Notes
	Blank Test	
A8.10	Repeat the above steps substituting 200 ml of water for the sample. Let the weight of the blank crucible weights from step A8.6 be m_{2b} and step A8.9 by m_{1b} respectively. Then the blank value m_3 is given by $m_3=m_{1b}-m_{2b}$.	
	Calculation	
A8.11	If clear sample solutions were used (step A8.4 omitted) calculate the weight of barium sulphate (M) in mg precipitated from V ml of sample: $M=(m_1-m_2-m_3)\times1000$, where m_1, m_2 and m_3 are expressed in grams (see steps A8.9, A8.6, and A8.10).	
A8.11a	If step A8.4 was used $M=(m_1-m_2-m_3-S)\times1000$ (M, m_1, m_2, m_3 and S are as in step A8.11 and A8.4).	
A8.12	Sulphate in mg/l SO_4^{2-} is given by $\frac{M}{V}\times411{\cdot}5$.	

A9 Insoluble Sulphate Procedure

Recovery and determination of sulphate present in the insoluble material filtered off at step A8.4.

The presence of insoluble sulphate in the insoluble material obtained at step A8.4 of the procedure is very unlikely in most samples. If this is suspected, however, proceed as follows:

Place the paper and precipitate reserved at step 8.4 in a platinum crucible and heat over a low bunsen flame to burn off the paper. Calcium and/or barium sulphates, which will be the most likely insoluble sulphates present, do not lose sulphur trioxide on heating but can be reduced to sulphide if ignited with carbon in the absence of air. Mix the ignited residue with $4{\cdot}0\pm0{\cdot}1$ g anhydrous sodium carbonate and fuse the mixture. Extract the cooled melt from the crucible with water, remove the crucible, neutralize the solution with dilute (10% V/V) hydrochloric acid and acidify the solution to 0·05M. If silica was originally present in the insoluble material, fusion will render it soluble and acidification using dilute acid will not re-precipitate it. Proceed with the precipitation and determination of barium sulphate in 0·05M 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 sample. For additional information see specialized texts[1].

A10 Reference

(1) WF Hillebrand, GEF Lundell, HAB Bright and JI Hoffman, *Applied Inorganic Analysis (2nd Edition)* Chapman and Hall Ltd, London, Wiley, New York, 1953.

Method B Sulphate in Waters and Effluents by Indirect Titrimetry with Disodium Ethylenediaminetetraacetate 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:	Soluble sulphate ion.
B1.2	Type of sample:	Raw and potable waters, sewage effluents and saline waters.
B1.3	Basis of method:	Interfering cations are first removed by ion exchange, then sulphate ions are precipitated by excess barium chloride and the residual excess determined by titration with disodium ethylenediaminetetraacetate (EDTA).
B1.4	Range of application:	Up to 1400 mg/l SO_4^{2-} without prior dilution.
B1.5	Standard deviation (a) (on synthetic solutions of magnesium sulphate):	Sulphate concentration mg/l SO_4^{2-} / Total standard deviation mg/l SO_4^{2-} 19·6 / 0·36 48·1 / 0·26 98·4 / 0·68 (All with 9 degrees of freedom.)
B1.6	Limit of detection (a):	1·5 mg/l SO_4^{2-} for a 100 ml sample.
B1.7	Sensitivity:	1 ml of 0·01M disodium EDTA is equivalent to 0·961 mg SO_4^{2-}.
B1.8	Bias (a):	None known.
B1.9	Interference (a):	Phosphate and chromate are known to interfere, but compensation procedures are available (see Section B3). Coloured substances may interfere with the end-point detection.
B1.10	Time required for analysis (a):	For a batch of 10 samples, using 5 ion exchange columns. Operator time —about 60 minutes. Total analytical time—about 150 minutes.

(a) The data quoted were obtained by the Yorkshire Water Authority.

B2 Principle[1]

Cations are replaced by hydrogen ions on passing the sample through a column containing a strong acid cation exchange resin in the hydrogen form. Sulphate ions in the eluate are then precipitated using excess barium chloride and the solution volume reduced by evaporation. An ethanolamine/ethanol solution is added to raise the pH to 11–12 and also reduce the solubility of the barium sulphate precipitate. The excess barium is determined by titration with 0·01M EDTA (disodium ethylenediaminetetraacetate) solution using o-cresolphthalein complexone screened with naphthol green B as indicator. (The EDTA is used as a primary standard.)

B3 Interferences

The effect of other substances on the determination is set out in Table 1 below. (Data obtained by Yorkshire Water Authority, SE Division)

Table 1

Substance tested (concentration expressed as indicated in brackets)	Concentration in sample mg/l	Effect in mg/l SO_4^{2-} of other substances at 100 mg/l (a)
Potassium dihydrogen orthophosphate (as PO_4^{3-})	3	+ 3·4
	30	+40
Potassium dichromate (as $Cr_2O_7^{2-}$)	1	+ 1·8
	10	+ 9·1
	10(b)	+ 2·0
Sodium fluoride (as F^-)	1	+ 1·1
	10	+ 1·7
Sodium nitrite (as NO_2^-)	1	+ 0·1
	30	+ 0·7

(a) (If the other substance did not interfere, the expected effect (with 95% confidence limits) would be 0·0±2·0 mg/l SO_4^{2-} at 100 mg/l SO_4^{2-}.

(b) The potassium dichromate was reduced with stannous chloride prior to the ion exchange step in this test (see B9.2).
Phosphate and dichromate show significant interference effects and procedures for dealing with them are given in Section B9.

For information on other sulphur compounds see Section A3 as the solution conditions are similar.

B4 Hazards

Barium chloride and ethanolamine are toxic substances and should be handled with care. Skin contact with these chemicals should be avoided.

B5 Reagents

Analytical reagent grade chemicals and distilled and/or deionized water should be used throughout. Store reagents at room temperature unless otherwise stated. (See step B8.9 note (e)).

B5.1 Approximately 1 M Hydrochloric acid

Carefully add 176±2 ml of hydrochloric acid (d_{20} 1·18) to 1000±100 ml of water, cool, transfer to a 2-litre calibrated flask and dilute with water to the mark, stopper and mix thoroughly. Store in a glass bottle. The solution is stable for at least six months.

B5.2 Approximately 0·01M Barium chloride solution

Dissolve 2·443±0·001 g of barium chloride dihydrate in 500±50 ml of water. (Hazard, see B4.) Transfer quantitatively to a 1-litre calibrated flask. Add 2·0±0·1 ml of hydrochloric acid (d_{20} 1·18) and dilute with water to the mark, stopper and mix thoroughly. Store in a polyethylene bottle. The solution is stable for at least six months.

B5.3 0·01M EDTA solution

Dissolve 3·7224±0·0005 g of disodium ethylenediaminetetraacetate dihydrate (dried for 1 hour at 80±2°C) in water. Transfer to a 1-litre calibrated flask and dilute with water to the mark, stopper and mix thoroughly. Stored in a polyethylene bottle, this solution is stable for at least two months.

B5.4 Ethanolamine/ethanol buffer

(HAZARD, SEE B4)

Add 200±2 ml of ethanolamine (reagent grade) to 800±5 ml of industrial methylated spirit (non-mineralized). Store in a glass bottle. This reagent is stable for at least three months.

B5.5 **o-Cresolphthalein complexone/naphthol green B indicator**

Grind together 0·150±0·001 g of o-cresolphthalein complexone (metalphthalein), 0·080±0·001 g of naphthol green B and 20±1 g potassium chloride until a uniform fine grained powder is obtained. Store in a tightly closed amber glass bottle. The indicator is stable for at least one year.

B5.6 **Standard sulphate solution** (1 ml contains 250 µg SO_4^{2-})

Dissolve 0·4536±0·0005 g of potassium sulphate (dried for 1 hour at 110±5°C) in water, transfer quantitatively to a 1-litre calibrated flask and dilute with water to the mark, stopper and mix thoroughly. Prepare fresh solution each week.

B5.7 **Phosphate solution** (1 ml contains 200 µg P)

Dissolve 0·8788±0·005 g of potassium dihydrogen ortho-phosphate in water. Transfer quantitatively to a 1-litre calibrated flask, add 1·0±0·2 ml of chloroform and dilute with water to the mark, stopper and mix thoroughly. Store in a glass bottle at 4°C. The solution is stable for at least one month.

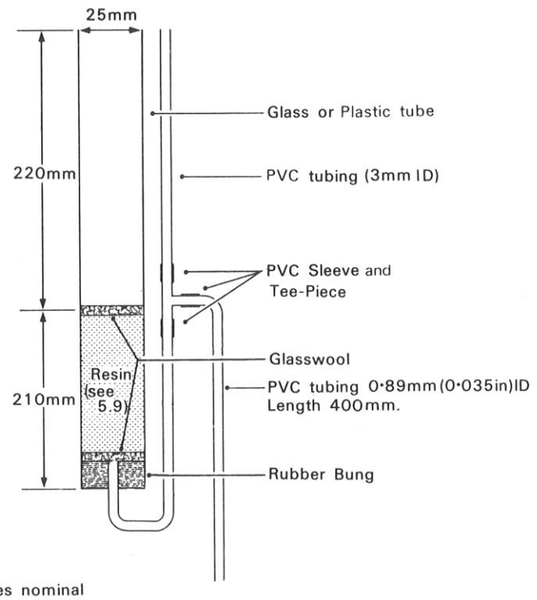
B5.8 **Cation exchange resin**

A strongly acidic cation exchange resin in the hydrogen form (BSS mesh size 10–50) is preferred. Amberlite IR120H is suitable. (See also Section B11.)

B6 Apparatus

B6.1 **Automatic ion exchange columns**

These may be constructed as indicated in figure 1.



Not to scale, sizes nominal

Figure 1 A typical 'automatic' ion exchange column

B6.2 **Burette type ion exchange column**

Alternatively, a 50- or 100-ml burette may be used instead of the column described in Section B6.1 and figure 1. A 200±10 mm long column of resin (see Section B5.8) retained by small plugs of glass wool above and below should be placed at the bottom end of the main burette tube.

B6.3 **Preparation and regeneration of ion exchange resin** (see also Section B11)

B6.3.1 Place a volume of the fresh resin in a beaker and add 4–5 volumes of distilled water. Swirl vigorously, allow to settle and then decant the liquid. Repeat the operation four times, then transfer the resin to the column with distilled water. Ensure that all air bubbles are removed.

B6.3.2 Pass a volume of 1M hydrochloric acid solution equal to three times the resin volume through the column.

B6.3.3 Wash the resin with water until the pH of the water rises above pH 5·5 (test with pH paper). The volume of water required will be approximately twice the volume of acid used. Do not allow the liquid surface in the column to fall below the resin level.

B6.3.4 The total ion exchange capacity is about 140 milliequivalents for the automatic column and about 30 milliequivalents for the 50-ml burette column. Before reaching 50% exhaustion, the columns should be regenerated using the procedure given in Sections B6.3.2 and B6.3.3.

B6.4 **The other apparatus required** includes the following:

B.6.4.1 *25-ml burette.*

B6.4.2 *Hot plate.*

B6.4.3 *400-ml tall form beakers.*

B6.4.4 *Anti-bumping granules* (sulphate free).

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. To eliminate risk of air oxidation of samples containing sulphide or sulphite, sample bottles should be filled to exclude air.

B7.2 Samples containing suspended matter should be filtered through a well-washed glass fibre filter capable of retaining particles of over about 1µm size before analysis.

B8 Analytical Procedure

READ SECTION B4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
B8.1	Pipette a volume, V ml, (note a) containing not more than 14 mg of sulphate SO_4^{2-} into a prepared ion-exchange column (note b).	(a) Normally 100 ml for 2–140 mg/l SO_4^{2-} and 10 ml for 140–1400 mg/l SO_4^{2-}. For a burette column the sample may be added in portions. (b) If the sample pH-value is outside the range 6–8, it must be adjusted to within this range prior to pouring the sample onto the column. Either measure the volume V ml into a small beaker and adjust the pH-value with a small amount of hydrochloric acid or sodium hydroxide solution, pour the sample onto the column, rinse the beaker thoroughly with a small volume of water and add the rinsings to the column, then continue with step B8.2; or, alternatively, adjust the pH-value of a known large amount of sample prior to pipetting the V ml and, if necessary, make a correction for any significant volume change, multiply the sulphate concentration from Section B 10 by the ratio: pH-corrected sample volume/original sample volume (see also Section C7.4).
B8.2	Allow the sample to run through the column at a rate of 10±2 ml/minute and collect the effluent in a 400-ml tall form beaker.	
B8.3	Wash the column 3 times with 50±5 ml volumes of water and collect the washings in the beaker used in step B8.2.	
B8.4	Add 5–10 well washed anti-bumping granules to the beaker and boil on a hot plate.	
B8.5	Add slowly by pipette, 15·00±0·05 ml (note c) of 0·01M barium chloride solution. Stir the solution with a glass rod during the addition.	(c) Smaller volumes of the barium chloride solution may be used where the concentration of sulphate in the sample permits, but an excess of at least 1·0 ml must be used.
B8.6	Evaporate the sample without boiling to 10±2 ml, cool to 20–25°C and add 25±1 ml of ethanolamine/ethanol buffer (note d).	(d) Maintain the sample to buffer volume ratio given otherwise problems will arise due to drifting end-points, particularly when phosphate is present.
B8.7	Stir just enough complexone indicator into the solution to give a strong purple colour. (Less than 0·1 ml of powder often suffices.)	
B8.8	Titrate the solution with 0·01M EDTA. The purple colour fades rapidly near the end point, which is marked by a sharp change to pale green. Let the volume of titrant be T ml.	
B8.9	Pipette 15·00±0·05 ml of 0·01M barium chloride solution into a beaker (notes e and f), followed by 25±1 ml of ethanolamine/ethanol buffer. Then carry out steps B8.7 and B.8. Let the volume of titrant be B ml.	(e) If samples are analysed regularly, step B8.9 need only be carried out daily. Results should be compared with those from previous days and the cause of any variation ascertained at once. With new batches of reagent carry out this step in triplicate prior to commencing analysis. (f) If a smaller volume than 15 ml of 0·01M barium chloride solution is used in step B8.5 the same volume should be used at this stage.

Step	Experimental Procedure	Notes
	Quality Control	
B8.10	Periodically a blank and a standard solution of sulphate should each be carried through the whole procedure in steps 8.1 to 8.9 inclusive to check on the efficiency of the ion exchange column which normally should be better than 99%.	

B9 Special Procedures

For samples with phosphate, chromate or dichromate concentration such that unacceptably biased results would be obtained (see Section B3, table 1), the following special procedures may be adopted:

B9.1 **Compensation for phosphate interference**

B9.1.1 Pipette 0·00, 0·50, 1·00, 2·00, 3·00, 4·00, 5·00 ml of working phosphate solution into a series of 250-ml beakers.

B9.1.2 Pipette 20·0 ml of standard sulphate solution into each beaker and make the volume in each case to 100±2 ml with water.

B9.1.3 Pass each solution through an ion exchange column as in step B8.2 and wash the column as in step B8.3, but rinse each of the beakers (step B9.1.1) with the first of the triple 50-ml portions of wash water. Collect the samples and their rinsings in 400-ml tall form beakers.

B9.1.4 Continue as for procedure steps B8.4, B8.5, B8.6, B8.7 and B8.8.

B9.1.5 From the titration for the solution containing 0·0 ml of phosphate solution subtract each of the other titrations and plot a graph of ml of 0·01M EDTA versus µg of phosphate as phosphorus.

B9.1.6 For samples with known phosphate concentration (determined separately, if necessary, for details see another method in this series) calculate the µg phosphate as phosphorus present in the aliquot of sample taken for analysis and read off the correction to be applied C_p ml from the graph.

B9.2 **Prevention of interference by chromate and dichromate**

Chromate and dichromate may be reduced by dropwise addition of tin II chloride solution to a simmering sample, prior to carrying out step B8.1. Use a slight excess of tin II chloride beyond that needed to cause the disappearance of the chromium VI colour. Then cool the sample to room temperature and proceed with step B8.1. No specific tin II chloride solution strength is stipulated; the strength should so match the chromium level that the resultant volume change is negligible. The reaction is stoichiometric:

$$3\,Sn^{II}+2Cr^{VI}=3\,Sn^{IV}+2Cr^{III}.$$

If phosphate is also present, it is precipitated during the reduction of the chromium; hence Sections B9.1 and B10.2 can be ignored.

B10 Calculation

B10.1 **In the absence of phosphate**

$$\text{Sulphate concentration}=\frac{(B-T)}{V}\times 961\ \text{mg/l}\ SO_4^{2-}$$

B10.2 **In the presence of phosphate**

$$\text{Sulphate concentration}=\frac{(B-T-C_p)}{V}\times 961\ \text{mg/l}\ SO_4^{2-}$$

B11 Resin Column Life

Resin columns are normally regenerated when about half the capacity has been used up (see step B6.3). This is usually determined from the theoretical capacity of the resin bed and knowledge of the calcium and magnesium content of the samples. However, should a column become exhausted prematurely, there will be difficulty with the blank and standard solution end-points (step B8.10); in which case, regenerate the column and repeat the immediately preceding samples.

B12 Reference

(a) G Schwartzenbach, H Flaschka, *Complexometric titrations*, p 318, 2nd Edition translated by HMNH Irving. Interscience Publishers Inc, New York, Methuen & Co Ltd, London. (1969).

Method C Sulphate in Most Waters and Effluents by Direct Barium Titrimetry Tentative Method

C1 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)

C1.1	Substance determined:	Soluble forms of sulphate.
C1.2	Types of sample:	Raw, potable, waste and saline waters.
C1.3	Basis of method:	Sulphate ions are titrated with barium chloride using a suitable indicator.
C1.4	Range of application:	Up to 200 mg/l, without the use of dilution or smaller aliquots, using the 0·005M barium chloride titrant; up to 20 mg/l using 0·0005M barium chloride.
C1.5	Standard deviation (a) (total and within batch, on synthetic solutions of sodium sulphate):	(b) Sulphate concentration mg/l SO_4^{2-} / Standard deviation mg/l SO_4^{2-} 5 / 0·15 50 / 0·45 (All with 10 degrees of freedom).
C1.6	Limit of detection:	(b) 0·2 mg/l sulphate as SO_4^{2-}.
C1.7	Sensitivity:	1 ml of 0·005M barium chloride is equivalent to 24 mg/l sulphate as SO_4^{2-}.
C1.8	Interference:	Several common anions cause interference including phosphate, fluoride, chromate, sulphide and various oxy-acids of sulphur. Strongly coloured waters may interfere. See Section 10.
C1.10	Time required for analysis:	5 minutes for 1 sample using a prepared column; using 2 columns, 10 samples in 30 mins.

(a) The method varies slightly with the expected range, see step C8.5, note f; both variants are given here.
(b) These data were obtained by North West Water Authority.

C2 Principle

After removing interfering cations by a preliminary ion-exchange stage, the sulphate ions are titrated with barium chloride using carboxyarsenazo as indicator (for the full name see Section C5.8).

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 serves two purposes. The bromocresol purple serves both as an acid-base indicator and as a colour screen for the carboxyarsenazo.

C3 Field of Application and Interferences

C3.1 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.

C3.2 Utilizing the more dilute titrant barium solution, the method is particularly useful for low levels of sulphate, for example in rain water.

C3.3 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.

C3.4 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 them or to apply corrections. See Section C9.

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.

C4 Hazards

Carboxyarsenazo indicator and barium chloride are toxic substances and should be handled with care.

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.

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

C5 Reagents

C5.1 Analytical reagent grade chemicals and distilled or de-ionized water should be used throughout.

C5.2 **Approximately 1·0M Ammonium hyrdoxide**
(HAZARD, SEE SECTION A4)

Dilute 60±5 ml ammonia solution (d_{20} 0·88) with water to 1000±10 ml. The solution is stable for at least one month.

C5.2.1 In laboratories where the use of ammonia is undesirable, it can be replaced by tetra-n-butylammonium hydroxide of equivalent strength.

C5.3 **Approximately 0·1M Ammonium hydroxide**

Dilute 50±5 ml of Solution C5.2 with water to 500±5 ml. The solution is stable for at least one week.

C5.4 **Approximately 1·0M Hydrochloric acid**

Carefully add 176±2 ml of hydrochloric acid (d_{20} 1·18) to 1000±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 six months.

C5.5 **Solvent buffer solution** (HAZARD, SEE SECTION C4)

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.

C5.6 **Standard sulphate solutions**

C5.6.1 *Solution A* 1 ml contains 1 mg SO_4^{2-}

Dissolve 1·814±0·001 g potassium sulphate (dried for 1 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.

C5.6.2 *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.

C5.6.3 *Solution C* 1 ml contains 0·01 mg SO_4^{2-}

Pipette 50·0±0·1 ml of solution B into a 500-ml calibrated flask, dilute with water to the mark, stopper and mix thoroughly. This solution is stable for at least one week.

C5.7 **0·005M Barium chloride** (HAZARD, SEE SECTION C4)

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.

C5.7.1 *0·0005M Barium chloride* (HAZARD, SEE SECTION C4)

Pipette 50·0±0·1 ml of 0·005M barium chloride solution into a 500-ml calibrated flask, dilute with water to the mark, stopper and mix thoroughly. This solution is stable for at least one week.

C5.7.2 *Standardization of the 0·005M or 0·0005M barium chloride solutions*

Pipette 20·0±0·1 ml of standard sulphate solution (either solution B for standardizing 0·005M barium chloride, or solution C for standardizing 0·0005M barium chloride) into a 250-ml conical flask. Carry out steps C8.4 and C8.5. Record the titre T_1. (T_1 is used directly in the final calculation).

C5.8 **Indicator Solution** (HAZARD, SEE SECTION C4. THIS SOLUTION IS TOXIC)

Dissolve 0·06±0·01 g carboxyarsenazo (disodium 2-(2-arsenophenylazo)-7-(2-carboxyphenylazo)-1, 8-dihydroxynapthalene-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.

C5.9 **A strongly acidic cation exchange resin in the hydrogen form** (BSS mesh size 10–50 is preferred); Amberlite IR120H is suitable.

C5.10 **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.

C5.11 **pH paper** to indicate pH 5·5.

C6 Apparatus

C6.1 **10-ml Burette** reading to 0·1 ml.

C6.2 **10-ml Microburette** reading to preferably 0·02 ml.

C6.3 Burette type ion-exchange column

To a 100-ml burette reading to ±0·2 ml, fitted with a small glass wool plug positioned just above the tap, add 30±5 ml of resin (see Section C6.5) and insert another glass wool plug above the resin column.

C6.4 Automatic ion-exchange column

This type of column may be used if desired. It may be constructed and prepared as indicated in the method B (Section B6.1, figure 1), but substituting a 100-ml burette or 15 mm diameter glass tube for the larger (25 mm diameter) tube shown in the diagram; the column should contain the same amount of resin as described in Section C6.5.1.

C6.5 Preparation and regeneration of ion-exchange resin

C6.5.1 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 four times, and, for either column design, transfer 30±5 ml of resin to the column with water. Ensure that all air bubbles are removed.

C6.5.2 Pass a volume of 1·0M hydrochloric acid solution through the column, equal to three times the resin volume.

C6.5.3 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 C6.5.2 will be required. When using the burette, do not allow the liquid surface to fall below the resin level.

C6.5.4 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 1·0M hydrochloric acid as in C6.5.2. 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 (C5.5) represents a convenient stage to regenerate the column.

C7 Sample Collection and Preservation

C7.1 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.

C7.2 To eliminate risk of air oxidation of samples containing sulphide or sulphite, sample bottles should be filled to exclude air.

C7.3 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 solution with 1·0M hydrochloric acid before ion-exchange.

C7.4 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 C8.7 note h).

C8 Analytical Procedure

READ SECTION C4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
C8.1	Run the water level just below the top plug level in the burette column (note a).	(a) The 'automatic column' is already adjusted.
C8.2	Pour in 40±2 ml of sample (note b).	(b) For very high sulphate levels, the sample should be diluted appropriately. See note d.
C8.3	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.
C8.4	Add 0·05±0·01 ml of bromocresol purple solution and, using a burette (C6.2), neutralize with 1·0M or 0·1M ammonium hydroxide solution to a purple end point (note e).	(e) The stronger ammonia solution should be used for highly saline waters.
C8.5	Add 50±2 ml of solvent buffer followed by 0·25±0·02 ml of carboxyarsenazo indicator. Then using a microburette (C6.2) titrate with standard barium chloride solution to a permanent grey colour which remains after 5 secs swirling. Note the titre T_2 ml (notes f and g).	(f) The weaker barium chloride should be used for sulphate concentrations less than 25 mg/l. (g) There is a small indicator blank hence amounts of indicator should be accurately controlled, and be the same for all samples. For work with very low concentrations of sulphate, the indicator blank can be eliminated by adding the calculated amount of 0·005M barium chloride to a bottle of solvent buffer.
C8.6	Blank Test Repeat steps C8.3, C8.4 and C8.5 using 20·0±0·1 ml water in place of the sample. Note the titre T_3 ml (note g).	
C8.7	Calculation (note h). (i) When using 0·005M barium chloride Concentration of sulphate in sample is: $\frac{100(T_2-T_3)}{(T_1-T_2)}$ mg/l SO_4^{2-} or if an aliquot (V ml) was taken at step C8.3 (note d): $\frac{2000(T_2-T_3)}{V(T_1-T_3)}$ mg/l SO_4^{2-} (ii) When using 0·0005M barium chloride Concentration of sulphate in sample is: $\frac{10(T_2-T_3)}{(T_1-T_3)}$ mg/l SO_4^{2-} or if an aliquot (V ml) was taken at step C8.3 (note d): $\frac{200(T_2-T_3)}{V(T_1-T_3)}$ mg/l SO_4^{2-}	(h) 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 C7.4) and the volume change was significant, correct the sulphate concentration found by multiplying by the ratio: $\frac{\text{pH-corrected sample volume}}{\text{original sample volume}}$

C9 Special Procedures

C9.1 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.

C9.1.1 Set out five sets of five 50-ml calibrated flasks (25 flasks in all). Prepare five 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 five series prepare five 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.

C9.1.2 Carry out steps C8.1 to C8.5.

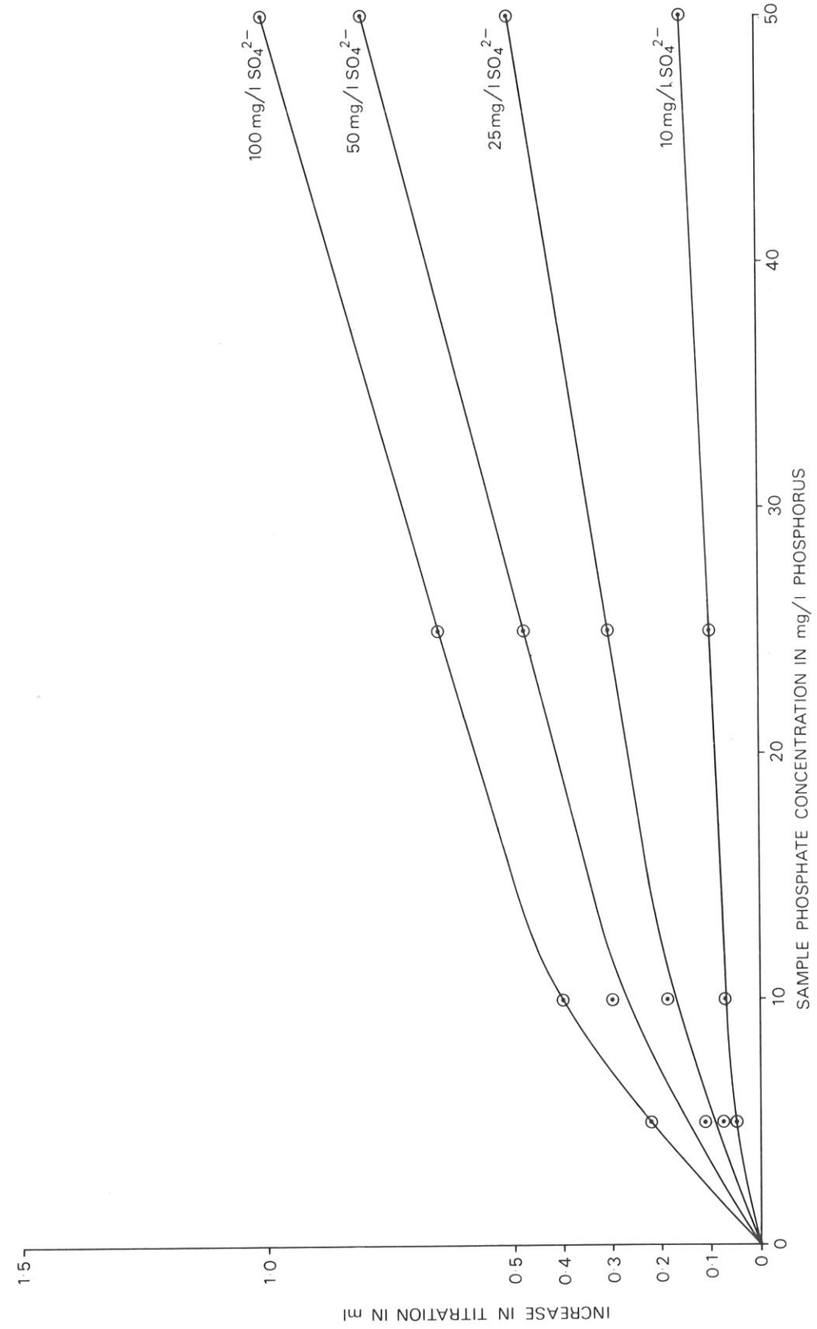


Figure 2 A typical set of phosphate correction curves

C9.1.3 From the results of the titrations, evaluate the increase in titre volumes over and above the titre with no phosphate present.

C9.1.4 For each sulphate concentration, plot a curve of phosphate concentration against increase in titration. An example is shown in figure 2.

C9.1.5 Determine the orthophosphate concentration in the sample (see another method in this series).

C9.1.6 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.

C9.2 Chromate

Chromate may be reduced with tin II chloride prior to the analysis, as described in Section B9.2.

C9.3 Sulphite

This will quickly become oxidized to sulphate. The sulphite concentration should be determined separately by another method in this series 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.

C9.4 Other sulphur oxy-acids

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

C9.5 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.

Method D Sulphate in Waters and Effluents by Indirect Atomic Absorption Spectrophotometry of Excess Barium Tentative Method

D1 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)

D1.1	Substance determined:	Soluble sulphate ion.
D1.2	Type of sample:	Potable waters, river waters, sewage effluents and some trade effluents.
D1.3	Basis of method:	Barium chloride solution is added to the sample and after precipitation of barium sulphate the excess barium is measured using atomic absorption spectrophotometry with an air-acetylene flame.
D1.4	Range of application (c):	Up to 175 mg/l (see Section D3).
D1.5	Calibration curve (c):	Linear to 175 mg/l.
D1.6	Total standard deviation (a) (b) (c):	Sulphate concentration mg/l / Standard deviation mg/l (b) 20 / 1·2 30 / 1·2 60 / 1·0 120 / 1·1 150 / 1·1 175 / 1·6 (All with 9 degrees of freedom).
D1.7	Limit of detection (b) (c):	Approximately 5 mg/l.
D1.8	Sensitivity (b) (c):	The blank solution* containing $1{\cdot}666 \times 10^{-3}$M barium chloride should give an absorbance of approximately 0·20.
D1.9	Bias:	No bias detected except when interferences occur (see Section D4). (b) (c)
D1.10	Interference:	Calcium exerts a complex effect and levels greater than 200 mg/l will cause marked interference. The levels of other matrix elements normally found in natural waters should cause no significant interference (see Section D4 and Table 2). (b) (c)
D1.11	Time required for analysis:	The total sample preparation time, standing time and analytical measurement time for 35 samples and associated calibration standards are 2·5 hours, 2·5 hours plus overnight and 1 hour respectively. (b) (c)

(a) River water and river water spiked with sulphate.
(b) Results obtained on a Varian AA6 Instrument.
(c) These data were obtained by the Severn Trent Water Authority Regional Laboratory at Malvern.

*Note, as this method relies on reduction of the barium concentration, the blank sensitivity is important. The concentration given here is that in a normal sample blank carried through the analytical procedure.

D2 Principle

An excess of acidified barium chloride is added to the sample, resulting in the precipitation of barium sulphate. After the precipitation is complete and after the addition of lanthanum chloride to the solution in order to minimize interelement effects that occur in the air-acetylene flame the residual barium in the solution is determined by atomic absorption spectrophotometry. Filtration is not required as a relatively coarse dense precipitate is formed and any traces of barium sulphate which may be carried through from the settled solution will not appreciably affect the air-acetylene flame.

D3 Range of Application

The procedure given can be used to determine the sulphate concentration given in Section D1. When the sulphate concentration exceeds 175 mg/l an appropriately smaller aliquot of the sample must be taken for analysis. To this volume of sample add water so that the total volume is 35–40 ml.

D4 Interferences

Except for calcium, substances usually present in river and potable waters at their typical concentrations were found not to interfere. (See Table 1).

Similar interference results have been observed for most of these substances by another laboratory using an atomic absorption spectrophotometer of different manufacture. However, differing interelement effects may be observed for other instruments and combination interelement effects in atomic absorption can differ from single interelement effects. Table 2 shows the effect of various levels of calcium on the concentration of sulphate observed. All the interference tests were carried out by adding the interferent (as the chloride unless stated otherwise) to deionized water and deionized water containing 100 mg/l sulphate. It should be noted that the calibration standards were prepared as detailed in the method and contained 75 mg/l calcium and 37·5 mg/l sodium. This was found to compensate for the effect of calcium in the samples.

Table I Effects of various other ions on the determination

Substance tested (concentration expressed as indicated in brackets)	Concentration in sample mg/l	Effect in mg/l SO_4^{2-} of other substances at a sulphate concentration of: 0·0 mg/l SO_4^{2-}	100·0 mg/l SO_4^{2-}
(as single salts)			
None		+2·2	+2·6
Ammonium nitrate (as N)	45 and 45 (of each ion)	+0·3	+2·2
Potassium dichromate (as Cr^{3+})	25	+1·2	+3·2
Copper chloride (as Cu^{2+})	12·5	+1·0	+2·2
Iron III chloride (as Fe^{3+})	25	+2·2	+2·8
Magnesium chloride (as Mg^{2+})	50	+2·5	+2·0
Di-sodium hydrogen Orthophosphate (as PO_4^{3-})	50	+2·2	+1·8
Potassium chloride (as K^+)	100	+0·7	+1·8
Sodium metasilicate (as SiO_2)	100	+0·8	+1·8
Sodium chloride (as Na^+)	400	+1·0	+2·6
(as Cl^-)	615		
Zinc chloride (as Zn^{2+})	12·5	+2·0	+2·4
(as a mixture)			
Calcium chloride (as Ca^{2+})	75		
Magnesium chloride (as Mg^{2+})	10		
Di-sodium hydrogen orthophosphate (as PO_4^{3-})	10	+0·5	0·0
Sodium metasilicate (as SiO_2)	20		
Sodium chloride (as Na^+)	10		

Table 2 Effect of calcium ion interference on determination

Calcium mg/l	Effect in mg/l SO_4^{2-} at a sulphate concentration of: 0·0 mg/l SO_4^{2-}	100·0 mg/l SO_4^{2-}
0	+2·2	+2·6
100	−1·1	−1·5
150	−2·1	−2·5
200	−4·0	−4·0
300	−7·0	−9·5

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

0·0±2·4 mg/l at the 0·0 mg/l SO_4^{2-} level, and

0·0±2·2 mg/l at the 100·0 mg/l SO_4^{2-} level.

If any sample contains more than 150 mg/l calcium, it is advisable to take a smaller sample aliquot. The effect of calcium is likely to differ slightly from instrument to instrument, thus it is worthwhile investigating the effect of various calcium levels on the sulphate result at various sulphate levels so that a correction can be applied if required.

D5 Hazards

Barium and lanthanum chlorides are toxic substances and should not be pipetted by mouth. An efficient fume extraction system should be used to vent the exhaust gases from the atomic absorption spectrophotometer.

D6 Reagents

Analytical reagent grade chemicals should be used.

D6.1 **Water**

The water used for the blank determination and for preparing reagents and standard solutions should have a negligible sulphate level (0·2 mg/l). Deionized or distilled water is suitable.

D6.2 **Barium chloride – hydrochloric acid** ($1{\cdot}666\times10^{-2}$M $BaCl_2$, 0·5M HCl)

Dry some barium chloride dihydrate at 300°C for 2 hours and cool in a desiccator. Dissolve 6·937±0·002 g of the anhydrous barium chloride in approximately 1 litre of water, add 85±2 ml of hydrochloric acid (d_{20} 1·18) and dilute with water to the mark in a 2-litre calibrated flask.

THIS SOLUTION IS TOXIC AND SHOULD BE LABELLED 'POISON'.

D6.3 **Potassium sulphate** (400 mg/l sulphate)

Dry some potassium sulphate at 300°C for 2 hours, cool in a desiccator. Dissolve 0·725±0·001 g of the anhydrous potassium sulphate in water and dilute with water to the mark in a 1 litre calibrated flask.

D6.4 **Calcium – sodium buffer solution** (3000 mg/l Ca and 1500 mg/l Na)

Dissolve 11±0·05 g calcium chloride dihydrate and 3·81±0·05 g sodium chloride in water and dilute with water to the mark in a 1-litre calibrated flask.

D6.5 **Lanthanum chloride solution** (10% m/V La)

This solution is available commercially.
Alternatively, weigh out 26·9±0·1 g of lanthanum chloride heptahydrate, dissolve in about 50 ml of water and make up to 100±5 ml with water.

IT SHOULD BE LABELLED 'POISON'.

D7 Apparatus

D7.1 **An atomic absorption spectrophotometer** equipped with an air-acetylene flame and a barium hollow-cathode lamp.

D7.2 **50-ml borosilicate calibrated flasks** with tight-fitting stoppers.

D7.3 **Water bath** set to 85–90°C. This should be placed in a fume cupboard.

D7.4 **1-ml automatic pipette** with disposable plastic tips.

D8 Sample Collection and Preservation

No special sample collection or preservation techniques are normally required. Clean plastic or glass bottles should be used. If anaerobic conditions are likely to occur in the sample it should be stored at 4°C and analysed within 24 hours.

D9 Sample Pre-Treatment

Samples containing large amounts of suspended matter should be filtered. If the suspended matter is suspected of containing sulphate, it should be analysed separately. Sections A9 and E11 of other methods in this booklet give a procedure for dissolving such materials.

D10 Analytical Procedure

READ SECTION D5 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
D10.1	Pipette 40±0·2 ml of each sample (filtered if necessary) into the calibrated flasks (note a).	(a) If the sample is thought to contain more than 175 mg/l sulphate or 150 mg/l calcium, a suitable dilution should be made. (Section D4 and step D12.2).
D10.2	Place the flasks in a water bath maintained at 85–90°C.	
D10.3	Carry out the following step on each flask before making the addition to the next flask in the series. After a period of at least ten minutes to allow the flask contents to warm up, add 5·00±0·03 ml of the $1{\cdot}666\times10^{-2}$M barium chloride—0·5M hydrochloric acid solution to each flask. Replace the stoppers and, whilst firmly holding the stopper in, carefully swirl each flask immediately after the barium chloride addition.	
D10.4	Immediately replace each flask in the water bath for at least 2·5 hours. The flasks should then be removed from the water bath, allowed to cool for five minutes, carefully shaken and allowed to stand overnight.	
D10.5	Add 1·00±0·02 ml of 10% m/V lanthanum solution to each flask, and dilute with water to the 50-ml mark. The flasks must then be thoroughly shaken and left for ten minutes prior to nebulization (note b).	(b) There is no necessity to filter the final solutions prior to measurement.
	Blank Determination	
D10.6	Two blanks must be run with each batch of determinations. Pipette 1·00±0·02 ml of the calcium-sodium buffer solution into a 50-ml calibrated flask and add 37±2 ml of water. Repeat steps D10.2 to 5. (note c).	(c) The calcium-sodium buffer is added to the blank and standards in order to minimize the effect of calcium (see Section D4).

Step	Experimental Procedure	Notes
	Calibration Standards	
D10.7	Pipette 1·00±0·02 ml of the calcium-sodium buffer solution into each of the five 50-ml calibrated flasks. Pipette 2·50±0·03 ml, 5.00±0·03 ml, 10·00±0·04ml, 15·00±0·05 ml and 17·50±0·10 ml of the 400 mg/l sulphate standard solution into separate flasks, dilute with water to 37±2 ml. Repeat steps D10.2 to 5. (note c). These standards correspond to 25, 50, 100, 150 and 175 mg/l sulphate.	
	Atomic absorption stage : Optimization of instrumental conditions	
D10.8	Set up the atomic absorption spectrophotometer as detailed in the manufacturer's handbook and in Section D11.	
	Method of Measurement	
D10.9	The nebulizer capillary is inserted down into the bulb of the flask. It should not be allowed to contact the precipitate at the bottom of the flask or the sides of the flask, or erratic readings will be observed, due to mechanical blocking of the capillary (note d).	(d) It is permissible to decant a small amount (10 ml) of the solution into a small beaker and use this.
D10.10	The scale expansion control should be adjusted so that the blank solution ($1·666\times10^{-3}$M Ba) gives a suitable output reading, such as 1000. (This should be checked after every sixth sample and reset if necessary. Distilled (or deionized) water should give a reading of zero. A distilled (or deionized) water measurement should be made between every sample or blank measurement (note e).	(e) If a reading of less than 125 is obtained, the procedure should be repeated using a reduced sample volume (see Section D3).
Note:	*Barium sulphate can be removed from volumetric glassware by the procedure given in A8.6 note e.*	
	Calculation of Results	
D10.11	The result can be obtained from a plotted calibration graph. Alternatively, if a sample gives a reading of x and the blank solution ($2·666\times10^{-3}$M Ba) gives an average reading of y, the theoretical sulphate level assuming complete precipitation is: $\frac{(y-x)}{5}\times\frac{1000}{y}$ Note: The barium added to the test solution is equivalent to 8000µg of sulphate. The actual sulphate level can then be calculated by multiplying the result by the ratio of the observed to the theoretical slope of the calibration graph. The slope of the calibration graph should be 97±1% of that of the theoretical slope for sulphate levels above 20 mg/l. At levels below this the calibration graph should be used.	

D11 Optimization of Instrumental Conditions

THIS IS EXTREMELY IMPORTANT. CONSIDERABLE CARE MUST BE EXERCISED WHEN SETTING UP THE ATOMIC ABSORPTION SPECTROPHOTOMETER, OTHERWISE PRECISION AND ACCURACY WILL INEVITABLY SUFFER. THE BURNER HEAD SHOULD BE WASHED OUT USING HOT WATER PRIOR TO EACH RUN.

D11.1 **Wavelength**

Set wavelength to 553·6 nm.

D11.2 **Spectral slit width**

Set the spectral slit width to 0·5 nm.

D11.3 **Burner height setting**

Set the burner height just (1 mm) below the setting where the burner grid begins to obstruct the light from the hollow-cathode lamp as registered on the output meter of the AAS instrument. The flame should be lit at least 20 minutes prior to use. The barium response is markedly dependent on the burner head temperature.

D11.4 **The acetylene flow rate**

This rate should be optimized for maximum response. This should result in a slightly luminous flame. The barium response should not be very dependent on the acetylene flow rate at the burner height used (Section D11.3). Correct alignment and satisfactory nebulizer performance can be checked prior to each run by noting the absolute absorbance for the blank solution (Section D1.8).

D12 Sources of Error

The attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. The following sub-sections summarize the main sources of error.

D12.1 **Optimization of instrumental conditions**

This is very critical (see Section D11) and care should be taken to ensure that these conditions are carried out properly.
If excessive baseline drift is observed, recheck the wavlength setting. Some instruments suffer from wavelength drift even for small temperature fluctuations. The reading for the blank solutions (containing $1·666\times10^{-3}$M Ba, 2000 mg/l La, 60 mg/l Ca, 30 mg/l Na and 0·05M HCl) should be checked after every five or six measurements.

D12.2 **Interfering substances**

The only commonly occurring matrix element in natural waters that should result in interference is calcium. The calibration standards are prepared in a 75 mg/l calcium matrix* in order to minimize the effect of calcium. The effect of various calcium levels is shown in Section D4, Table 2.
It is probable that interference effects would be similar on other instruments, but this must not be assumed and must be checked. It is possible to work out a correction factor for calcium if the calcium level is known.

D12.3 **Precipitation conditions**

In order to obtain a high degree of precipitation of barium sulphate and to minimise co-precipitation effects, the precipitation is carried out in a hot, acidified solution (85–90°C). The resultant solution is digested at this temperature for 2·5 hours and then allowed to stand overnight.

D13 Reference

(1) KC Thompson and K Wagstaff. *A method for the determination of sulphate in natural waters and some effluents by atomic absorption using the air-acetylene flame.* (Paper presented at the meeting of the Institute of Water Engineers and Scientists, Scientific Section, October 1979. To be published later).

*Based on the initial 40 ml sample.

Method E Sulphate in Waters, Effluents and Some Insoluble Matter by Indirect Spectrophotometry using 2– aminoperimidine Tentative method

This method has two different quantification procedures, both of which have two useful concentration ranges. It can be automated.

E1 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)

E1.1	Substance determined:	Soluble sulphate ion.
E1.2	Type of sample:	Raw, potable and waste water. This method was developed for soluble samples. If the sample should contain insoluble matter, it should be filtered off. If the insoluble matter is likely to contain sulphate, it is suggested that it be brought into solution using the procedure given in Section E.11 and the result either returned separately as insoluble sulphate or added to the soluble value.
E1.3	Basis of method:	Precipitation of sulphate with 2-aminoperimidine, followed by UV or colorimetric determination of the excess reagent.
E1.4	Range of application (a): (See Section E.8)	(i) 10–120 mg/l. (ii) 4–30 mg/l.
E1.5	Calibration graph (a):	Linear to 120 mg/l SO_4^{2-}

E1.6 Total standard deviation (a):

Sample Type	Sulphate Concentration mg/l SO_4^{2-}	Total Standard Deviation mg/l SO_4^{2-}	Degrees of Freedom
Range (i) 10–120 mg/l			
(*EA*) UV determination			
	0 (b)	1·07	9
	50 (b)	1·73	9
	42 (c)	1·88	5
	93 (c)	1·70	9
	100 (b)	1·33	8
(*EB*) Colorimetric determination			
	0 (b)	1·66 (within batch)	9
	50 (b)	1·99	9
	47 (c)	2·27	9
	65 (c)	3·29	9
	100 (b)	2·28	9
Range (ii) 4–30 mg/l			
(*EA*) UV determination			
	0 (b)	0·446 (within batch)	9
	25 (b)	0·429	9
	10 (b)	0·772	9
	16 (d)	0·643	9
(*EB*) Colorimetric determination			
	0 (b)	0·79 (within batch)	8
	25 (b)	1·31	9
	10 (b)	1·23	9
	21 (c)	0·33	9

E1.7	Limits of detection (a):	Range (i) 10 mg/l or better (ii) 4 mg/l see Section E1.6
E1.8	Sensitivity (a):	Range (i) 0·4 absorbance units=1000 mg/l for either variant (ii) 0·5 absorbance units=25 mg/l.
E1.9	Bias (a):	No bias detected.
E1.10	Interference (a):	No significant interference from commonly occurring constituents of raw, potable and waste water. (See Section E3)
E1.11	Time required for analysis (a):	Approximately 1 hour for a batch of 20 samples.

(a) These data were obtained at Thames Water Authority, Directorate of Scientific Services, New River Head Laboratory, London.
(b) Distilled water with potassium sulphate.
(c) Potable water.
(d) Well water.

E2 Principle

Sulphate is precipitated by 2-aminoperimidine[1], and the precipitate is removed by means of a centrifuge. The precipitation reaction in natural waters is pH-dependent and is best carried out at a carefully controlled pH of between 3·5 and 4·5 (±0·1). The specified buffer gives a pH approximately 4·1±0·1 in samples with alkalinities of up to 1000 mg/l as $CaCO_3$ (or 20 m eq/l CO_3^{2-}).
The excess reagent in the supernatant liquid is determined by one of two methods, either (*EA*) direct UV absorbance measurements at 305 nm[2], or (*EB*) treatment with nitrous acid and alkali to give a red colour, whose absorbance at 525 nm is proportional to the concentration of excess reagent[3]. Method (*EB*) is applicable only to samples with low amounts of organic matter, while method (*EA*) is more generally applicable.

E3 Interferences

E3.1 The UV determination may suffer from interference arising from sample absorption at the analytical wavelength. In such cases the colorimetric version of the method should be employed. An assessment of the extent of this type of interference can be made by carrying a portion of the sample through the analytical procedure but replacing the 2-aminoperimidine reagent with the same quantity of water. An optical density of 0·004 in the final solution measured against distilled water would correspond to a suppression of about 1 mg/l SO_4^{2-} in the analytical result.

E3.2 The effects of commonly occuring constituents of raw, potable and waste water upon range (i) of the colorimetric determination are listed in table 1. Similar effects are encountered when using the UV determination, and are also representative of the likely effects to be expected with the colorimetric determination in range (ii).