Determination of Sulphite, Sulphur Dioxide, Thiosulphate and Thiocyanate, with Notes on the Determination of Total Sulphur and Other Sulphur Compounds 1985

Methods for the Examination of Waters and Associated Materials

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Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office

This booklet supplements the booklets in this series on the determination of sulphates and sulphides. It contains much general information of use in the analysis of samples containing other forms of sulphur. Five specific methods for Sulphite and Sulphur Dioxide, Thiosulphate and Thiocyanate are given. This is followed by a section on ways of determining the total sulphur content of a variety of samples followed by a review type discussion of ways of proceeding should a significant amount of the sulphur present be in other forms than those mentioned and there be a need to know either what forms are present, or whether the sample contains certain specific sulphur compounds. The layout is as follows:

Introduction, including
(i) suitability of the methods given,
(ii) a list of forms in which sulphur has been found to occur in water, sludge and sediment samples, and
(iii) a note on ultra-precise titration.

A. A spectrophotometric method for Sulphite and Sulphur Dioxide using pararosaniline
B. A titrimetric method for Sulphite and Sulphur Dioxide by iodometry
C. A titrimetric method for Thiosulphate in simple solutions by iodometry
D. Manual colorimetric and volumetric methods for thiocyanate using ferric ions
E. An automated colorimetric method for Thiocyanate using ferric ions
F. Methods for the determination of Total Sulphur
G. Notes on other methods for analysing complex mixtures of sulphur compounds
H. Notes on Analytical Quality Control

References

Although many of the methods in this booklet are well known and widely used, due to a scarcity of test data all must be regarded as tentative.

Contents

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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 a 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 7 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
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological 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
1 July 1986

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. See specific advice in the Hazards section.

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 checklist, 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 a 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. 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

Sulphur is a ubiquitous element occurring in oxidation states from minus two to plus six and also forms peroxysalts. In water, it usually occurs as part of a negative ion (anions) but neutral compounds and even positive ions can occur. The free element and its compounds can also be encountered in sludges and solids, oils and gases. It is a component of living matter, hence the form in which it is present can be changed by natural processes. Its chemistry is complex and sulphur can occur in more than one oxidation state in the same compound. Sample preservation may be difficult. Waters are known in which sulphur cycles between insoluble metal sulphide in the bottom mud and soluble sulphate, depending on the time of the day. Variations in the reduction–oxidation potential, which often changes with depth, are also important in deciding the form in which sulphur may occur. The free element can occur in volcanic, and thermal waters and fumes.

Very rarely is the nature of a sample completely unknown. There is usually some information available as to its origin and probable contents which the analyst can use when planning the analysis. Even so surprises can occur. The worst problems are usually encountered in the analysis of effluents and natural waters which are anoxic or at least oxygen deficient. If sulphur compounds other than sulphide and sulphate may possibly be present in such a water or sediment, the presence or absence of other forms of sulphur can be ascertained by first determining these two anions using the appropriate methods given in the booklets in this series (1, 2), and then determining the total sulphur content by a procedure suggested in this booklet. A major positive discrepancy between the total sulphur balance and the sulphur present as sulphide and sulphate (and other known forms of sulphur), indicates the presence of additional sulphur compounds in the sample. A detailed investigation of the sulphur compounds present can be a research operation, but as such information may be necessary, the second part of this booklet gives advice on some of the procedures which analysts have found most helpful. For guidance, a summary of the types of sulphur compounds which have been found in samples in the past follows this introduction.

In many instances, especially in water purification, the compounds present are known and the analyst may only be required to determine whether sufficient chemical has been added or removed. The first part of this booklet contains specific methods for a number of sulphur anions other than sulphide and sulphate, some of which may also be of use for more complex mixtures. Table 1, lists the suitability of the various methods and procedures given in this booklet. Some of the methods given in the second part of the booklet are also very suitable for the determination of the anions for which methods are given earlier, provided that the equipment is available and the sample is suitable.

Table 1 Suitability of Methods given in this Booklet

Note – some compounds are listed more than once in the Determinand column. Methods are listed in the order in which they appear in this booklet.

Determinand	Method	Sample type	Comments	See Section
Sulphite and Sulphur Dioxide	by Pararosaniline Colorimetric	Most waters and effluents	The effects of sulphide, nitrite and colour are negligible or removable	A
	by Iodometry	Clean waters	Sulphide, thiosulphate and related anions must be absent or known. Thiocyanate does not interfere	B
Thiosulphate	by Iodometry	Clean waters	Sulphite and related anions must be absent (sulphide can be removed)	C
Thiocyanate	2 colorimetric methods, one volumetric method	Most waters and effluents	Should not be highly coloured, mercury salts and oxalates interfere	D, E
Total Sulphur	by Bromine Oxidation	Only relatively clean waters and solutions	Not suitable for most organic forms of sulphur, will analyse for the free element	F4

Determinand	Method	Sample type	Comments	See Section
	by Hydrogen Peroxide oxidation	Only relatively clean waters and solutions	Suitable only for inorganic forms of sulphur, will not oxidize the free element	F5
	by Peroxide Fusion	Solids and liquids capable of evaporation without loss of sulphur	Will analyse non volatile forms of sulphur, care would be necessary for combustible material. Will attack sulphide minerals and scales	F6
	Oxygen Flask Method	Solids and can be adopted to liquids	Will analyse organic forms of sulphur, not good for non combustible material	F7
	Other Combustion Methods	Solids and liquids, including waters	Not suited to non combustible forms of sulphur. Samples high in salts will cause problems unless the sulphur is solvent extractable in a sulphur free non halogen containing solvent	F8
	X-ray Fluorescence Spectroscopy	Solids and some waters	Will quantify all sulphur compounds given standards of similar type, the limit of detection is not low	F9.1
	Vacuum U V Emission Spectroscopy	All liquid and solid samples	Will quantify all sulphur compounds	F9.2
	Inductively coupled Plasma Emission Spectroscopy	All liquid and soluble solid samples	Will quantify all sulphur compounds	F9.3
	Flame (Band Spectra) Photometry	as ICP	Rarely used as not very sensitive	F9.4
Dithionites and Formaldehyde Sulphoxylates	Methylene Blue Colorimetry	Waters and effluents	Very strong reducing agents interfere	G1
Trithionates and higher, also free sulphur and polysulphides	Cyanide Colorimetric Method	Water and effluents	Needs initial separation, for example by chromatography but can be used to identify fractions isolated	G2
Ionic forms	by ion chromatography	Many waters and effluents	The sample must not foul the column. Basically a separation procedure, not suitable for complex mixtures	G3
Series of Compounds inorganic and organic	HPLC	Many waters and effluents	The sample must not foul the column. Basically a separation procedure	G3
Soluble Sulphides and Mercaptans	by potentiometric titration	Many waters and effluents	Needs good ventilation, will not identify individual mercaptans	G4
Ionic forms	by electrophoresis	Many waters and effluents	Basically a separation procedure	G6
Sulphide, Sulphite, Thiosulphate and Thiocyanate	by polarography	Many waters and effluents	The sample must be free from oil and grease	G5
Many compounds soluble in water or organic solvents	Column and TL Chromatography	Many waters and effluents	Basically a separation procedure, using more than one column can separate some difficult mixtures	G7
Volatile compounds	Gas Chromatography with or without solvent extraction and derivatization	Many waters and effluents	Basically a separation procedure	G7

Some sulphur compounds such as hydrogen sulphide are toxic, many such as sulphur dioxide and sulphuric acid are harmful irritants, or like sulphates, physiologically active in large doses, but it must not be forgotten that some very hazardous organic compounds as well as some much used pharmaceuticals and natural organism metabolites contain sulphur. Care should be taken when handling samples of doubtful toxicity to avoid inhalation, ingestion or skin contact.

Although a method for one determinand may suffer from an interference effect due to another substance being present, if the effect is quantitative, and the interferant can be determined separately, corrections can be made, although with reduced accuracy and precision for the final result. Attention should also be paid to the other easily detected ions present, when analysing complex mixtures, as some combinations of ions are not possible in samples at equilibrium. Thus sulphite will only have a transient existence in the presence of iron III or chromium VI. In some instances the compatability of two ions is dependent on pH or complexation. There are too many such interferences, which can be discovered from the literature, to give a detailed list and analysts faced with such a problem should check the more detailed reference works, and also try a few laboratory tests with known substances as the literature is not always correct.

Sulphur Compounds Which May Be Present In Samples

As mentioned earlier, sulphur usually occurs in water as negative ions which vary in oxidation state from minus two to plus six, which latter state may also have peroxy groups attached. Neutral molecules and positive ions also occur in the natural aqueous environment. The oxidation state can vary between different sulphur atoms in the same compound without reaction occurring. Thus the minus two and plus six states can co-exist in one compound or in mixtures even though under certain conditions reaction does occur. The products of reactions between sulphur compounds, especially those found in effluents, can be very complex indeed, and may often be mixtures. Some, especially those of intermediate oxidation state, may react with the oxygen in air, though usually only slowly. Although many sulphur compounds are too reactive to exist in the presence of water indefinitely, some only react slowly and may be found in some effluents.

Insoluble sulphur compounds occur in river muds and sediments and in minerals found in stream beds. Those likely to be of analytical interest are mentioned. There are, in addition, a large number of other sulphur compounds with other elements such as the halogens and nitrogen, reactive to air or water, which are only likely to be encountered in containers and after spillages. These are not mentioned here. The free element can also occur in the aqueous environment. Sulphur can form the following types of bonds in its compounds:-

1. co-ordination by oxide (or peroxide) with up to 4 oxygen atoms per sulphur atom, the same sulphur atom may also have covalent bonds as well;
2. covalent bonds to hydrogen, carbon, oxygen, etc, usually the maximum number per sulphur atom is 2, 3 is the limit;
3. covalent chains of sulphur atoms, usually up to 6 in number, chains with more than 8 consecutive sulphur atoms tend to split out free sulphur and form compounds with less sulphur;
4. covalent pi-bonded systems, especially heterocyclic ring molecules;
5. covalent double bonds, usually to carbon;
6. a simple negative ion, often with a single covalent bond as well, but the doubly negative sulphide ion is common;
7. co-ordination of a sulphide ion to transition or b sub-group metal or metalloid, sulphur itself, carbon and phosphorus, and, as with oxygen, similar co-ordination by polysulphide ions can also occur with a few metals;
8. monopositive ions in which the sulphur is also triply covalent, analogous to oxonium, ammonium and phosphonium ions.

Typical compounds are given in Table 2, almost all of which could occur at least in effluents.

As mentioned in the introduction, a sample about which absolutely nothing is known is very rare. Not all the compounds mentioned in Table 2 can co-exist in one sample. Some cannot exist in alkaline, or in acid solution, others are readily oxidized or reduced. Some have an obnoxious smell. Although reactions, including alkylation, especially methylation, to mercaptans and sulphonium ions occur readily, knowledge of the types of industrial processes or compounds involved often reduces the possibilities. Consultation of the chemical literature, organic as well as inorganic, is often helpful. The reactions of sulphur compounds are often reported under other elements than sulphur.

Table 2

Typical Compounds	Formulae of typical ions or compounds	Remarks
Sulphates	$SO_4^{=}$	
Polysulphates	$S_2O_7^{=}$ $(O_3S.O.SO_3)$	Higher are known
Acid sulphates	HSO_4^- $(HO.SO_3)^-$	
Fluosulphonates	FSO_3^-	Once formed are only slowly hydrolysed by water
Sulphate esters	$C_{12}H_{25}SO_4^-$ $(C_{12}H_{25}O.SO_3)^-$ $(CH_3)_2SO_4$ $(CH_3O.SO_2O.CH_3)$	
Permonosulphates	$SO_5^{=}$ $(O_2SO_3)^{=}$	
Perdisulphates	$S_2O_8^{=}$ $(O_3SO_2SO_3)^{=}$	
Sulphonates	$C_6H_5SO_3^-$	

Table 2 – *continued*

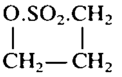
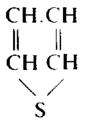
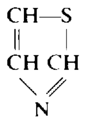
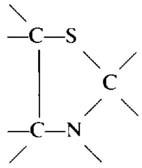
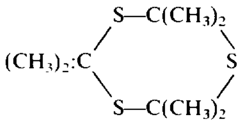
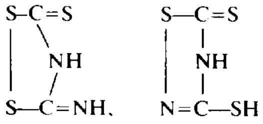
Typical Compounds	Formulae of typical ions or compounds	Remarks
Sulphonamides	$C_6H_5SO_2NH_2$	
Sulphamates	$NH_2SO_3^-$	
Nitroso and Hydroxamino Sulphonates	($N(SO_3)_3^{\equiv}$ $ON(SO_3)_2^{=}$ ($(ON)_2\,(SO_3)_4^{4-}$ ($ONO.SO_3^-$ ($HO.N(SO_3)_2^{=}$ ($HO.NH.SO_3^-$	
Betaines (see also sulphonium salt betaines)	$^+NH_3\,CH_2\,SO_3^-$	Occur in some plants
Sulphones	$(H_2N\,C_6H_4)_2SO_2$	These need not contain nitrogen. The one shown is an important pharmaceutical
Sulphites	$SO_3^{=}$	
Metabisulphites	$S_2O_5^{=}\,(O_2S.O.SO_2)^{=}$	
Acid (or bi) sulphites	$HSO_3^-\,HS_2O_5^-$	
Sulphur dioxide	SO_2	
Aldehyde bisulphites (hydroxy sulphonates)	$(CH_3CH(OH).SO_3^-$ $(CH_2(OH)SO_3^-$	Unlike other sulphonates are reducing agents
Sulphinates	$C_6H_5SO_2^-$	
Sulphoxylates	$CH_3(OH)SO_2^-$	
Sulphoxides	$(CH_3)_2SO$	
Sultones	 $\begin{array}{ll} O.SO_2. & CH_2 \\ \vert & \vert \\ CH_2- & CH_2 \end{array}$	Analogous to lactones. Very soluble in water
Polythionates	$S_2O_6^{=}\,(O_3S.SO_3)^{=}$ $S_3O_6^{=}\,(O_3S.S.SO_3)^{=}$ $S_4O_6^{=}\,(O_3S.S.S.SO_3)^{=}$ $S_5O_6^{=}\,(O_3S.S_3SO_3)^{=}$ $S_6O_6^{=}\,(O_3S.S_4SO_3)^{=}$	Dithionates are more stable than other polythionates. Tri and higher polythionates tend to decompose in very acid solution. Tri and tetrathionates are not readily oxidized. Salts with chains longer than $S_6O_6^{=}$ are unstable and rare, but exist
Thiosulphates	$S_2O_3^{=}\,(O_3S.S.)^{=}$	Higher $O_3S.S_2^{=}$ are known but rare, $^-O_3S.S_4CH_3$ etc are also known
Selenosulphates	$SeSO_3^{=}$	
Sulphides	$S^{=}$ also $(CH_3)_2S^{*\dagger}$	Insoluble sulphides occur in sediments and minerals eg FeS, CuS, As_2S_3, HgS. The sulphide compounds marked with an asterisk occur naturally in marshes. †Some halo-alkyl sulphides are vesicant such as the 2-chloroethyl
Hydrosulphides	SH^-	
Hydrogen Sulphide	H_2S^*	
Mercaptides	CH_3S^-	
Mercaptans	CH_3SH^-	
Polysulphides	$S_2^{=},S_3^{=},CH_3S_2^-,(CH_3)_2S_2^*$ $(CH_3)_2S_3$	Higher are known. Insoluble Iron II disulphide is the mineral Pyrite
Carbon disulphide	CS_2^*	
Carbon oxysulphide	COS^*	
Dithionites	$S_2O_4^{=}\,(O_2S.SO_2)^{=}$	
Thiols and Related Compounds:		
Toluene dithiol	$CH_3.C_6H_3{:}(SH)_2$	Also the proteins, casein in milk and keratin in skin, hair and horn
Methionine	$CH_3.S.(CH_2)_2.CH(NH_2).CO_2H)$	
Cysteine	$HS.CH_2.CH(NH_2).CO_2H$	
Cystine	$(.SCH_2.CH(NH_2).CO_2H)_2$	
Thiogylycollic acid	$HS.CH_2.CO_2H$	

Table 2 – *continued*

Typical Compounds	Formulae of typical ions or compounds	Remarks
Thiophene		Stable pi bond aromatic ring structures. Related polycyclic compounds also occur
Thiazole		
		Saturated rings such as this occur in antibiotics such as pencillin, often with additional sulphide bonds in the side chains
Thioketones	$R_2{:}CS$	May also exist as cyclic trimers, stability depends on substitutions, simple aliphatic are the least stable
Thioaldehyde trimers		Some Thioaldehydes R.CHS do exist, but are unstable and have an obnoxious smell. The trimers do not
Mercaptals	$(CH_3)_2C(SC_2H_5)_2$	
Thioureas	$((CH_3)_2N)_2CS$	
Thiocarbamates Xanthates	$(CH_3)_2N.CS_2^-$ $C_2H_5.O.CS_2^-$	
Thiocyanates	SCN^-	The esters occur in two isomeric forms with very different properties
Thiocyanogen	NCS.SCN, $(CNS)_2$	Tends to behave like a halogen with a redox potential between bromine and iodine; but can form relatively stable linear and heterocyclic derivatives some of which are dyestuffs
	$S(CN)_2$ $S(SCN)_2$, $Se(SCN)_2$	
		
Thiomolybdates	$MoS_4^=$, $MoOS_3^=$, $MoO_2S_2^=$, MoO_3S^-	This is only a small selection of typical simple compounds. Many pesticides contain thio groups of this type
Thioarsenate	$AsS_4^\equiv$	
Thioarsenite	$AsS_3^\equiv$	
Thiocarbonates	CS_3^-	
Polythioplatinates	$Pt(S_x)_3^=$	
Thiophosphates	$PS_4^\equiv$	
Sulphonium salts and betaines	$(CH_3)_3S^+\ Cl^-$ $(CH_3)_2S^+\ CH_2.CH_2.CO_2^-$ (dimethylpropiothetin)	Substituted salts of this type have been found in marine plant toxins, and hence in waters
Sulphur Hexafluoride	SF_6	Very inert, sometimes used as a gaseous tracer
Free Sulphur		Chain and cyclic allotropes occur

Note on Accurate Measurement Using Burettes and Pipettes

Several of the methods in this booklet are titrimetric. The performance characteristics of such methods in well run laboratories are often determined by only four criteria. These are the inherent bias of the method, the indicator blank, the ability to measure accurately a liquid volume and the constancy of measurement.

The inherent bias of the method is determined by solubility and equilibrium constants, etc, and will not be discussed further.

The indicator blank should be as small as possible, but for some indicators it may not be negligible and may vary between technicians. There are various techniques for sharpening the detection of the end point, such as the use of xylene cyanol with methyl orange, and starch with iodometry. If there is sufficient sample, a helpful practice is to run a preliminary titration which indicates to within one millilitre the volume of titrant required for the end point, subsequent titrations being taken dropwise through this last stage. This technique can be repeated using extreme care to note the volume immediately before and after the end point. With some but not all reactions, it is possible to obtain the mean position of the end point by back titrating with sample from a second burette. Titrations with silver nitrate, and with acids or alkalis, are examples where this is possible, some iodometric titrations where there is risk of a drifting end point with time are examples where this back titration technique is not possible. If there is some marked instrumentally measurable change associated with the end point such as colour (absorption) or conductivity (precipitative silver titrations are an example of this latter), then graphing the measure of this variable from well before to well after the end point, followed by determination of the point of inflection or minimum will give a sharp indication of the end point. In many analyses, the indicator blank is actually included in the reagent blank correction. For very precise work, narrow bore burettes with tips immersed in stirred sample, with PTFE plug non-stick taps with long carefully balanced handles are recommended.

However sharply the end point of a titration may be detected, comparable accuracy of reading the burette or pipette is necessary for high precision. Reading with the eye level with the meniscus, without distracting background is essential, as is always reading the same part of the meniscus, which part is best for taking a reading varies with titrant. For clear solutions the bottom of the meniscus is the rule, but for very dark, intensely coloured or opaque solutions, reading the top rim may be necessary. Be consistent for the same reagent, even when it is necessary to vary between reagents. The size of the surface being read is important, within reason, the narrower the tube at point of reading the more accurate the reading is. Accuracy is often, but not always dependent on the ratio of the minimum discrimination interval readable to the size of the burette reading. Inspection of the calculation will show whether this is the case. Ordinary burettes and calibrated pipettes usually have 0.1 ml calibrations, which with good tips and taps can be subdivided at least into thirds by drop counting or by eye. Location of the exact position of a meniscus by eye is often aided by mounting a vertical strip of white card, with thin black lines drawn on it at 45° to the horizontal, behind the burette and illuminating it from the front. The lines appear to bend at the meniscus. For exceedingly precise measurement the exact location of the meniscus, so indicated, can be measured relative to the scale divisions with a small travelling microscope, or more usually with a hand lens with engraved scale. The lens is clipped to the burette for steadiness during reading and slides along it. If a screw-threaded device is used, always approach the meniscus from the same direction when taking readings to minimise error from the whiplash on screw-threads. The burette and microscope should have absolutely parallel mountings.

If the amount of titrant required is small, the analyst may have two choices for improving accuracy, either to use a more dilute solution to get a bigger titration, provided that this does not seriously increase the reagent blank, or to use a more precise narrower bore burette or pipette. Such burettes are not always available and can be fragile and unwieldy, but burettes of 5 ml capacity calibrated to 0.02 or even 0.01 ml have been used. They are usually filled through the tap by suction, like pipettes. Initial and final readings should always be rechecked after the walls of the tube have had time to drain. Repeat readings to constancy if unsure.

Analytical glassware is normally calibrated to either of two standards of accuracy – grades A (with the tightest tolerances) and B (for routine use). However, for very precise work, pipettes especially, and burettes can be calibrated by delivering measured amounts of pure water into pre-weighed stoppered bottles which are then weighed at known temperature. Each operation is repeated several times to ensure accuracy. Volumes are calculated from the mean masses using water density–temperature tables. Operator skill with burettes and pipettes can also be assessed this way.

The weights in modern high precision substitution balances which are not handled are usually highly accurate, but a set of weights can be calibrated against national standards by standards laboratories, for a fee, and these secondary standards used solely to check other weights including automatic balances. Given care and air-conditioned balance rooms, automatic balance weights should stay constant for at least 30 years, but occasional checking is recommended even for the best systems. Finally, calibration scales should be checked on all new apparatus. Errors in calibration do occasionally occur and invariably cause big errors if undetected.

Note that one set of test data quoted in this booklet (Thiosulphate by Iodometry Cl.5.2) was obtained using highly refined analytical techniques, with, for instance, measurements of c20 ml titrations to ±0.005 ml.

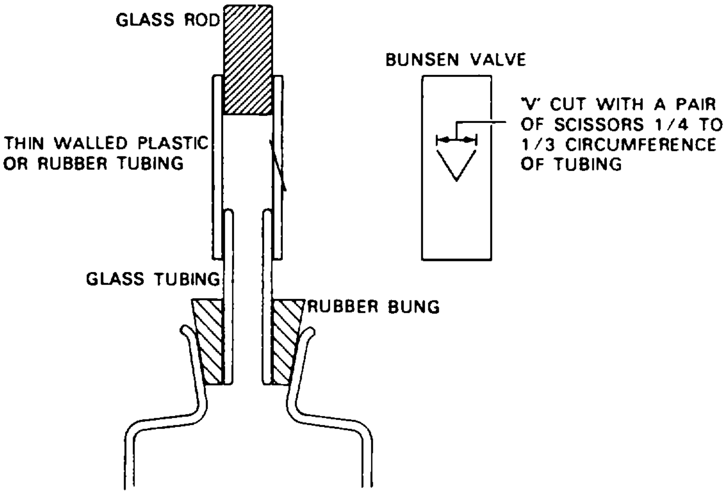


Figure 1 Typical bunsen valve

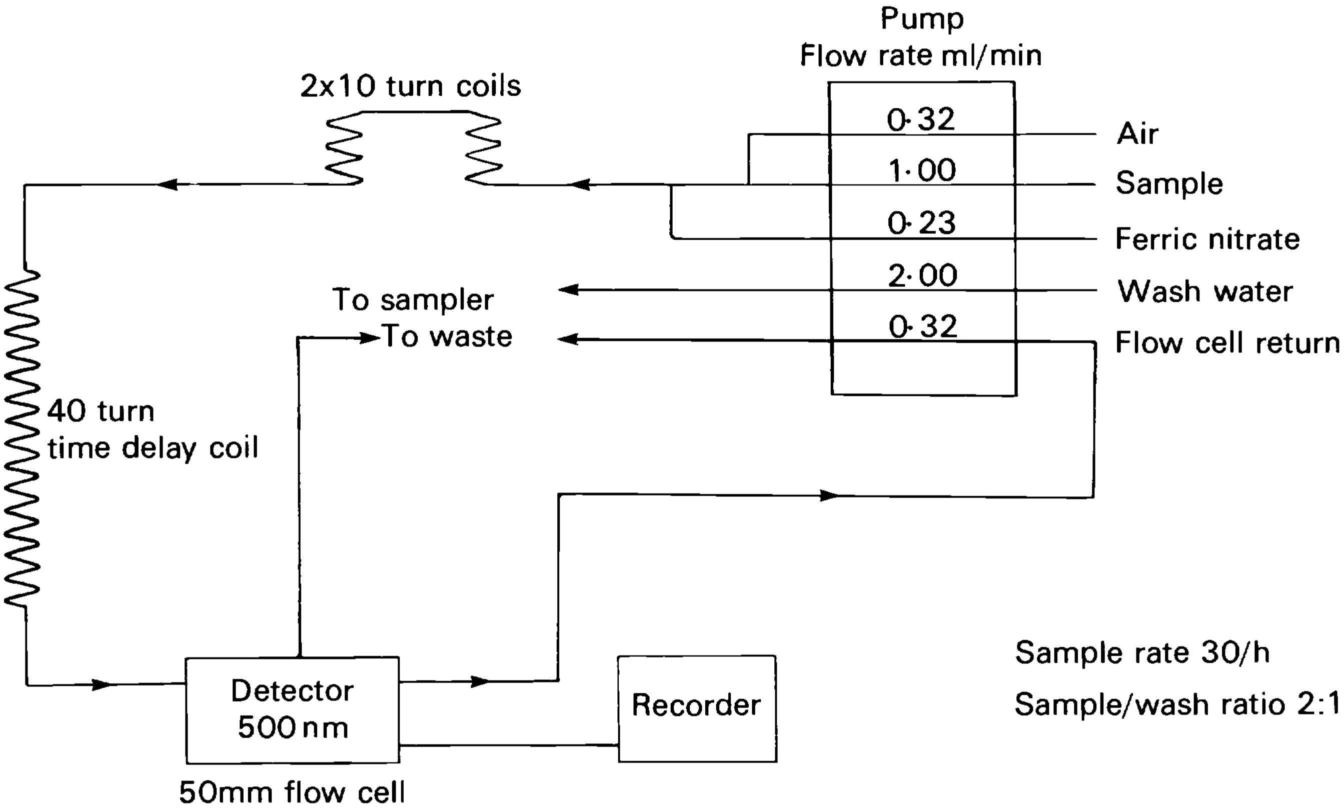


Figure 2 Analytical manifold for the automated determination of thiocyanite

A Determination of Sulphite and Sulphur Dioxide by Pararosaniline Spectrophotometric Method

A1 Performance Characteristics

<table>
<tr><td>A1.1</td><td>Substance Determined</td><td>Total sulphur dioxide liberated by acid (sulphite and sulphur dioxide interconversion dependent on pH).</td></tr>
<tr><td>A1.2</td><td>Types of Sample</td><td>Most types of water including sea water.</td></tr>
<tr><td>A1.3</td><td>Basis of Method</td><td>Sulphite is stabilized by complexation with potassium tetrachloromercurate at the time of sampling. The sulphite complex reacts with formaldehyde and acid-bleached pararosaniline to form the intensely coloured pararosaniline methyl sulphonic acid (Refs 3–8).</td></tr>
<tr><td>A1.4</td><td>Range of Application</td><td>Up to 40 μg $SO_3^=$ in a test portion of volume not exceeding 10 ml. For a 10 ml sample this corresponds to 4 mg/l $SO_3^=$. It is recommended that for higher concentrations (above 25 mg/l $SO_3^=$), a measured volume of sample be accurately diluted to a known volume with water (see Section A5.1) prior to addition to the stabilizer in the sample bottle (see Section A7.5).</td></tr>
<tr><td>A1.5</td><td>Calibration Curve</td><td>Linear up to at least 0.95 absorbance.</td></tr>
<tr><td>A1.6</td><td>Standard Deviation</td><td>
<table>
<tr><td>Sulphite Concentration mg/l</td><td colspan="2">Standard Deviation mg/l for 10 ml samples</td></tr>
<tr><td></td><td>Within-batch</td><td>Total</td></tr>
<tr><td>0.5 (a)</td><td>0.0096 (5)</td><td>0.052 (9)</td></tr>
<tr><td>2.0 (b)</td><td>0.035 (8)</td><td>0.132 (11)</td></tr>
<tr><td>4.0 (a)</td><td>0.0098 (5)</td><td>0.11 (9)</td></tr>
</table>
Degrees of freedom in brackets</td></tr>
<tr><td>A1.7</td><td>Limit of Detection[a]</td><td>0.02 mg/l (9 degrees of freedom).</td></tr>
<tr><td>A1.8</td><td>Sensitivity</td><td>10 ug $SO_3^=$ (1 mg/l $SO_3^=$) gives a net absorbance of 0.24 units.</td></tr>
<tr><td>A1.9</td><td>Bias</td><td>Not known.</td></tr>
<tr><td>A1.10</td><td>Interferences</td><td>Most possible interferents can be removed. Colour is an occasional problem. See Section 3.</td></tr>
<tr><td>A1.11</td><td>Time Required for Analysis</td><td>About 15 minutes working time plus 30 minutes waiting time per sample.</td></tr>
</table>

(a) Data obtained at Nalfloc Ltd on stabilized solutions.
(b) Data obtained at Chelsea College of Technology on stabilized solutions.

A2 Principle

A2.1 Sulphite is readily oxidized by atmospheric oxygen and therefore must be stabilized with potassium tetrachloromercurate in the sample bottle at the time of sampling. A dichlorosulphitomercurate complex is formed which is stable to strong oxidants.

A2.2 Intensely coloured pararosaniline methyl sulphonic acid is formed by the reaction of sulphite with formaldehyde and acid-bleached pararosaniline. The pH of the final solution is adjusted to 1.6 ± 0.1 by the use of 3M phosphoric acid solution in the pararosaniline reagent. The absorbance at 548 nm is measured using a spectrophotometer.

A3 Interferences

A3.1 The method is applicable to most types of water. Errors may occur due to the colour of highly-coloured waters and turbidity.

A3.2 Nitrite severely depresses the intensity of the developed colour. If present, it must be destroyed by the addition of sulphamic acid.

A3.3 Sulphide and mercaptides could interfere with the formation of the coloured derivative to an extent which has not been reliably quantified. Unverified results indicate that 5 μg $S^=$ enhances the developed colour by about 0.02 absorbance units and that there is a progressive increase in absorbance with increasing sulphide concentration. However, as a mercuric compound is used as sample stabilizer and any sediment is filtered off prior to use, sulphide should not be present during colour formation.

A3.4 Thiosulphates – No interference to 1 mg/l $S_2O_3^=$. At higher concentrations interference may occur especially in the absence of tetrachloromercurate.

A3.5 Sulphates do not interfere.

A3.6 Thiocyanates do not interfere at up to 100 μg/l CNS^-.
Above this concentration a marked positive bias is evident the effect increasing with thiocyanate concentration, being about +15 μg/l $SO_3^=$ at 1 mg/l SCN^-.

A4 Hazards

A4.1 Hydrochloric and phosphoric acids are corrosive.

A4.2 Mercury compounds are highly poisonous and should be handled as such. If potassium tetrachloromercurate solution is spilt on the skin it must be flushed off with water immediately. For disposal of waste solutions containing mercury see Reference 9.

A4.3 There is some evidence that some of the intermediates used in some but not all methods for the preparation of pararosaniline may be carcinogenic. As the method of preparation is not always known, and as the purity of the commercially available reagent is variable, it is recommended that skin contact with pararosaniline itself and its solutions, and inhalation of pararosaniline dust should be avoided.

A4.4 Formaldehyde is a suspected carcinogen for some but not all species, and is also an irritant poison, it should therefore be treated with extreme care. It is unlikely that formaldehyde and hydrochloric acid will react to form bis-chloro methyl ether (BCME) under the aqueous conditions used in this procedure, but, since chloro methyl ethers are known carcinogens, the use of a fume hood is obligatory in order to avoid inhalation of the vapour. Rubber gloves should be used to avoid skin contact. Do not pipette by mouth. Wastes containing formaldehyde should be disposed of with care, using copious amounts of water.

A4.5 Supplies of gas from cylinders and other sources under pressure should always be fitted with a lute or similar pressure relief device. (A lute is a tee tube with a side arm dipping sufficiently into a suitable liquid to give a head slightly greater than required by the apparatus.) If the gas is toxic, proper venting is essential.

A5 Reagents

All reagents should if possible be of analytical grade.

A5.1 Water

Use good quality distilled water which has been freshly de-oxygenated by sparging with oxygen-free nitrogen for 5 to 10 minutes or by boiling and cooling. Prepare fresh water as required. For oxygen free nitrogen see Section B11.

A5.2 Glycerol solution 25%v/v

Dilute 250 ml glycerol to 1000 ml with water. Mix well. Stored in a glass bottle this reagent is stable for several months.

A5.3 Potassium Tetrachloromercurate Solution, 0.1M

Dissolve 14.9 ± 0.2 g potassium chloride in approximately 750 ml water. Add to this solution 27.2 ± 0.1 g mercuric chloride and mix to dissolve, add 3.7 ±0.1 g ethylenediaminetetra acetic acid disodium salt (EDTA), allow to dissolve and dilute to 1000 ± 10 ml with water. Mix well. (NB This solution is 0.01M with respect to EDTA.) This reagent is stable indefinitely. Replace if a precipitate forms.

A5.4 Potassium Tetrachloromercurate Solution, 0.01M

Dilute 100 ± 1 ml of 0.1M potassium tetrachloromercurate solution to 1000 ± 10 ml with water and mix well. Replace if a precipitate forms.

A5.5 Hydrochloric Acid, 1M Solution

Dilute 86 ±1 ml concentrated hydrochloric acid ($d_{20}1.18$) to 1000 ± 10 ml with water and mix well. This reagent is stable indefinitely.

A5.6 Pararosaniline Stock Solution

Dissolve 0.20 ± 0.01 g pararosaniline hydrochloride or acetate in 100 ± 1 ml of 1M hydrochloric acid. Mix well. This reagent is stable for several months. Not all sources of pararosaniline hydrochloride or acetate are satisfactory as a reagent. Reference 6 gives tests of reagent purity and methods of reagent purification. As a guide, blank values (steps A8.5 and A8.6) should have an absorbance of about 0.15–0.2 and 40 μg of sulphite should give an absorbance of about 0.95. Solutions of specially purified reagent are commercially available.

A5.7 Phosphoric Acid, 3M Solution

Dilute 205 ± 5 ml concentrated phosphoric acid ($d_{20}1.7$) to 1000 ± 10 ml with water. This reagent is stable indefinitely.

A5.8 Pararosaniline Reagent

Pipette 20.0 ± 0.1 ml of pararosaniline stock solution and 25.0 ± 0.1 ml of 3M phosphoric acid into a 250 ml calibrated flask and make up to the mark with water. This reagent is stable for several months, if stored in the dark.

A5.9 Sulphamic Acid, 0.6 per cent solution

Dissolve 0.6 ± 0.05 g sulphamic acid in 100 ± 2 ml water. Prepare fresh weekly.

A5.10 Formaldehyde 0.2 per cent solution

Pipette 5.0 ± 0.1 ml of 40 per cent w/v formaldehyde into a 1 litre volumetric flask and make up to the mark with water. Prepare fresh solution daily.

A5.11 Potassium Iodate-Iodide 0.025N solution

M/240 approximately 0.0042M (see also the next method B4.3).

Dissolve 0.892 ± 0.001 g potassium iodate (previously dried for 1 hour at 120°C), 8.7 ± 0.1 g potassium iodide and 0.62 ± 0.02 g sodium bicarbonate in water and dilute to 1 litre in a calibrated flask.

A5.12 Sodium Thiosulphate 0.0125M solution

Nominal (see also the next method (A4.4) for an alternative strength solution).

Dissolve 3.125 ± 0.001 g sodium thiosulphate pentahydrate in water and make up to 1 litre with water in a calibrated flask. Add 1 ml chloroform as a preservative and store in a dark glass bottle. Discard if turbid.

A5.13 Starch Indicator

See the next method (B4.5) for preparation.

A5.14 Sulphite Stock Solution

Introduce about 100 ml water and 50 ml glycerol solution (B5.2) into a 500 ml volumetric flask. Add 0.2 g anhydrous sodium sulphite or 0.4 g of the heptahydrate and mix to dissolve. Make up to the mark with water and mix again. This solution deteriorates on storage and should be standardized on the day of use.

A5.14.1 Standardization

See also the next method in this booklet for a variant using 0.025M thiosulphate.

Introduce 10.0 ± 0.2 ml 1M hydrochloric acid (A5.5) and 10.00 ml ± 0.02 ml 0.0042M potassium iodate-iodide solution (A5.11) into each of two conical flasks. Dilute both solutions to about 200 ml and swirl to mix. Add to the first flask only, 25.00 ± 0.05 ml stock sulphite solution. Titrate both solutions with 0.0125M sodium thiosulphate (A5.12) adding starch indicator when the solution colour is reduced to pale straw. Continue the titration until the blue colour just disappears and record the titres in the presence (A ml) and absence (B ml) of added sulphite.

Calculate the strength of the sulphite solution as follows:-

$$0.4\left(1-\frac{A}{B}\right) = \text{mg/ml } SO_3^{=}$$

A5.15 Sulphite Working Solution 1 ml = 4 μg $SO_3^{=}$

Introduce 50 ml 0.1M potassium tetrachloromercurate (A5.3) into a 500 ml calibrated flask. Add approximately 425 ml water. The water may be de-oxygenated as described under A5.1, or preferably by sparging with oxygen-free nitrogen for 5 to 10 minutes after introduction into the volumetric flask. From a burette, add a volume of stock sulphite solution (A5.14) containing 2 mg $SO_3^{=}$. Dilute to the mark and mix.

A6 Apparatus

Volumetric glassware should be to Class B tolerance in the relevant British Standards. In addition to general laboratory glassware the items listed below are required.

A6.1 Sloping-shouldered glass bottles

For sample collection (a capacity of 100–250 ml is suitable).

A6.2 A completely closed box

In which to store sample bottles without exposure to sunlight.

A6.3 Spectrophotometer

With matched 10 mm cells.

A7 Sampling and Sample Preservation

A7.1 Use sloping-shouldered glass sample bottles (A6.1). For each 100 ml of sample to be collected, put 10 ml of potassium tetrachloromercurate solution (A5.3) into the bottle. Store all samples out of direct sunlight, preferably in the dark. Sample deterioration is retarded by refrigeration. Do not freeze.

A7.2 Samples from a Tap or Sample Point

Fix a length of clean sulphur free tubing to the tap, sufficiently long enough to reach the bottom of the sample bottle. Sample points should be fitted with permanent tubes. Thoroughly purge the sample tube, then insert the outlet to the bottom of the sample bottle, whilst the sample is still flowing. If the water to be sampled is at a temperature about 25°C cool it to between 15°C and 20°C by inserting a stainless steel cooling coil in the sample line. (No action is necessary to warm colder samples.)

A7.3 Samples from Open Water

Taking care to avoid aerating the sample, thoroughly rinse a beaker fitted with a handle, or a similar ladle of capacity greater than the sample bottle. Then scoop up a beaker or ladle full of sample and gently pour into the sample bottle using a funnel, pre-rinsed with sample, which dips to the bottom of the sample bottle. When full, remove the bottle, stopper securely and mix.

A7.4 Potassium tetrachloromercurate-stabilized samples may be stored for several days if refrigerated (see A7.5). They should be filtered, if necessary, to remove suspended matter, whether present initially, or generated on standing. As oxidation of sulphite is catalysed by UV light, exposure of the samples to direct sunlight should be minimized by storing samples in a dark box. Exposure to artificial lighting should be limited to a few hours. Heavy metals which might otherwise catalyse the oxidation of sulphite, are complexed by the addition of ethylenediaminetetra acetic acid (EDTA) which is included in reagents A5.3 and A5.4.

A7.5 Samples stabilized in the recommended manner may suffer loss of sulphite at a rate of between 1 and 3% per day if stored at 25°C but less than 1% per day if stored at 5°C. However, if the concentration of sulphite exceeds 500 mg/l, a rapid redox reaction occurs between Hg(II) and $SO_3^=$. Immediate quantitative dilution is then suggested as an alternative.

A8 Analytical Procedure

(See notes at Steps A8.7 to A8.9)

Step	Procedure	Notes
	Analysis of Samples	
A8.1	Transfer a measured volume, V, of sample not exceeding 10 ml and containing not more than 40 µg $SO_3^=$ to a 25-ml calibrated flask. Dilute, if necessary, to approximately 10 ml using 0.01M potassium tetrachloromercurate (A5.4).	
A8.2	Add by pipette 1 ml of 0.6% sulphamic acid solution (A5.9) to the flask and stand for 10 minutes (note a).	(a) This stage may be omitted if it is known that nitrite is absent.
A8.3	Add by pipette 2 ml of 0.2% formaldehyde (A5.10) and 5 ml of pararosaniline reagent (A5.8). Dilute to volume with water and mix. Stand for 30 ±5 minutes at the temperature at which the calibration was prepared, and out of direct sunlight (notes b and c).	(b) The pipetting of the pararosaniline must be done accurately. (c) The temperature of the calibration and of the analyses should not differ by more than ±2°C. For maximum accuracy a constant temperature for both should be used.
A8.4	Measure the absorbance A_S, at 548 nm using 10 mm cells with distilled water in the reference cell (note d).	(d) Do not allow the coloured solution to stand in the cell otherwise a film of dye will be deposited.
	Blank Determination (note e)	
A8.5	Add 10 ml of 0.01M potassium tetrachloromercurate (A5.4) into a 25-ml volumetric flask (note e).	(e) A blank determination must be run with each batch of samples using exactly the same reagent solutions.

Step	Procedure	Notes
A8.6	Repeat steps A8.2–A8.4 inclusive. Let the absorbance of the blank be A_B (note e).	
	Preparation of Calibration Graph (prior to the analysis of samples)	
A8.7	Add from a burette 0.0, 2.0, 4.0, 6.0, 8.0 and 10.0 ml (all ±0.005 ml) of freshly prepared sulphite working solution (A5.15) into a series of 25 ml calibrated flasks.	
A8.8	Carry out steps A8.2–A8.4 (notes b, c, d, e, and f) at least in duplicate on these solutions and repeat at least once on another occasion, and then again, as required, until the calibration graph is defined with the required precision.	(f) Omit stage A8.2 if it is known that nitrite is absent from the samples.
A8.9	Subtract the mean absorbance of the solution containing no added sulphite (note g) from the mean absorbances of the other solutions and plot a calibration graph of blank-corrected absorbances against amount (in μg) of sulphite ie 8, 16, 24, 32 and 40 μg (note c).	(g) The absorbance should be approximately 0.2.
A8.10	Calculate the sulphite concentration, C, in the sample from $C = \frac{A_S - A_B}{KV}$ mg/l where K is the absorbance of 1 μg $SO_3^=$ as obtained from the calibration graph and V is the volume of sample expressed in millilitres.	

A9 Sources of Error

A9.1 Oxygen Pick Up

Care and attention to detail is essential in order to avoid solution of oxygen in the water, reagent solutions and even samples, which will lead to low results. Nitrogen used for sparging should be oxygen free. See Section B.11 for details of preparation. If water is degassed by boiling, care is essential during cooling not to redissolve oxygen. Cooling and subsequent storage under oxygen-free nitrogen is suggested.

A9.2 Quality and Quantity of the Pararosaniline Reagent

As both the reagent and the substances formed for measurement are coloured, it is essential that the calibration curve be checked for each new batch of reagent and regularly in between, that the solution be accurately made up each time, and accurate amounts be dispensed to the samples and standards in the analysis.

A9.3 Spectrophotometer Cell Match

Cell match should be checked prior to use and regularly thereafter, using distilled water. Cells must be cleaned thoroughly, or changed if their spectrophotometer readings do not agree.

A9.4 Constancy of Temperature during Colour Development

This is a mjaor cause of variation in colour development. A water bath is recommended, the accuracy of the setting of which should be checked daily.

A9.5 Stability of Sulphite Standards and Samples

There is a tendency for these solutions to lose sulphur dioxide or pick it up from the atmosphere if any free sulphur dioxide is present (even from other samples). Standard solutions and samples should be kept in tightly stoppered bottles with as little free air space at the top as possible. Standards should be checked regularly before use (see Section A5.14) and samples analysed as soon after collection as possible. Samples and standards should be kept cold, without freezing to minimize loss of determinand (see Section A7.5).

A9.6 Use of Alternative Stabilizers

Other stabilizers for sulphites than chloromercurates are known, but their use is not recommended as, besides stabilizing, chloromercurates minimize some interferences.

A9.7 Nitrites

Nitrites must be absent or removed.

A10 Checking the Accuracy of Analytical Results

See part H.

B Determination of Sulphite and Sulphur Dioxide by Iodometry

B1 Performance Characteristics

B1.1	Substance Determined	Total sulphur dioxide liberated by acid.
B1.2	Types of Sample	Clean waters, including sea water but especially potable waters treated with sulphur dioxide.
B1.3	Basis of the Method	The sample is acidified and treated with potassium iodate-iodide. The iodine or iodine chloride formed oxidizes the sulphite to sulphate. Excess iodine is then titrated with a sodium thiosulphate solution which is itself standardized against a potassium iodate primary standard.
B1.4	Range of Application	2 to 150 mg/l on a 250-ml sample. For higher concentrations use a smaller sample.
B1.5	Standard Deviation	Not determined experimentally. Estimates based on the indicator uncertainty and the discriminatory interval for the various critical measurements indicate that the co-efficient of variation will vary between 25% at 4 mg/l to under 5% at 190 mg/l.
B1.6	Limit of Detection	About 1 mg/l based on the limiting discriminatory interval and indicator uncertainty.
B1.7	Bias	The method has an inherent negative bias due to loss of sulphur dioxide, oxidation of sulphur dioxide, and the effect of air on the end point. Interferants usually cause high results, many directly quantitatively.
B1.8	Interferences	Sulphide, thiosulphate and similar substances which react with iodine and iodate give quantitatively high results. Thiocyanate does not react. Substances such as copper which liberate iodine from iodide give almost quantitatively low results. Copper and cobalt also cause low results by catalysing the oxidation of sulphite by air. Nitrate, mercuric ion and similar oxidants will oxidize sulphite on acidification causing low results. Iron interferes in a complex manner.
B1.9	Time Required for Analysis	About 5–10 samples per hour excluding reagent preparation time.

B2 Principle

The sample is acidified with hydrochloric acid and then an excess of potassium iodate-iodide mixture is added. In acid solution, iodate and iodide react to form iodine or in the presence of chloride at higher acidity, iodine chloride. These oxidize sulphite to sulphate reforming iodide which can react with more iodate, and so on until all the sulphite is oxidized or the iodate is exhausted. In the latter event the solution would become colourless and a further addition of iodate would be indicated. The excess of iodine, iodine chloride and iodate is determined by titration with sodium thiosulphate solution. The sodium thiosulphate solution is standardized by the titration, in the presence of acidified iodide, of a known amount of potassium iodate, which is an analytical primary standard substance. The brown to yellow to straw coloured end point of the iodine titration is sharpened by the addition of soluble starch which reversibly gives a blue colour with iodine.

The equations for the reactions involved are:

$IO_3^- + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2$
$SO_3^= + I_2 + H_2O \rightarrow SO_4^= + 2H^+ + 2I^-$

and

$2S_2O_3^= + I_2 \rightarrow S_4O_6^= + 2I^-$

or

$IO_3^- + 2I^- + 6H^+ + 3Cl^- \rightarrow 3ICl + 3H_2O$
$SO_3^= + ICl + H_2O \rightarrow SO_4^= + 2H^+ + I^- + Cl^-$

and

$2S_2O_3^= + ICl \rightarrow S_4O_6^= + I^- + Cl^-$

or overall

$IO_3^- + 3SO_3^= \rightarrow 3SO_4^= + I^-$

and

$IO_3^- + 6H^+ + 6S_2O_3^= \rightarrow 3S_4O_6^= + I^- + 3H_2O$

B3 Interferences

B3.1 The following interferants titrate quantitatively:-

Sulphide is oxidized to sulphur
1 mg/l $S^=$ causes an apparent gain of 2.5 mg/l $SO_3^=$

Thiosulphate is oxidized to tetrathionate
1 mg/l $S_2O_3^=$ causes an apparent gain of 0.5 mg/l $SO_3^=$

Copper II is reduced by iodide to Copper I, quantitatively if thiocyanate is present, and almost quantitatively otherwise. Insoluble copper I iodide absorbs slight amounts of free iodine which will not then react with either sulphite or thiosulphate. 1 mg/l Cu^{++} causes an apparent loss of 0.63 mg/l $SO_3^=$ (but see also B3.3 below).

B3.2 Many organic compounds also react with iodine and so cause high results, the amount depending on the compound, however sulphite can sometimes be separated from interfering organic matter by distilling an acidified solution, collecting the sulphur dioxide in dilute alkali and using this distillate as sample. A suitable apparatus is that used for the converse separation of ammonia (Ref 12). Alternatively see Ref 13.

B3.3 In the presence of air, cobalt and copper salts catalyse the oxidation of sulphite causing low results. This can be minimized by reducing contact with air.

B3.4 Nitrite and mercuric ions can also oxidize sulphite in acidic solutions but the degree of oxidation is very dependent on conditions. If these ions are present in significant amounts compared with the desired precision, use method A. Nitrite also liberates iodine from iodide stoichiometrically.

B3.5 Iron III reacts quantitatively with both sulphite and iodide forming sulphate and iodine respectively. As the former reaction would prevent sulphite being in the sample if iron III were in excess, and the latter causes a low result, negative analytical results might then be caused. If such a result were obtained and iron III was present initially, the sample contained no sulphite or sulphur dioxide.

Iron II is oxidized by iodate forming iron III and iodine. Hence the effect of iron II, under the conditions of these titrations, would be similar to that of extra iodide and would not affect the analytical result (contrary to the report in 'Analaysis of Raw, Potable and Waste Waters (p239)).

B3.6 Thiocyanate does not interfere.

B4 Reagents

B4.1 Water

The water used in this analysis should be free of organic matter, sulphur dioxide and chlorine. Distil water containing just sufficient potassium permanganate to give a faint pink colour, reject the first 5% of distillate and leave a similar volume of undistilled residue.

B4.2 Hydrochloric acid $d_{20}1.18$

B4.3 Potassium Iodate-Iodide Solution, M/240

Dry potassium iodate to constant weight at 120°C, weigh out 0.8917 ± 0.0005 g and dissolve in 200 ml of water. Add 9 ± 1 g potassium iodide and 0.5 ± 0.1 g sodium bicarbonate, dissolve and make up quantitatively to 1 litre in a calibrated flask, with water. This solution should be stable for at least 3 months, but discard earlier if it turns slightly yellow.

B4.4 Sodium Thiosulphate Solution, M/40 (0.025M)

(Other strengths may be prepared by dilution, or by changing the weight of sodium thiosulphate taken, see previous method Section A5.12). Dissolve 6.3 ± 0.1 g of sodium thiosulphate pentahydrate in water, and make up to 1 litre in a calibrated flask, with water. Add not more than 1 ml of chloroform as stabilizer. Store in a brown bottle. Check the titre at least weekly. Discard if even slightly turbid.

B4.5 Starch Indicator Solution

Grind about 1 g of soluble starch into a smooth paste with a little cold water and pour into 200 ± 10 ml of boiling water, with constant stirring. Boil for 1 minute and cool before use. Store in a glass bottle. Discard if growth of micro-organisms becomes apparent, or a test sample fails to give a blue colour with acidified potassium iodate-iodine solution (B4.3). Commercial preparations are also satisfactory (See method for Thiosulphate determination Section C4.5).

B4.6 Inert Gas

Carbon dioxide, or oxygen/free nitrogen.

If the supply of nitrogen is not oxygen-free, bubble through a solution of chromium II solution prior to use. See Sections B11 for details.

B5 Apparatus

B5.1 Standard laboratory glassware, cleaned and then rinsed thoroughly in distilled water. British Standards to class B tolerances usually suffice for volumetric glassware.

B5.2 For accurate results the whole analysis from taking of the sample and sample measurement to titration should be carried out in as oxygen-free conditions as possible, with minimum risk of loss of sulphur dioxide to the atmosphere above the sample.

Samples can be transferred through a tube dipping to the bottom of the bottle, using inert gas pressure supplied by a tube ending flush with the bottom of the stopper. Sample volumes can be taken using a similar device with the dip tube sufficiently above the bottom of the bottle to leave the required volume remaining in the bottle. The stopper dip tube should be so fixed in that it always leaves the same volume in the bottle. For accurate work ground glass joints and accurate calibration of the volume remaining are necessary. Gas pressurizing lines must be fitted with lutes (vent tubes dipping into water of somewhat greater depth than the maximum head required for any sample transfer and capable of carrying all the gas in the event of closure of the sample transfer tubes).

Similarly, titrations can be started in flasks with the burette passing through the stopper provided there is also a suitable vent dipping into a water seal to prevent ingress of air. Once the sulphite has reacted with the iodate, the flask can be opened and excess iodate-iodine titrated in the above more normal manner.

However, with care, it is possible to measure sample volumes using measures and titrate in narrow necked flasks containing an atmosphere of carbon dioxide.

Sample volume measurements should not be made by pipette.

B6 Sampling and Sample Preparation (See also Section B5 above)

B6.1 For techniques for taking the sample see the proceeding method, Section A7, but omit the potassium tetrachloromercurate stabilizer.

B6.2 If the sample is acidic, loss of sulphur dioxide can be minimized by the addition of just sufficient sodium hydroxide to make the sample alkaline. For accurate work this volume should be measured.

B6.3 Sample bottles should be of glass and filled as full as possible commensurate with not bursting.

B6.4 The analysis should be made as soon after sampling as possible. If necessary samples may be stored for a few hours at about 4°C.

B7 Analytical Procedure

Step	Procedure	Notes
	Titration of Sample	
B7.1	Measure out, in an inert atmosphere, 250 ± 1 ml of sample (V_3) (note a).	(a) See Section B5.2.
B7.2	Add 2.0 ± 0.2 ml of hydrochloric acid (note b), followed by 50.00 ± 0.01 ml of M/240 potassium iodate-iodine mixture. Mix by gentle swirling (note c).	(b) If the samples contain more than 20 milliequivalents per litre of alkali, add extra hydrochloric acid to bring the sample to neutrality or slight acidity and then the 2 ml excess. (c) If there is no free iodine left after mixing, add further 50 ml portions of iodate-iodine until the brown colour of free iodine is obtained. Note how much is needed (V_1).
B7.3	Titrate the excess iodine formed with M/40 sodium thiosulphate solution. When the brown iodine colour becomes amber, add a few drops of starch indicator solution and continue titration until the resultant blue colour disappears completely (note d). Note the volume of thiosulphate solution used (V_2).	(d) The blue colour may return on standing in air. This should be ignored as it is due to oxidation of iodide by air.
	Standardization of Thiosulphate (B4.4)	
B7.4	Using 250 ± 1 ml of water carry out steps B7.2 and B7.3 and note the volume of thiosulphate required (V_4) for 50.00 ± 0.05 ml of the M/240 iodate-iodine.	

B8 Calculation

B8.1 Sulphite Concentration $= \dfrac{\left(V_1 - \dfrac{50}{V_4} V_2\right)}{V_3} \times 1000$ mg/l $SO_3^{=}$

Where: V_1 is the volume of M/240 iodate-iodine used with the sample (usually 50 ml).

V_2 is the volume of M/40 thiosulphate used to back titrate the excess iodine from the sample.

V_3 is the volume of the sample.

and V_4 is the volume of M/40 thiosulphate required for the standardization step B7.4.

All volumes being in ml.

B8.2 For sulphur dioxide concentration the formula is:

$$\frac{\left(V_1 - \frac{50}{V_4} V_2\right)}{V_3} \times 800 \text{ mg/l } SO_2$$

B9 Sources of Error

B9.1 Oxygen Pick Up

See Section A9.1 of the previous method. There is also a risk of error due to drift back of the end point after titration due to atmospheric oxidation of iodide in acid solution. This is obviated by using the first clear end point with starch indicator, and ignoring any drift back.

B9.2 Loss of Iodine Vapour

Titration should not be delayed after addition of the iodate-iodide mixture. Samples should also be kept cool and not aerated.

B10 Checking the Accuracy of Analytical Results

See Part H.

B11 Preparation of Oxygen-Free Nitrogen (See Section B4.6)

If guaranteed oxygen-free nitrogen is not available, remove any traces of oxygen by bubbling the gas through 2 gas bubblers containing chromium II solution (B11.1). Regenerate the absorbant when the solution becomes markedly green or mauve in colour. A lute should be fitted between the gas supply and the first bubbler. (See Section A4.5 of the Pararosaniline Method for safety precautions).

A lute is a water sealed safety vent such as a long tee piece dipping into a jar or cylinder filled with a suitable inert liquid such as water, oil or mercury.

B11.1 Chromium II Oxygen Absorbing Solution

The following reagents are required for its preparation:

B11.1.1 Chromium III chloride, hexahydrate

B11.1.2 Mercury metal

B11.1.3 Zinc granules (1.7–2.8 mm)

B11.1.4 Hydrochloric acid, $d_{20}1.18$

B11.1.5 Hydrochloric acid, c2M

Dilute 200 ± 10 ml of hydrochloric acid $d_{20}1.18$ to 1 litre with water using measuring cylinders. Stored in a glass bottle this solution will keep indefinitely.

B11.1.6 Sulphuric acid $d_{20}1.84$.

B11.1.7 Sulphuric acid cM.

Put 1 litre ± 10 ml of cold water into a 2 litre beaker and slowly and carefully stir in 28 ± 2 ml of sulphuric acid $d_{20}1.84$. Stored in a glass bottle this solution will keep indefinitely.

B11.1.8 Preparation of the absorbant solution:

B11.1.8.1 Wash 16 g of zinc granules (1.72–2.8 mm) with hydrochloric acid (2M approximately). Add 500 g of pure mercury, cover with 10 ml of hydrochloric acid (2M approximately) and heat for one hour on a boiling water bath in an efficient fume cupboard. Allow to cool, wash the amalgam with sulphuric acid (1M approximately) and then with water.

B11.1.8.2 Transfer the amalgam to a 400 ml reagent bottle, add 100 g of chromic chloride hexahydrate, 260 ml of water and 40 ml of hydrochloric acid ($d_{20}1.18$). Stopper the bottle with a rubber bung carrying a bunsen valve (Figure 1) and shake the bottle until the contents assume the characteristic blue colour of a chromous solution. The absorbing power is about 25 ml of oxygen per millilitre of solution. Store this solution only in bottles fitted with bunsen valves, or similar, as it may slowly evolve hydrogen.

B11.1.9 Regeneration of spent amalgam and absorbant:

B11.1.9.1 Recovery of the mercury from the amalgam.

Gently swirl spent amalgam with portions of c2M hydrochloric acid, decanting off spent acid (first into a beaker to catch any accidental spillage of mercury which should be returned to the bulk in the original beaker). When the mercury is free flowing and bright, wash once with water in the same manner and reuse as in Section B11.1.8.1 for preparing fresh zinc amalgam.

B11.1.9.2 Regeneration of chromium II solutions.

Return spent solution from the bubblers to a bottle containing amalgam, as in Section B11.1.8.2, add 40 ml of hydrochloric acid $d_{20}1.18$, stopper and shake as detailed in B11.1.8.2. Regeneration can be repeated until the solution becomes turbid. It should then be discarded.

C Determination of Thiosulphate by Iodometry

C1 Performance Characteristics of the Method

Note – this method is intended for the determination of thiosulphate when used as a treatment chemical and in photographic industry effluents. It is usually unsuited for use with complex mixtures such as coke oven liquors.

C1.1	Substance Determined	Thiosulphate	
C1.2	Types of Sample	Clean waters and some effluents.	
C1.3	Basis of the Method	The sample is added to a known excess amount of iodine generated from iodate-iodine by acidification. This oxidizes the thiosulphate to tetrathionate. The excess of iodine is back titrated with a thiosulphate solution prestandardized against iodate-iodine.	
C1.4	Range of Application	10–1000 mg/l $S_2O_3^=$ depending on sample size.	
C1.5	Standard Deviation (a) For main method, Steps C7.1–C7.4	Thiosulphate Concentration mg/l	Maximum Probable Standard Deviation mg/l
		35.0	1.15
		168.0	2.15
	C1.5.1 Standard Deviation including Step C7.5.	Indications are that the precision is only marginally worse than for the main method.	
	C1.5.2 Standard deviation including Step C7.6(c)	Thiosulphate Concentration mg/l	Total Standard Deviation mg/l
		11,200	154
C1.6	Limit of Detection (b)	Approximately 7 mg/l.	
C1.7	Bias	Not determined for the main method. For the formaldehyde procedure there is a risk of low results if there are delays or the solution is too acid (Ref 15).	
C1.8	Interference	Sulphide and Sulphite interfere but can be removed. Thiocyanate does not interfere. Other substances such as copper II and iron III which react with iodide to form iodine cause low results, substances such as unremoved sulphide and sulphite and some phenols which react with iodine cause high results.	
C1.9	Time required for analysis	About 5–10 samples per hour.	

Notes

(a) Estimated from experimental data for the simple titration of iodine (from iodate-iodide) by thiosulphate in Panel 5.5 records.

(b) Based on the Discriminatory Interval and a Relative Standard Deviation of 10% with the method as written. This limit can be lowered to about 2 mg/l $SO_3^=$ by using 1 litre samples.

(c) In the presence of 0.4–1.6 g/l sulphite or bisulphite, using a stronger iodine and thiosulphate than here because of the higher concentration (M/10 $S_2O_3^=$). Data from A Kurtenacker (Ref 15).

C2 Principle

Iodine is formed stoichiometrically by reaction of a primary standard iodate solution and iodide in the presence of sulphuric acid. This reacts with the thiosulphate in the sample to form tetrathionate and iodide. Excess iodine is back titrated against sodium thiosulphate, which has been prestandardized against the same potassium iodate-iodide solution.

C3 Interferences

C3.1 Sulphide, Sulphite and Dithionite

Sulphide and sulphite interfere quantitatively see Sulphite and Sulphur Dioxide by Iodometry Sections B2 and B3. Dithionites also interfere quantitatively. Sulphide may be removed by shaking the sample with lead carbonate and filtering (Step C7.5).

Sulphite may be removed by reaction with 2 ml of 40% w/v formaldehyde solution in dilute acid solution to form formaldehyde bisulphite ($HO\ CH_2\ SO_3\ H$) which does not titrate. Sulphide and thiosulphate can form the cyclic trithiane ($C_3H_6S_3$) but only slowly in highly acid solutions or on heating. The method given in step C7.6 relies on titrating after the bisulphite formation is virtually complete but before trithiane formation ceases to be negligible. Acidity control and avoidance of undue delay is therefore very important.

Dithionites react quantitatively. One $S_2O_4^=$ ion is equivalent to one IO_3-ion. If present, determine dithionite, see Other Techniques, Section G1, and if the amount present is significant, correct the thiosulphate titration accordingly.

C3.2 Phenols

Phenols such as resorcinol and 3,5-dimethyl catechol and some other organic compounds are iodinated and give high results. Increased acidity may suppress this reaction but does not completely eliminate it. Rapid titration also helps. If accurate analyses are required use either polarography or HPLC/Ion Chromatography described in part G of this booklet (G3 and G5) instead of this method.

C3.3 Substances which liberate iodine from iodide

Also interfere causing low results. Nitrite, manganese III and higher oxidation states, chromate, iron III, copper II, or, very rarely, cerium IV can occur in samples of the type being analysed and may interfere. The extent of the interference will depend on the overall composition of the sample. If the amount of interferent is greater than 5 molar percent of the thiosulphate being determined use another method. If higher precision is required the limiting value of interferent should be lower still.

C4 Reagents

All chemicals should be of analytical reagent quality unless otherwise specified. Store reagents in glass bottles.

C4.1 Water

See Determination of Sulphite and Sulphur Dioxide by Iodometry, Section B4.1.

C4.2 Potassium Iodide, crystals

C4.3 Potassium Iodate 0.0208M (ie M/48)

C4.3.1 Dissolve 4.46±0.005 g of potassium iodate dried at 110±5°C for 1 hour, in about 200 ml of water, transfer quantitatively to a 1 litre calibrated flask, dilute with water to the mark and mix. Properly stored in a clean, glass stoppered, bottle the solution should be stable for at least 1 year.

C4.3.2 Potassium iodate 0.00208M (ie M/480)

Pipette 50.00±0.05 ml of potassium iodate 0.0208M into a 500 ml calibrated flask and make up to the mark with water. Properly stored in a clean, glass stoppered, bottle the diluted solution should be stable for at least one week.

C4.4 Sulphuric Acid c25 percent

Carefully, with cooling and with constant stirring, wearing goggles, slowly pour 100 ± 10 ml of sulphuric acid $d_{20}1.84$ into 300 ± 15 ml of cold water. Cool.

C4.5 Starch solution

Grind 0.5 ± 0.1 g of soluble starch into a smooth paste with a little cold water and pour into 100 ± 10 ml boiling water with constant stirring. Boil for one minute and allow to cool before use. The reagent remains stable for up to one week if stored in a refrigerator, otherwise prepare fresh solution as required. Solid indicators are available commercially and may be used in place of starch solution. Use in accordance with manufacturer's instructions.

C4.6 Sodium thiosulphate

C4.6.1 Sodium thiosulphate 0.125M

Dissolve 31.2 ± 0.05 g of sodium thiosulphate pentahydrate in about 200 ml of water, transfer quantitatively to a 1 litre calibrated flask, dilute with water to the mark and mix. Shelf life is variable and limited. Store in an amber glass bottle. Turbid solutions should be discarded. Also discard as soon as the dilute solutions prepared daily, show a signficant loss of strength (see Section C7).

C4.6.2 Sodium thiosulphate 0.0125M

Pipette 50.00 ml of sodium thiosulphate 0.125M into a 500 ml calibrated flask and dilute with water to the mark. Prepare fresh solution daily.

C4.7 Powdered Lead Carbonate

C4.8 Formaldehyde solution c40% w/v

The exact strenth is not critical (see Sulphite and Sulphur Dioxide by Pararosaniline Section 4.4 and Ref 2).

C4.9 pH Indicators

Phenolphthalein and Methyl Orange solutions or equivalent, including a pH meter, may be needed if sulphite is present and the samples are markedly acidic or alkaline.

C4.10 Standard Sodium hydroxide and acetic, phosphoric or hydrochloric acids

May be needed if sulphite is present and the samples are markedly acid or alkaline. Consistent use of the same quantity reagent of uniform strength is more important than exact standardization of the reagent strength.

C5 Apparatus

Unless otherwise specified all glassware for the handling of specified volumes of reagents should be accurate to a Class B tolerance or better as defined in relevant standards of the British Standards Institution.

Common laboratory glassware.

Including pipettes, conical flasks, measuring cylinders and beakers.

C6 Sampling and Sample Preparation

Samples should be stored in glass bottles and analysed as soon as possible. If necessary storage should be at 2–4°C. If stored, acidic samples should be made just alkaline with sodium carbonate or a few marble chips.

C7 Analytical Procedure

Step	Procedure	Notes
	Standardization of Sodium Thiosulphate 0.0125M (note a)	
C7.1	Pipette 25.00 ± 0.05 ml of 0.00208M potassium iodate into 200 ± 5 ml of water in a 1 litre conical flask. Add 0.5 ± 0.1 g potassium iodide crystals and 5 ± 1 ml sulphuric acid, mix and allow to stand for 60 ± 5 seconds.	(a) This should be carried out immediately before the use of sodium thiosulphate for the analysis of samples.
C7.2	Titrate with 0.0125M sodium thiosulphate until the colour of the liberated iodine is nearly discharged. Add 2 ± 0.5 ml starch solution (or its equivalent if using an alternative indicator) and titrate rapidly until the blue colour disappears for 30 seconds. Note the titration volume V_2 ml (note b).	(b) Any deviation from 0.0125M in the strength of the thiosulphate should be taken into account when making the final calculation.
	Analysis of Samples	
	No interference.	
C7.3	Using a measuring cylinder transfer 200 ± 1 ml or other volume V ml of sample to a 1 litre conical flask. Add 0.5 ± 0.1 g potassium iodide crystals and pipette in 25.0 ml of potassium iodate 0.00208M solution, followed by 5 ± 1 ml of sulphuric acid. Allow to stand for 60 ± 5 seconds. Mix by gentle swirling.	
C7.4	Titrate with standardized 0.0125M sodium thiosulphate (see steps C7.1 and C7.2) until the colour of the liberated iodine is nearly discharged. Add 2 ± 0.5 ml of starch solution (or its equivalent if using an alternative indicator) and titrate rapidly until the blue colour disappears (note c). Note the titration volume V_1 ml.	(c) Titrate to the first end point only, since problems may occur due to recurring end points caused by slow oxidation by air and other substances.
	Modifications in the Presence of Interferences (note d)	
	Sulphide Removal	
C7.5	Take at least 250 ml of sample in a stoppered bottle, add powdered lead carbonate a few grains at a time, stopper and shake vigorously. Add a little more lead carbonate. Repeat this until the last addition does not change colour on addition prior to shaking. Allow to settle, then filter using a qualitative grade filter paper. Discard the first 10 ± 1 ml of filtrate, collect the remainder and proceed as in steps C7.1 to C7.4, using this sample at step C7.3. If sulphite is also present use step C7.6 instead of steps C7.3 and C7.4.	(d) It is possible to obtain approximate values for sulphide, sulphite and thiosulphate from mixtures containing just these 3 iodine reactive anions. Three samples are titrated, one with no pre-treatment and one each with pre-treatments 7.5 and 7.6. Let these be A, B and C respectively. A is equivalent to $S^= + SO_3^= + S_2O_3^=$, B is equivalent to $SO_3^= + S_2O_3^=$, and C is equivalent to $S^= + S_2O_3^=$.

Step	Procedure	Notes
		Then A–B is equivalent to $S^{=}$ A–C is equivalent to $SO_3^{=}$ and B + C − A is equivalent to $S_2O_3^{=}$ If sulphide is not removed, the solution will become turbid during the titration, but the end point is not affected.
C7.6	Sulphite Removal (note e)	(e) The accuracy of this analysis is highly dependent on the acidity; the solution must be acid enough firstly to form formaldehyde bisulphite and secondly to form free iodine from the iodate-iodide mixture. Hence, it is essential to know approximately the amount of acid needed. If the sample is very acid, take a separate known volume, titrate to a pink phenolphthalein end point with standard alkali and back titrate to a methyl orange end point with standard acid. Very alkaline solutions should similarly be titrated first to a colourless phenolphthalein end point with standard acid and then more carefully with weaker standard acid to a methyl orange end point. Weakly acidic solutions may be brought just to a methyl orange end point with a dilute standard acid. Sodium hydroxide is the preferred alkali, acetic, phosphoric, or hydrochloric acids are the preferred acids.
C7.6.1	Carry out steps C7.1 and C7.2 using water (not sample and without formaldehyde).	
C7.6.2	Measure out 200 ± 1 ml of sample and, based on the preliminary tests with a known sample (note e), add the known amount of alkali and or acid to bring the sample to the methyl orange end point, preferably not using indicators with the analytical sample itself.	
C7.6.3	Add 10 ml of formaldehyde solution c40 percent w/v and swirl to mix. Allow the solution to stand at a temperature of not warmer than 20°C for 5 ± 0.5 minutes. Add 0.5 ± 0.1 g potassium iodide crystals and 5 ± 1 ml acetic acid, mix and allow to stand for 60 ± 5 seconds. Immediately titrate with 0.0125M sodium thiosulphate until the colour of the liberated iodine is nearly discharged. Add 2 ± 0.5 ml starch solution (or its equivalent if using an alternative indicator) and titrate rapidly until the blue colour disappears for 30 seconds. Note the titration volume V_1 ml.	

C8 Calculation

Thiosulphate concentration $= \frac{1400\,(V_2 - V_1)}{V}$ mg/l $S_2O_3^{=}$

(If the sodium thiosulphate at step C7.2 is not exactly 0.0125M,

Thiosulphate concentration is $\frac{35000}{V}\left(1 - \frac{V_1}{V_2}\right)$ mg/l $S_2O_3^{=}$)

where in either formula V ml is the volume of sample used (usually 200 ml).

V_1 ml is the volume of thiosulphate required for the sample (steps C7.3 and C7.4 or C7.6) and V_2 ml is the volume of thiosulphate required for the water (steps C7.1 and C7.2).

C9 Change of Range

Large changes of range are possible either by changing the amount of sample used in accordance with the following table, or by changing the strength of potassium iodate and sodium thiosulphate used and changing the calculation factor as detailed below.

Variations in Sample Volume

Thiosulphate Concentration mg/l $S_2O_3^=$	Sample Volume V ml	Titration Range (V_2-V_1) ml
10 to 100	200	1.4 to 14.3
100 to 250	100	7.1 to 17.9
250 to 500	50	8.9 to 17.9
500 to 3000	10	7.2 to 21.5

Variations in Solution Strength

Potassium Iodate Moles per litre	Sodium Thiosulphate Moles per litre	Calculation Factor (Section 8 above) (recalculate if the sodium thiosulphate titre is not exact)	Thiosulphate Concentration Range for 200 ml Sample mg/l $S_2O_3^=$
M/480	M/80	1,400	10–100
M/60	M/10	11,200	80–800

Smaller sample sizes may also be used, pro rata,
Above 2,400 mg/l $S_2O_3^=$ (M/60, M/10 reagent at 10 ml sample), it is suggested that the sample be quantitatively diluted and aliquots taken.

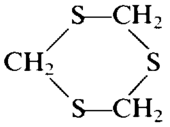
The interference removal steps C7.5 and C7.6 can also be adjusted (see Section C1.5.2 note c).

C10 Sources of Error

C10.1 Decomposition of Thiosulphate by acid on standing, with formation of sulphur and sulphur dioxide.

C10.2 Sections C9.1 and C9.2 of the Sulphite by Iodometry are applicable.

C10.3 If the sulphite removal step is used, excess acidity, and delay can cause loss of thiosulphate by formation of trithional



However the reaction is only rapid when the acidity reaches several moles per litre, but almost complete in minutes at 10M.

C10.4 Some phenols iodinate slowly and cause high results.

C11 Checking the Accuracy of Results

See Part H. Use a standard thiosulphate solution. Sulphide and Sulphite solutions may also be used to check the accuracy of the interference removal steps C7.5 and C7.6 (see also Refs 10 and 11).

D Determination of Thiocyanate, Manual Colorimetric and Volumetric Methods

The volumetric method is included chiefly for calibration of standards for the colorimetric method. However if the thiocyanate concentration is high and the chloride concentration is not excessive, a thiocyanate determination can be obtained by use of this method with correction for chloride interference. In which case Ref 9 Method A should be used including Section 13.4 to determine chloride. 1 mg/l Cl^- is equivalent to 1.18 mg/l SCN^-. Expected standard deviations will be at least twice those for the method without interference.

D1 Performance Characteristics

D1.1 Substance Determined — Thiocyanate

D1.2 Types of Sample

D1.2.1 Colorimetric — Waters and effluents.

D1.2.2 Volumetric — Clean waters and reagent solutions containing no other substances reacting with silver ions.

D1.3 Basis of Methods

D1.3.1 Colorimetric — Thiocyanate is reacted with an iron III solution to form a red complex and is determined spectrophotometrically.

D1.3.2 Volumetric — Thiocyanate solutions are used to titrate a primary standard silver nitrate solution to a brown end point using an iron III indicator. (Note that in this instance the sample is in the burette).

D1.4 Range of Application

D1.4.1 Colorimetric — Up to at least 32 mg/l.

D1.4.2 Volumetric — See Sections D1.5.2 and D1.6.2. Use of a precision 5 ml burette will improve accuracy at the higher range. Use of Molar Silver Nitrate will extend the range upward.

D1.5 Standard deviation

D1.5.1 Colorimetric
(a) Sample

	Thiocyanate Concentration mg/l CNS^-	Standard Deviation (within batch) mg/l CNS^-	Degrees of Freedom
Standard solutions	1.0	0.038	15
	9.0	0.104	15
Industrial effluent (b)	1.17	0.037	15
Spiked effluent (c)	6.07	0.040	15

D1.5.2 Volumetric — The sample being in the burette reverses the normal accuracy limits. Data, based on the discriminatory intervals to which good equipment can be read and the end point detected are summarized in Section D1.6.2.

D1.6 Limit of Detection	
D1.6.1 Colorimetric (a)	0.15 mg/l with 15 degrees of freedom.
D1.6.2 Volumetric	(i) For the method as given with 20 ml of 0.1M AgNO$_3$, precision improves to below 10% if the thiocyanate concentration exceeds about 50 g/lSCN$^-$. A 50 ml burette will determine down to about 2 mg/lSCN$^-$ with precision much better than 10%. (ii) If 5 ml of 0.01M AgNO$_3$ is used, precision improves to below 10% above 2 g/lSCN$^-$ and the limit of detection using a 50 ml burette is about 0.05 g/lSCN$^-$. (iii) Use of more dilute or less silver nitrate or even bigger sample burettes lowers the limit of detection.
D1.7 Bias	Not known.
D1.8 Interference	Substances reducing the iron III indicator interfere if present in sufficient amount, but see Section 3.
D1.8.1 Colorimetric	Mercuric salts and oxalates suppress colour formation, silver if present lowers the possible soluble thiocyanate concentration below the limit of detection. Ferro-cyanide, ferricyanide, chromium, alkalinity and sulphide may interfere but can be removed (see Section 3).
D1.8.2 Volumetric	Chloride, bromide, iodide and other substances precipitating or reducing silver ions from acid solution interfere quantitatively. Sulphide can be removed. Thiosulphate and similar substances forming strong soluble complexes with silver may also interfere if they dissolve silver thiocyanate in acid solution.
D1.9 Time required for Analysis	
D1.9.1 Colorimetric	With solutions already made up, standardization and 10 samples will take about 3 hours, longer if filtration or sulphide removal is required.
D1.9.2 Volumetric	With solutions already made up, 10 samples will take about 1 hour.

Overall reagent preparation time about 2 hours.

(a) This data supplied by Northumbrian Water Authority, Howden Laboratory.
(b) The concentration given was determined by this method.
(c) This is the preceding sample spiked with 5 mg/l SCN.

D2 Principle

Volumetric

Pure silver nitrate is a primary analytical standard substance which is used to standardize a solution of potassium thiocyanate by titration. Highly insoluble silver thiocyanate is precipitated; only when this is complete is the first excess of thiocyanate sufficient to form permanently a detectable amount of an iron III thiocyanate complex. Nitrobenzene is added to coagulate the precipitate.

Colorimetry

Standard thiocyanate solutions are prepared by dilution of this standardized solution. These standards and samples are reacted with iron III nitrate in very dilute nitric acid solution to form one of the several iron III thiocyanate complexes. Light absorption is measured at 515 nm (see Section E6.1 of the automated method which follows) and the sample concentrations determined by comparison with the subsidiary standard solutions.

A few samples may be determined directly by titrimetry, but most samples encountered will contain too many interferences for direct titration (See Section D3.1).

D3 Interferences

D3.1 Volumetric

Chloride, Bromide and Iodide react quantitatively with silver as if thiocyanate and must be absent or predetermined and corrected for. Sulphide is similar but can be removed with lead carbonate.

Fluoride may interfere by reacting with the indicator. If this occurs add extra iron III indicator. Substances which reduce the iron III indicator will likewise cause problems if present in sufficient amounts and are not removable (see above). See Step D8.2 (note (b) for a simple method of detecting and controlling such interferences, but, if the amount of indicator becomes too high see 'Other Techniques', for example, Section G3.

Any other substance precipitating or reducing silver from dilute acid solution will likewise interfere as will any substance forming a soluble complex more stable than silver thiocyanate. This latter may be ascertained by seeing whether the substance will redissolve a small amount of silver thiocyanate.

D3.2 Colorimetry

D3.2.1 The following substances or ions do not interfere at up to at least the concentrations stated for any concentration of thiocyanate within the range of this method:

	mg/l	
Sulphate	1,000	
Orthophosphate	300	
Fluoride	50	(see also the automated method Section E3)
Phenol	300	
o Cresol	1,000	
m Cresol	1,000	
p Cresol	200	
Catechol	1	
Resorcinol	50	
Quinol	50	
1 Naphthol	1	
2 Naphthol	50	

D3.2.2 The following interference are known:

Mercuric salts and oxalates suppress the reaction, mercury by complexing thiocyanate, oxalate by reacting with iron. Sulphides, which obscure the absorbance measurement by the formation of a colloidal precipitate on acidification, can be removed by prior precipitation with lead carbonate (see Section D10).

Reducing agents may also interfere. If not readily removable consider another method, such as Ion Chromatography. Sulphites and Thiosulphates may cause such problems, but may be removable by warming after slight acidification. Thiosulphate will give some turbidity which may not be tolerable.

Ferricyanides and ferrocyanides interfere by reacting with iron to form highly coloured complexes. The limiting tolerances are 15 and 4 mg/l respectively. For a removal procedure see the Automated Colorimetric method Section E9.1. Resume this manual procedure at the addition of iron III nitrate in Step D9.2. If cyanide is present and reacts to form ferricyanide, it is suggested that this be removed in the same way, the sample solution volume measured and the analysis restarted at the addition of iron III nitrate, correction being made for volume change.

Some coloured solutions absorb at 515 nm. A colour correction procedure is given.

D4 Hazards

Mercury, Lead and Cadmium which are used in some of the interference removal procedures are toxic and notifiable wastes which should be recovered either for approved disposal or recycling.

Nitrobenzene is toxic, slightly volatile, not very soluble and heavier than water. It should not be disposed of to drain.

D5 Reagents

(Reagents not required for the Volumetric Method are indicated by an asterisk.)

D5.1 Water

Distilled Water is preferred

D5.2 Silver Nitrate 0.1M

Dissolve 8.495 ± 0.001 g of silver nitrate in about 100 ml of water, transfer quantitatively to a 500 ml calibrated flask and make up to the mark with water. Stored in the dark in a stoppered brown glass bottle this solution keeps for at least one year.

D5.2.1 For the direct titration of samples other strengths of silver nitrate may be more suitable.

D5.3 Nitric Acid c25% w/v.

Add 40 ± 1 ml nitric acid $d_{20}1.42$ to 100 ± 2 ml of water and mix well. Stored in a glass stoppered bottle this solution keeps indefinitely.

D5.4 Iron III nitrate solution

Dissolve 100 ± 1 g of iron III nitrate nonahydrate in a mixture of about 200 ml of water and 25 ± 1 ml of nitric acid $d_{20}1.42$, transfer quantitatively to a 500 ml calibrated flask and make up to the mark with water. Discard when sediment forms or the glass becomes stained.

(Iron stained glassware may be cleaned by rinsing with concentrated hydrochloric acid and then copiously rinsing with water.)

D5.5 Nitrobenzene, or Amyl alcohol

See Section D4.

D5.6* Potassium thiocyanate standard solutions

D5.6.1* 5000 mg/l SCN^-

Dissolve 4.50 ± 0.05 g of potassium thiocyanate in about 100 ml of water, transfer quantitatively to a 500 ml calibrated flask and make up to the mark with water. Stored in a stoppered glass bottle the solution is stable for at least 6 months. Standardize this solution by the Volumetric Method (Section D8).

D5.6.2* 100 mg/l SCN^-

Calculate to two decimal places the volume of solution D5.6.1 required to give 100 mg of thiocyanate ion (about 20 ml). Measure out this volume to the nearest 0.05 ml into a 1 litre calibrated flask and make up to the mark with water. Prepare fresh solution each month, or sooner if it becomes discoloured or turbid.

D5.7* Mercuric Chloride c6 g/l

Weigh out 6.0 ± 0.5 g of mercuric chloride, dissolve in about 90 ml of water, by warming, cool and make up to 100 ± 1 ml. Stored in a stoppered glass bottle this solution should keep indefinitely.

D5.8 Lead Carbonate powder

D6 Apparatus

D6.1 Normal laboratory glassware

See Section D5.4 above for removal of iron stains. Grade B is usually satisfactory.

D6.2 A spectrophotometer

with 1 cm cells, measuring absorbance at 515 nm.

D7 Sample Storage and Preservation

Samples should be kept in stoppered glass bottles preferably at 2–4°C. If they contain dissolved volatile inflammable substances a flameproof refrigerator must be used.

D8 Volumetric Analytical Procedure

Step	Procedure	Notes
D8.1	Pipette 20.0 ± 0.05 ml of silver nitrate solution (D5.2) (note a) into a 250 ml conical flask. Add 5.0 ± 0.5 ml of nitric acid (D5.3) and 0.5 ± 0.1 ml of iron III nitrate (D5.4), followed by 1.0 ± 0.2 ml of nitrobenzene or amyl alcohol and shake well (note b).	(a) This strength of silver nitrate is used for the standardization of solution D5.6.1. Other strengths may be more suitable if a direct titrimetric analysis is being made of a sample. See Note on the Reading of Burettes and Pipettes at the beginning of this booklet. (b) High fluoride content can complex iron and prevent a colour being given with thiocyanate. Substances which reduce iron III have a similar effect. If this occurs the simplest procedure is to continue to add iron until a typical colour is obtained, if necessary repeat the analysis with a fresh sample with this amount of iron added in one go at this stage. A simple control, when such interference is suspected is to carry out a parallel titration using water instead of silver nitrate in step D8.1 and to note whether the brown end point colour which should form almost immediately subsequently fades, showing that more indicator is needed for both sample and control.
D8.2	Titrate with potassium thiocyanate solution D5.6.1 to standardize it, or with sample if a direct analysis is being made. Titrate with shaking until the first permanent brown colour appears. Shake well to verify the permanency of the colour. Note the volume of thiocyanate or sample required V_1 ml.	

Step	Procedure	Notes
	Indicator Blank (For accurate analyses only)	
D8.3	In addition to repeating steps D8.1 and D8.2 also carry duplicate samples of water through the procedure to obtain indicator blank values V_2 ml (note c).	(c) If V_2 is only one drop, either ignore V_2 or for high precision, use a better quality burette and match blank titration colour to sample titration colour. Accurate burette reading is needed. (See note at the front of this booklet.)
	Calculation	
D8.4	Thiocyanate concentration of solution D5.6.1 is: $\frac{116200}{V}$ mg/l where V is either the mean value of V_1 above or if step D8.3 is used then $V_1 - V_2$, using mean values for V_1 and V_2.	

D9 Manual Colorimetric Analytical Procedure

If Sulphide removal is necessary first carry out Section D10.

Step	Procedure	Notes
	Calibration Samples	
D9.1	Measure out into six 100 ml calibrated flasks 0.00, 5.00, 10.00, 15.00, 20.00 and 25.00 ml, (all ± 0.05 ml) of 100 mg/l SCN^- solution D5.6.2.	
D9.2	To each flask add water to bring the volume to 80 ± 5 ml, followed by 2.00 ± 0.05 ml of dilute nitric acid, and 10.00 ± 0.05 ml of iron III nitrate solution (D5.4) and make up to 100 ml with water. Mix well. Keep flasks in the shade.	
D9.3	Transfer with an accuracy of ± 0.05 ml an aliquot of sample expected to contain not more than 3 mg of thiocyanate, but not greater than 80 ml in volume, to a 100 ml calibrated flask (note a). Let the volume of sample taken be V_m). Add 2.00 ± 0.05 ml of dilute nitric acid and 10.00 ± 0.05 ml of iron III nitrate solution and make up to 100 ml with water. Mix well.	(a) In cases of doubt a ranging procedure with a series of aliquots of different size may be necessary.
	Blanks	
D9.4	The nature of the blank is dependent on the need for colour correction or not. If no colour correction is needed run a blank consisting of 80 ml of water through the procedure from step D9.3 onwards.	
	D9.4.1 If colour correction is necessary prepare an additional sample as in D9.3, but prior to adding any reagents add 1.0 ± 0.1 ml of mercury chloride solution. Then continue as in step D9.3 and so on. This blank should only be used for calculating the concentration of the sample from which it was prepared.	

Step	Procedure	Notes
	Measurement	
D9.5	Measure the absorbance at 515 nm, of both standards and samples, and blanks using a spectrophotometer and 10 mm cells (note b).	
	Calculation	(b) Other size cells may be used if more convenient, but cells must be matched.
D9.6	The standards prepared in step D9.1 correspond to 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mg SCN^-. Plot a graph of absorbance versus mg SCN^-.	
D9.7	Determine the thiocyanate content of the samples and also that corresponding to the appropriate blank from this graph. Let these be W_s and W_b respectively. Then the thiocyanate concentration is: $\frac{1000\,W_s - W_b}{V}$ mg/l	

D10 Sulphide Removal Procedure

Take more than sufficient sample for all the aliquots required into a beaker and slowly add with stirring powered lead carbonate until the latest addition does not change colour. Allow the sample to settle, filter through a qualitative grade filter paper, rejecting the first 10 ml. Use the filtrate as sample.

D11 Analytical Quality Control

See Part H.

D12 Silver, Mercury and Cadmium Recovery

Silver thiocyanate is formed in the volumetric method, mercury and cadmium compounds including thiocyanates and ferrocyanides may be formed during interference removal. These are valuable materials and notifiable wastes. For decomposition of thiocyanates, ferricyanides and ferrocyanides see Ref 9 Section C12. For recovery of Mercury and Silver see Ref 9 Section H, for cadmium recovery see Ref 16 Section D12.

E Determination of Thiocyanate, Automatic Colorimetric Method

E1 Performance Characteristics of the Method

E1.1	Substance Determined	Thiocyanate ions
E1.2	Types of Sample	Raw, potable and waste waters
E1.3	Basis of Method	Continuous flow colorimetry using the reaction described in Section E2.
E1.4	Range of Application	Up to 2 mg/l
E1.5	Calibration Curve	Linear

E1.6 Standard Deviation: (within-batch)

Sample Type	Thiocyanate Concentration (mg/l)	Total Std. Dev. (mg/l)	Degrees of Freedom
Standard Solutions (a)(b)	0.04	0.003	7
	0.10	0.0035	11
	0.40	0.0045	11
	0.50	0.002	11
	1.0	0.006	11
	1.5	0.007	11
	2.0	0.012	11
Waste-water (b)(d)	0.81	0.0065	11
Standard Solutions (a)(c)	0.2	0.0058	15
	1.8	0.020	15
Industrial Effluent (c)(d)	0.74	0.20	15
Spiked Effluent (c)(d)(e)	1.72	0.20	15

E1.7	Limit of Detection (b)	0.014 mg/l (with 7 degrees of freedom).
E1.8	Sensitivity	A 2.0 mg/l standard gives an absorbance of approximately 0.84 units.
E1.9	Bias	No bias > 5% except when interferences occur (see Section E3).
E1.10	Interferences	Silver, cyanoferrates II and III, chromium VI, hydroxide 0.01M and iodide (see Section E3).
E1.11	Time required for Analysis	The automated system described is operated at 30 determinations per hour. Set up and wash through times are 30 and 15 minutes (total) respectively.

(a) Distilled water standards spiked with the stated quantity of thiocyanate.
(b) Data obtained by Stablex International Holdings Ltd.
(c) Data obtained by Northumbrian Water Authority, Howden Laboratory.
(d) Thiocyanate concentration as reported by this method.
(e) Preceding sample spiked with 1 mg/SCN$^-$.

E2 Principle

Thiocyanate ions in the sample are allowed to react with an acidic ethanolic solution of iron III nitrate. A strongly coloured reddish-brown solution of the iron III thiocyanate complex is produced and is measured spectrophotometrically. It is thought that the species $(Fe(CNS))^{+-}$ is formed at the low thiocyanate concentrations used in this method (see Ref 17).

The presence of ethanol in the iron III nitrate reagent eliminates interference due to chloride which would otherwise occur (see Table 3 for data using ethanol) and reduces fading of the complex. However, it is advisable to keep the instrumentation out of sunlight during analysis.

E3 Interferences

The effect of some other substances on the determination of thiocyanate is given in Table 3.

Table 3 Interference Test Data for the Automated Thiocyanate Method

Substance Added	Concentration of other Substance mg/l	Effect in mg SCN^-/l of other substance at a Thiocyanate concentration of		
		0.000 mg/l	0.400 mg/l	2.00 mg/l
Aluminium Nitrate	10 (Al)	0.000	−0.010	0.04
Ammonium Chloride	500 (N)	0.000	0.000	−0.03
Ammonium Molybdate	10 (Mo)	0.000	+0.005	+0.03
Arsenic Trichloride	10 (As)	0.000	−0.010	+0.04
Barium Nitrate	10 (Ba)	0.000	−0.020	+0.01
Beryllium Sulphate	10 (Be)	0.000	+0.005	+0.03
Bismuth Nitrate	10 (Bi)	0.000	−0.010	−0.02
Cadmium Chloride	10(Cd)	0.000	0.000	0.00
Calcium Chloride	500 (Ca)	0.000	0.000	−0.04
Cobalt Nitrate	10 (Co)	0.000	−0.007	+0.03
Copper Nitrate	10 (Cu)	0.000	−0.030	−0.02
Iron II Chloride	100 (Fe)	−0.030	−0.020	−0.05
Iron III Nitrate	100 (Fe)	0.000	−0.010	−0.06
Lead Nitrate	10 (Pb)	0.000	0.000	−0.04
Magnesium Chloride	500 (Mg)	+0.020	−0.010	−0.01
Manganese Nitrate	10 (Mn)	0.000	0.000	0.00
Manoxol O.T.	10	0.000	0.000	−0.04
Mercury II Chloride	10 (Hg)	0.000	0.000	−0.01
Nickel Nitrate	10 (Ni)	0.000	0.000	0.00
Orthoboric Acid	50 (B)	0.000	+0.007	+0.01
Phenol	50 (C_6H_5OH)	0.000	0.000	0.000
Potassium Antimonyl Tartrate	10 (Sb)	+0.010	+0.02	
Potassium Cyanate	500 (CNO^-)	+0.060	0.000	−0.04
Potassium Cyanide	10 (CN^-)	0.000	0.000	0.00
Potassium Dichromate	10 (Cr)	+0.15	+0.13	+0.16
Potassium Cyanoferrate III	10 (CN^-)	+1.250	+1.27	>+0.5
Potassium Cyanoferrate II	10 (CN^-)	+0.400	+0.405	>+0.5
Potassium Nitrate	1,000 (N)	0.000	−0.010	−0.05
Potassium Sulphate	500 (SO_4^{2-})	0.000	+0.010	+0.01
Selenous Acid	10 (Se)	0.000	0.000	+0.02
Silver Nitrate	10 (Ag)	+0.340	+0.330	+0.08
Sodium Bicarbonate	1,000 (HCO_3^-)	+0.070	0.000	+0.04
Sodium Chloride	10,000 (Cl^-)	+0.010	0.000	−0.01
Sodium Fluoride[†]	20 (F^-)	0.000	0.000	+0.03
Sodium Iodide	5 (I^-)	0.000	−0.170	−0.46
Sodium Nitrite	20 (N)	0.000	+0.020	−0.01
Sodium Nitroprusside	100	0.000	+0.008	+0.02
Sodium Orthophosphate	500 (PO_3^{4-})	0.000	+0.040	+0.04
Sodium Sulphide	10 (S^{2-})	0.000	−0.020	−0.02
Sodium Tungstate	10 (W)	0.000	0.007	+0.02

Table 3 *continued*

Strontium Chloride	20 (Sr)	0.000	0.000	−0.04
Tin Chloride	10 (Sn)	0.000	−0.004	0.00
Urea	20 (N)	0.000	0.000	+0.04
Ammonium Vanadate	10 (V)	0.000	0.000	0.00
Zinc Chloride	10 (Zn)	0.000	0.000	−0.01

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

0.000 ± 0.006 mg/l SCN^-
0.400 ± 0.009 mg/l SCN^-
2.00 ± 0.024 mg/l SCN^-

[†] See end of this section

Both potassium hexacyanoferrate II and potassium hexacyanoferrate III (potassium ferro and ferricyanide) interfere positively in the method. A strong blue colour is developed with potassium hexacyanoferrate II and a yellow-green colour with potassium hexacyanoferrate III.

When 50 ml portions containing 2.00 mg/l potassium thiocyanate and 100 mg/l of potassium hexacyanoferrate II and hexacyanoferrate III were separately treated with solid cadmium acetate as in Section E9.1, the following results were obtained. The blank and 2.0 mg/l standard solution were similarly treated with cadmium acetate.

Solution	Concentration Thiocyanate added mg/l	Concentration of other substance mg/l	Concentration Thiocyanate found mg/l
Blank	0.000	0.0	0.000
Standard Solution	2.00	0.0	2.02
Standard Solution	2.00	100*	2.05
Standard Solution	2.00	100**	2.00

* potassium hexacyanoferrate II
**potassium hexacyanoferrate III

If the presence of either of these substances is suspected in the sample, then the treatment procedures given in Section E9.1 should be applied.

Alkalinity at 0.01M and above causes positive interference in the method. Samples with high pH values (pH12) should have the pH value adjusted according to the method given in Section E9.1. Tests using a standard with 2.00 mg/l CNS^- showed complete removal of interference without loss of thiocyanate.

Hexavalent chromium interferes positively and should be removed by the method given in section E9.3. Tests using 2.00 mg/l CNS^- gave 1.97 mg/l CNS^- found. Tests on a blank without added ferric nitrate but with acid showed that much of this interference is due to absorption at 500 nm by the chromate ion.

Silver interferes positively and iodide interferes negatively in the method. Silver should be removed by the method given in Section E9.4 and iodide by the method given in Section E9.5. Test using 2.00 mg/l CNS^- gave 1.98 mg/l found. Some highly coloured waters may cause interference. A method of correction is given in Section E9.6.

Some non British waters and some industrial effluents contain so much fluoride that the colorimetric determination of iron by thiocyanate gives no absorption at all; however tests show that the iron to sample ratio used in the procedure below is sufficiently high for problems to be unlikely below 500 mg/l F^-. Such interference can be removed completely by addition of a beryllium salt to the ferric nitrate solution. A beryllium concentration in the final solution equal to that for fluoride in the same solution would be more than adequate. Scrupulous cleanliness and care is then essential due to the dangers from inhaled beryllium.

Should substances such as sulphite and thiosulphate be present in sufficient amounts to significantly reduce the iron III concentration, they may cause interference giving lower or nil results. This can be detected by running a sample spiked with a small amount of thiocyanate. If the effect is significant, consider another method, such as are given in Other Techniques, Section G3.

Coke oven effluents often contain substances which cause positive interference, the amount varying with the particular effluents. The dialysis procedure (Section E10), though less sensitive than that in Section E7, will often remove these interferences. The detection of such positive interferents in real samples is not easy but may sometimes be made by noting changes in the overall absorption spectrum of the sample. Cyanoferrates are one known interferent removed by dialysis.

E4 Hazards

E4.1 The precautions given in reference 18 should be observed.

E4.2 Nitric acid, hydrochloric acid and iron III nitrate are corrosive. Eye protection and gloves should be worn when handling them and any spillages washed away with copious amounts of cold water.

E4.3 Ethanol is a fairly volatile, flammable solvent and should be handled with care in a fume cupboard ensuring that no naked flames are in the vicinity.

E4.4 Sodium hydroxide and solutions of it are caustic, eye protection and gloves should be used when handling them. All reagents should be prepared in a well ventilated fume cupboard.

E5 Reagents

Analytical grade reagents should be used where possible. Volumetric (calibrated) glassware should meet the recognised criteria for accuracy.

E5.1 Water

Distilled or deionized water is normally suitable. The wash water should contain about 0.2 ml per litre of a suitable wetting agent. Anionic surfactants of the polyoxyethylene alcohol type are normally suitable.

Evaluate wetting agents for freedom from interference before use.

E5.2 Iron III Nitrate Reagent

To about 400 ml water in a 1 litre flask add 23 ± 0.5 ml concentrated ($d_{20}1.42$) nitric acid and 35 ± 0.5 ml concentrated ($d_{20}1.16$) hydrochloric acid. Add 169 ± 1 g iron III nitrate nonahydrate and dissolve. Add with cooling, 300 ± 5 ml absolute ethanol and make up to the mark with water. Store in an amber glass bottle. This reagent is stable for at least one week when stored at 2–4°C.

E5.3 Stock standard thiocyanate solution

1 ml contains 1 mg thiocyanate.

Dissolve 1.673 ± 0.0005 g potassium thiocyanate (dried at 105°C to constant weight) in about 800 ml water in a 1-litre volumetric flask. Make up to the mark with water. This solution is stable for at least one month. (If there is doubt as to the quality of the thiocyanate used, standardize as in the preceding method, section D8).

E5.4 Working standard thiocyanate solution

1 ml contains 0.01 mg thiocyanate.

Dilute 10 ml stock standard thiocyanate solution (E5.3) to 1 litre with water. Prepare fresh on the day of use.

E5.5 Calibration standard thiocyanate solutions

Prepare a series of thiocyanate solutions containing 0.1, 0.5, 1.0, 1.5 and 2.0 mg/l thiocyanate by pipetting 1, 5, 10, 15 and 20 ml working standard solution (E5.4) to 100 ml volumetric flasks. Make up to the mark with water and mix. Prepare fresh on the day of use.

E5.6 Nitric acid solution 50% V/V

To 500 ± 10 ml water in a 2-litre beaker add slowly with continuous stirring and external cooling 500 ± 10 ml nitric acid ($d_{20}1.42$).

E5.7 Sodium Hydroxide 1.0M

Dissolve 40 ± 1 g sodium hydroxide pellets in 1000 ± 20 ml water in a 2-litre beaker with continuous stirring and external cooling. When cool, store in a polyethylene bottle with a polyethylene screw top.

E5.8 Litmus paper

E5.9 Silver Nitrate 0.6% m/V

Dissolve 0.40 ± 0.01 g silver nitrate in about 200 ml water contained in a 250 ml volumetric flask. Make up to the mark with water and mix. When stored in an amber bottle, this reagent is stable indefinitely.

E6 Apparatus

The following apparatus, shown diagrammatically in figure 2, is required:

Sample presentation unit (Sampler)
Multi-Channel peristaltic pump with air inlet valve attachment
Analytical cartridge including pump-tubes and mixing coils
Colorimeter incorporating a 50 mm path length flow-cell (Detector Unit)
Single-pen recorder output or printer unit (Recording Unit).

E6.1 Wavelength setting

The wavelength for maximum absorption is 450–480 nm depending on the relative concentrations of thiocyanate and iron III. The absorption band extends to 630 nm. At 500 nm, the wavelength of the instrument used to evaluate the method, the intensity of absorption is approximately 76% of the maximum.

E7 Analytical Procedure

Step	Procedure	Notes
	Starting Operation	
E7.1	Connect the system as shown in the flow diagram (Fig 2). (Notes a and b).	(a) Follow the manufacturer's general operating instructions. (b) See reference 18.
E7.2	Place the reagent tube in the reagent bottle with the sample probe in the wash water container. Start pump (note c). Switch on recording and detector units. Allow at least 30 minutes for the equipment to warm up.	(c) With a newly constructed manifold, pump-test to ensure hydraulic continuity. Check that bubbles do not accumulate in the flow-cell and eliminate any problems before proceeding to the next step.

Step	Procedure	Notes
	Initial Sensitivity Setting	
E7.3	When a satisfactory baseline has been obtained with water for 15 minutes, adjust the baseline to about 5 percent of full scale (note d) with the zero control. Aspirate a 2 mg/l standard for about 3 minutes. Return the sample proble to the rest position (note f). After 12 minutes have elapsed after the initial standard aspiration, a positive response appears on the chart. Adjust the response to give a reading of about 90 percent full scale (note e).	(d) An elevated baseline allows for any negative drift that may occur. (e) A setting 10 percent less than full scale allows for any increase in sensitivity that may occur. (f) Remove traces of standard solution from probe before replacing it.
	Analysis of Samples	
E7.4	Arrange the standards, blanks and samples on the turntable and start the sampler with the sampling rate at 30 samples per hour (notes g and h).	(g) The samples and standards can be loaded on the turntable during the initial setting up period (steps 7.2 and 7.3). (h) Alternative loading arrangements are given in reference 18.

Suggested Position on turntable	Solution	
1 - 5	Calibration standards in ascending order of concentration.	
6	Blank (note j)	(j) Use the same water as used to prepare the calibration standards.
7	Calibration standard (note k)	(k) Use the standard which occupies position No 4 to check the calibration.
8 - 17	Samples (note l)	(l) A quality control standard should be included in one batch as a check on the system. See references 10 and 11. The standard solution used should be different from that used for the calibration standards but should be stored under identical conditions.
18	Blank	
19	Calibration standard	
20 - 29	Samples	
30	Blank	
31	Calibration standard	

Step	Procedure	Notes
	Repeat the sequence 8–31 until all the samples have been analysed (note m). If it is thought necessary, repeat the calibration standards 1–5 at the conclusion of the run of samples.	(m) If cross-contamination is seen to occur (incomplete peak separation) either separate the samples by blanks and reanalyse them or reanalyse in reverse order.
E7.5	When the last sample or standard has been analysed and the final baseline obtained and all responses have been registered on the recording unit, switch off this unit.	
	Shut-Down Procedure	
E7.6	Remove reagent lines, wipe dry with a tissue and transfer to a beaker containing water and allow to pump through for 15 minutes (note n).	(n) Pumping water through the system removes reagent solution from the tubing.

E7.7 Switch off pump and detector units. Check all pump tubes for wear, replace any worn tubes with new flow-rated tubes.

Calculation of Results

E7.8 Plot a calibration curve of measurement unit responses (y axis) against concentration (x axis) of the calibration standard solutions (note o).

(o) Providing that the responses due to the blanks and calibration standards are acceptably close to their respective initial blank-corrected values. If not, refer to reference 18 for suggested alternative procedures to obtain calibration curves.

E7.9 Using the calibration curve convert the measurement unit responses due to the samples into concentration of thiocyanate in the samples (notes p and q).

(p) The measurement unit responses of the samples must first be corrected for any baseline and sensitivity changes.

(q) Allow for dilution produced in any sample pretreatment procedures (section E9).

E8 Extending the Range of the Method Upwards

Samples with a thiocyanate concentration greater than 2 mg/l should be diluted accordingly and re-analysed. The result, corrected for blank and sensitivity should be multiplied by the dilution factor to obtain the thiocyanate concentration in the sample.

E9 Removal of Interferences

See also Section E10.

E9.1 Hexacyanoferrate II and hexacyanoferrate III

In a 100 ml beaker, place 25 ml of sample and a magnetic stirrer bar. Add about 30 mg powdered solid cadmium acetate ($Cd(CH_3COO)_2.2H_2O$) to the sample, two drops 50% V/V nitric acid (E5.6) and stir on a magnetic stirrer for about 30 minutes. Filter on a fine porosity paper and analyse the sample as from step E7.4.

E9.2 Caustic Alkalinity

For samples with an alkalinity of greater than 0.01M (pH 12), take 25 ml sample contained in a 100 ml beaker, acidify to litmus with dropwise addition of 50% V/V nitric acid (solution E5.6). Check total volume of acid added. Analyse sample as from step E7.4. Apply a dilution correction factor to the result obtained.

E9.3 Chromate and Dichromate

To a 25 ml sample in a 50 ml beaker add about 50 mg solid barium nitrate and add sodium hydroxide (E5.7) dropwise until alkaline to litmus. Stir on a magnetic stirrer for 5 minutes, filter on a fine porosity paper and acidify to litmus by adding nitric acid (E5.6). Note total volume of alkali and acid added. Analyse sample as from step E7.4 and apply a dilution correction factor for the volume change to the result obtained. Alternatively, treat as a coloured solution, see Section E9.6.

E9.4 Silver

Silver thiocyanate is insoluble but may react under the conditions of the test. Remove any silver thiocyanate precipitate by filtration of the sample prior to analysis. If silver is present in the sample and thiocyanate is absent, a positive result may still be given. Silver is removed by adding about 10–20 mg solid sodium chloride to 25 ml sample in a 50 ml beaker. Stir for 5 minutes, filter on a fine porosity paper and analyse the sample as from step E7.4.

E9.5 Iodide

To 25 ml sample in a 50 ml beaker, add about 0.2 ml of silver nitrate solution (5.9) and stir for 5 minutes. Add about 10–20 mg solid sodium chloride and stir for 5 minutes. Filter on a fine porosity paper and analyse the sample as from step E7.4. Apply a dilution correction factor to the result obtained.

E9.6 Colour

If the sample absorbs strongly at 500 nm, carry out an additional analysis with only wash water passing through the ferric nitrate line. Measure the peak height obtained and subtract this from that obtained using ferric nitrate, prior to calculating the thiocyanate. In the rare event that the sample contains organic matter complexing iron to give complexes absorbing strongly at the analytical wavelength, either use another method such as HPLC or Polarography (G3 or G5); or repeat the analysis with the addition of 1 ml of saturated mercuric chloride solution (see the preceding manual colorimetric method, reagent E5.7) to 100 ml of sample and mix well before loading. As mercury inhibits formation of ferric thiocyanate complexes the equipment will need a thorough cleaning afterwards.

E9.7 Fluoride

See Section E3 second from last paragraph for a procedure.

E10 A Dialysis Procedure for Coke Oven Effluents high in Thiocyanate

E10.1 Typical Performance Characteristics

E10.1.1	Calibration linearity	0 to 50 mgl^{-1}		
E10.1.2	Criterion of detection	0.2 mgl^{-1}		
E10.1.3	Standard deviation	Concentration (mgl^{-1})		σ_{wb}(mgl^{-1})
		0.5		0.074
		5.0		0.105
		45.0		0.211
E10.1.4	Speed of analysis	Sample time 90 sec. Wash time 60 sec. 24 cycles/hour		
E10.1.5	Interferences	Substantially less positive interference than that reported in Section E3, but fluorine causes minor problems		
	Interference	Fluoride Conc ng.l^{-1} as NaF	Effect on Blank in ppm CNS^{-}	Effect on 25 ppm CNS^{-} in ppm CNS^{-}
		100	+0.2	−0.2

E10.2 Reagents

E10.2.1 Ammonium perchlorate solution

Dilute 100 ± 1 ml of Spectroscopic grade ammonium perchlorate solution (10% w/v) to 1000 ml in a graduated flask with distilled water. Add 0.5 ml of Triton X100 or equivalent detergent.

E10.2.2 Dialyser recipient

To approximately 500ml of distilled water, add 95 ± 1 ml of conc. nitric acid. Dilute to 1000 ml in a graduated flask with distilled water. Add 0.5 ml of Triton X100 or equivalent detergent.

E10.2.3 Ferric nitrate solution

Dissolve 10.0 ± 0.1 g of ferric nitrate ($Fe(NO_3)_3.9H_2O$) in about 500 ml of distilled water. Add 95 ± 1 ml of conc. nitric acid. Dilute to 1000 ml in a graduated flask with distilled water.

E10.2.4 Potassium thiocyanate solution (1000 $mg.l^{-1}$ CNS^-)

Dissolve 1.800 ± 0.001 g of potassium thiocyanate in distilled water and dilute to 1000 ml in a graduated flask.

E10.3 Apparatus

Continuous flow analysis equipment, as shown in figure 3. Principally: sampler, pump capable of pumping 10 tubes, manifold, colorimeter with 480nm filters and chart recorder.

E10.4 Calibration Procedure

E10.4.1 Into a series of 100 ml graduated flasks add the volumes of solution shown in the following table:

Volume of thiocyanate solution E10.2.4 (ml)	Concentration $mgl^{-1}CNS^-$
1.0	10
2.0	20
3.0	30
4.0	40
5.0	50

Dilute to volume with distilled water

E10.4.2 Insert these standards in ascending order at the commencement of analyses.

E10.5 Procedure

E10.5.1 Place reagent lines in appropriate solutions and switch on pump. Allow 15 minutes pumping before making any adjustments.

E10.5.2 Adjust colorimeter and recorder in accordance with manufacturers instructions.

E10.5.3 Load sample tray. The actual order may be determined by the use of data processing facilities and the instructions for these should be followed.

E10.5.4 Complete analysis, and then shut down after flushing each line with water.

E10.6 Calculation

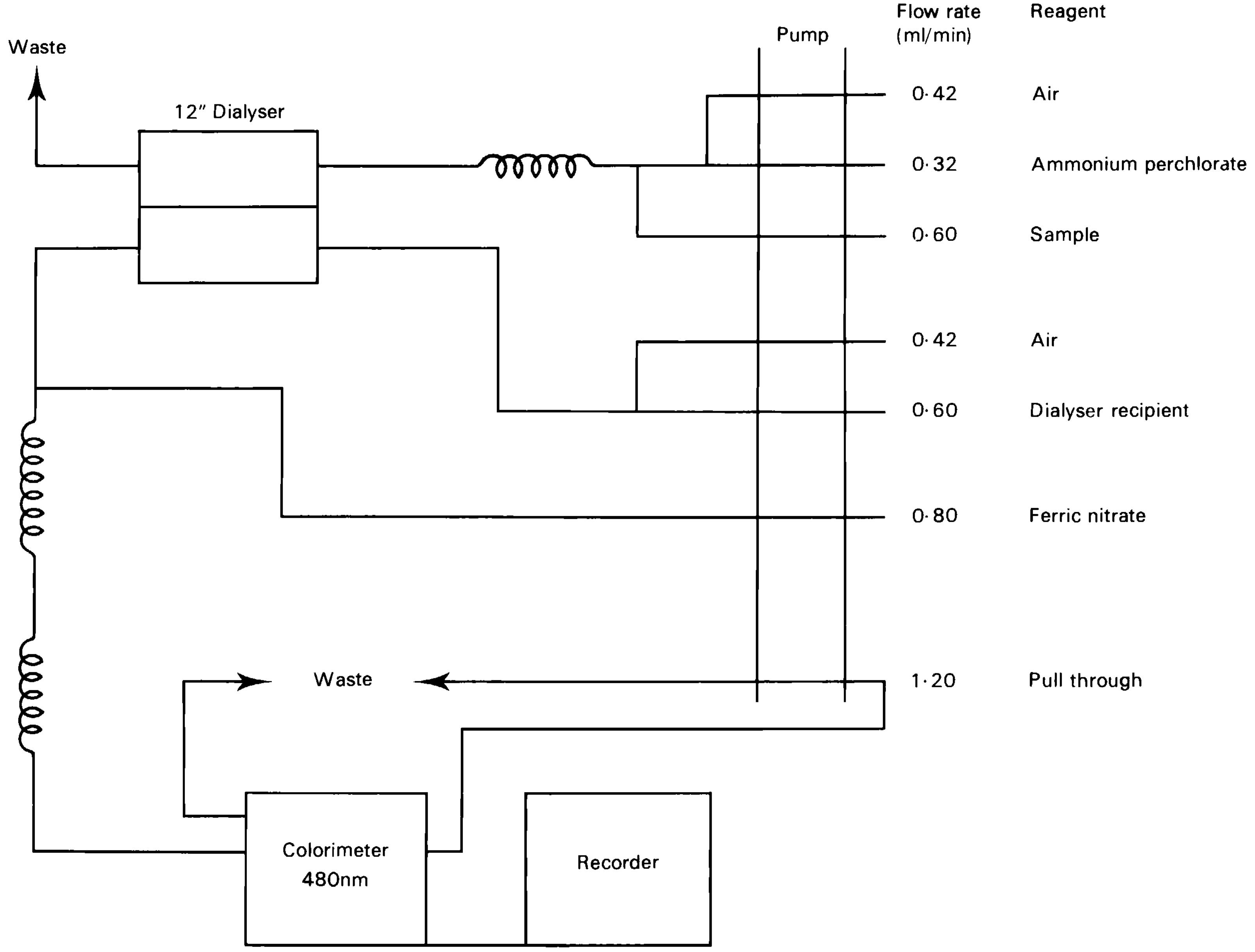
E10.6.1 Plot a calibration curve of scale divisions (y axis) against concentration (x axis) from the standard solutions.

E10.6.2 Calculate the concentration of thiocyanate (as CNS^-), in mgl^{-1} for the samples, from the calibration curve.

E11 Checking the Accuracy of Analytic Results

As there are many factors which can adversely affect the performance of the method, it is advisable to carry out experimental tests to check the sources of inaccuracy. Periodically, a series of replicate standards and samples should be analysed to obtain data on mean and standard deviations. In addition an analytical quality control standard should be analysed in duplicate at least once a day and the responses entered on an appropriate control chart. The control standard used in this method corresponding to 0.9C is 1.8 mg/l where C is the concentration of the highest working standard. See also Part H.

Figure 3 Analytical manifold for the determination of thiocyanate using a dialyser



F Determination of the Total Sulphur Content

Performance Characteristics of the Methods in this Section

Method	Suitable for	Typical Sulphur Recovery (as per cent of expected sulphate)		No of Samples per Day	Remarks
F4 Alkaline Bromine	Inorganic Sulphur and free element	$S_2O_8^{=}$	100–103%	10	Very poor recoveries with organic compounds 0–6%. Easy to determine when the reaction is completed. The equivalent AOAC method gave recoveries ranging from 0–86% dependent on compound.
		SCN^-	99–102%		
		$S_2O_6^{=}$	74–103%		
		$S_4O_6^{=}$	64–104%		
		$S_2O_3^{=}$	96–101%		
		$SO_4^{=}$	99–100%		
		$SO_3^{=}$	99–100%		
		S (free)	100–106%		
F5 Hydrogen Peroxide	Inorganic Salts (not free sulphur)	$S_2O_8^{=}$	102–103%	6	Poor recoveries with organic compounds 0–20%. Difficult to determine when the reaction is completed.
		SCN^-	101–102%		
		$S_2O_6^{=}$	92–98%		
		$S_4O_6^{=}$	92–98%		
		$S_2O_3^{=}$	99–100%		
		$SO_4^{=}$	99–100%		
		$SO_3^{=}$	99–100%		
F6 Sodium Peroxide Fusion		$S_2O_8^{=}$	100–101%	4	Not tested on organic compound.
		$S_2O_6^{=}$	100–101%		
		$S_4O_6^{=}$	100–102%		
		$SO_4^{=}$	100%		
		S (free)	100–102%		
		S_2 (Pyrite)	95–97%		
F7 Oxygen Flask		Ethyl methane sulphonate	97%		Not tested on Inorganic compounds. + good recover in many years routine use (BDH data) Blanks on the capsules or filter paper should be low. Typical blank values reported are 260 and 80 ppmS respectively on a 50 ul sample.
		Thiophene	91%		
		Thiooctic acid	+		
		Thiobenzamide	+		
		Thioacetic acid	+		
		Thionine	+		
		Biotin	+		

With the above methods, the range is dependent on the Sulphate method used for the final step.

F8 Oxygen Furnace	Most Compounds	Manufacturers data suggests a limit of detection of about 3 ppb.S.
F9 Emission and Fluorescence		The range is dependent on sample type Relative Standard Deviations for methods F9.1 and F9.3 should be better than 10%
F9.1 X-ray fluorescence	All Compounds	The limit of detection will be at lowest 20 ppmS. Interference and matrix wave length shifts are known. A rapid method.
F9.2 UV DCArc	All solids and substances convertible to solids	Methods F9.1 and F9.3 are usually preferred.
F9.3 ICPS Emission	All soluble samples	For liquid samples the limit of detection is about 1 mg/l, lower concentrations may be detected if sufficient sample is available, using integrating instruments, and special sampling techniques.
F9.4 Flame Band Emission	All soluble samples	Rarely used, precision may be poor.

F1 Objective

To determine the Total Sulphur content of either the sample or a fraction of the sample (soluble, sediment, suspended matter or oil), often in order to determine whether all the sulphur compounds present have already been determined by specific methods or whether a significant amount of sulphur is present in yet other forms.

F2 Principle

The sample is oxidized to sulphate which is then determined by the method given in Sulphate in Waters, Effluents and Solids 1979 (Ref 1) most suitable for the concentration of sulphate formed.

For mass balance purposes the concentrations of sulphur compounds already known are converted to concentration of sulphur present and the total compared with the total sulphur concentration found by this method.

If separation procedures are carried out on different portions of the sample, care is necessary in planning the analytical strategy to avoid either counting the same compound twice or missing a group of compounds entirely. No detailed advice can be given as the analytical strategy must be tailored to suit the sample. The following section discusses the various possible methods for determining Total Sulphur Content, and their limitations.

F3 Preliminary Discussion

Conversion of a sulphur compound to sulphate may involve not only the oxidation of the sulphur atom itself to the six positive valence state but also the breaking of sulphur-carbon, sulphur-sulphur, sulphur-hydrogen or other similar covalent bonds. Because some compounds contain chains or rings, the complete destruction of the molecule may be necessary. In other circumstances, such oxidations are often carried out in sulphuric acid solution, but in this case this is not possible as sulphate is the final determinand. There are added complications due to the volatility of some sulphur compounds, especially sulphur dioxide from acid solutions, the possibility of preparing toxic compounds such as thiocyanogen $(CNS)_2$ and some halo-organic sulphur derivatives, and finally the danger that some oxygen containing sulphur compounds, when undiluted may run away to explosion. When first ascertaining whether an oxidation method is suitable for a type of sample outside one's previous experience, always use very small quantities, wear protective clothing, eye and face protection, work over a safety tray, behind a safety shield and in a well ventilated place, and ensure that any possible fumes are adequately scrubbed. Use of a fume hood may not always be advisable if there is risk of channelling the hazard to others or of condensation in the ducting. Use of a suitable absorbent scrubber can also be an advantage in detecting whether volatile sulphur compounds are being given off. Sodium hypochlorite solution is usually an effective scrubbing agent. The nature of the sample and the method of oxidation being tested tend to dictate the precautions required for an initial investigation.

Oxidations are usually carried out with, if necessary, a gradually increasing oxidation potential. Details follow on the following techniques, which should suffice for most samples.

Alkaline Bromine Aqueous – for soluble samples.
Hydrogen Peroxide Aqueous – for soluble samples.
Sodium Peroxide fusion – for insoluble inorganic samples.
Oxygen Flask – for combustible samples.

There are, in addition, two non-oxidative techniques for total sulphur which can be used if the equipment is available. These are X-ray Fluorescence Spectrophotometry and Far Ultra-violet Emission Spectrophotometry, either carbon arc or I.C.P. sources can be used. Both XRFS and ICPS properly applied have proved more reliable than the other methods.

F4 Aqueous Alkaline Bromine Oxidation

F4.1 Hazards

Bromine is an irritant, corrosive poison, producing skin burns. Care is essential to avoid any contact. In the event of a spill on the person, wash copiously, removing all contaminated clothing at once and get informed medical assistance. Decontamination can be carried out using sodium carbonate or bicarbonate and water. It is recommended that laboratory first aid manuals be consulted prior to the use of bromine, so that personnel are familiar with procedures.

F4.2 Reagents

F4.2.1 Water

Good quality distilled water should be used throughout.

F4.2.2 Bromine

Sulphur free.

F4.2.2.1 Saturated Bromine Water (prepare the day before use). Half fill a glass stoppered bottle with water (the neck of the bottle should be about one third the bottle diameter in width. A glass bottle with a Polytetrafluoethylene stopper is equally acceptable. The stopper should be tight but easily removable. The bottle should be of a convenient size such that the technician can pour from it dropwise using only one hand). In a fume hood, over a safety tray, add sufficient bromine to the bottle to give a layer 1–2 cm deep under the water. Swirl gently at intervals to form a deep red solution with a faint orange fume above it.

Maintain this solution by addition of water or bromine as long as it is needed. Never add so much bromine that any would spill out of the neck if the bottle were lying on its side, but always have some free bromine present. Always swirl gently and allow the solution to become saturated before use after water addition.

Keep in a fume hood standing in a safety tray. Avoid smelling the vapour. Treat spillage as for bromine (section F4.1 above).

F4.2.3 Sodium Hydroxide solution 40% w/v

Weigh out 400 ± 10g of sodium hydroxide and add slowly to about 500 ml of water with stirring. Heat is evolved. Stir in water to a final volume of 1 litre ± 10 ml. Stored in a plastic bottle with tight plastic stopper this solution is usable indefinitely.

F4.2.4 Hydrochloric acid c5N

Stir 500 ± 10 ml hydrochloric acid d_{20} 1.16 into 500 ± 10 ml of water. Stored in a stoppered glass or plastic bottle this solution is usable indefinitely.

F4.3 Apparatus

F4.3.1 Glass Bottle

See 4.2.2.1 above for special requirements.

F4.3.2 Boiling water bath

F4.3.3 250 ml beaker or wide mouthed conical flask

F4.4 Procedure

Step	Procedure	Notes
F4.4.1	Measure out 50.0 ± 0.1 ml of sample into the beaker or wide mouthed conical flask (note a). Add slowly 20.9 ± 0.5 ml sodium hydroxide solution. Set the liquid in the flask gently swirling, place in the boiling water bath.	(a) If more convenient, use a larger known quantity, make up to a known volume with water in a suitable calibrated flask and use aliquots for the final sulphate analysis.

Step	Procedure	Notes
	Carefully add bromine water dropwise, replenishing as rapidly as it is used up (notes b and c).	(b) The absorption of bromine by the sample can usually be determined by observing the colour around the point of addition in the liquid. Keep the sample swirling slowly.
F4.4.2	After half an hour or when the sample has ceased absorbing bromine for at least 20 minutes, bring the sample to the boil and continue boiling until no more bromine vapour can be seen above the sample.	(c) Simmer but do not boil the sample.
F4.4.3	Carefully acidify the sample, adding the hydrochloric acid dropwise and continue boiling until all further bromine vapour has been boiled out.	
F4.4.4	If Sulphate is to be determined by direct Barium Precipitation Gravimetry (Method A of Ref 1), unless the sample is so high in sulphur that taking an aliquot is necessary, proceed directly to step A8.5 of that method. If the AAS–Barium method (Ref 1) is to be used, cool the sample transfer quantitatively to a convenient sized calibrated flask and make up to the mark with water. Start at step D10.1 of that method without further acid addition. If a 2–aminoperimidine method (Ref 1) is to be used, cool, then using a pH meter, adjust the pH to 4.1 ± 0.1. (With sodium hydroxide or hydrochloric acid, diluted further with water before use.) Quantitatively transfer a convenient volume to a calibrated flask and make up to the mark with water. Start at Step E8.1 of that method (Ref 1) and so on as directed in the appropriate versions of that method (see Ref 1, E8.8, E8.16 or E12).	
F4.4.5	Blanks. Carry a water blank through the entire procedure in order to correct for any sulphur in the reagents. Attempt to use the same amount of reagents, even though this means boiling off much bromine and the pH adjustment may require a different amount of acid. Alternatively, if the sulphur contents are known exactly for all reagents used, sum the sulphur contents of the amounts of reagents used and correct accordingly.	

F5 Hydrogen Peroxide Oxidation

This method is particularly suited to thiocyanate containing mixtures).

F5.1 Hazard

Strong solutions of Hydrogen Peroxide are skin irritants producing itchy white marks. Copious washing in cold water suffices.

F5.2 Reagents

F5.2.1 10, 20 or 30 "volume" hydrogen peroxide

Free from sulphur compounds.

F5.2.2 Sodium Hydroxide

See F4.2.3 above.

F5.2.3 Hydrochloric Acid

See F4.2.4 above.

F5.2.4 pH papers for the range 6–8pH units.

F5.2.5 Acid Iron III chloride solution

Dissolve about 1 g of Iron III chloride in 100 ± 10 ml of water and add 1.0 ± 0.1 ml of hydrochloric acid.

F5.3 Apparatus

F5.3.1 250 ml or 500 ml wide mouthed conical flasks.

F5.4 Procedure (see note d below)

Step	Procedure	Notes
F5.4.1	Accurately measure out a suitable quantity of sample into the wide mouthed conical flask (to ± 0.1 ml if possible).	
F5.4.2	Check that the pH is slightly greater (more alkaline) than 7 units (note a). Adjust if necessary using sodium hydroxide, or if exceedingly alkaline, with hydrochloric acid.	(a) Use a small rod to transfer the minimum of sample. Do not put paper into the sample, some indicators are sulphur compounds. Wash the rod before reuse.
F5.4.3	Simmer the sample on a hotplate, swirl and add hydrogen peroxide solution a few drops at a time. When at least 40 ml of hydrogen peroxide 30 vol (note c) have been added, check whether any thiocyanate or cyanides are present by removing one drop of sample to a drop of acid iron III chloride solution on a test plate. There should be no red, blue or green colour (note d).	(b) Periodically check that the solution is still slightly alkaline. If necessary add a few drops more sodium hydroxide solution as required. (c) If 10 vol Hydrogen Peroxide is used, about 150 ml of hydrogen peroxide will be required. (d) If other sulphur compounds are expected, run duplicate samples, stop one at this point, the other at double this amount. If the second sample has a higher sulphur content than the second, run two more samples using three and four times the hydrogen peroxide and so on.
F5.4.4	Continue the hydrogen peroxide additions until at least 10 ml have been added after the first negative test result with iron III chloride.	
F5.4.5	Boil to remove any unreacted hydrogen peroxide, cool, transfer quantitatively to a suitable calibrated flask and make up to the mark with water.	
F5.4.6	Proceed with the sulphate determination. See Ref 1, methods A, D or E.	

F6 Peroxide Fusion Method for Solid Samples

Aqueous samples may be processed by this method if they are either capable of evaporation to dryness without loss of volatile sulphur compounds in the steam or capable of absorption in a sulphur free inert material, without loss.

F6.1 Reagents

F6.1.1 Sodium Hydroxide

F6.1.2 Sodium peroxide

F6.1.3 Water

F6.1.4 Hydrochloric Acid $d_{20}1.16$

F6.2 Apparatus

F6.2.1 Nickel crucibles 50 ml, tongs and spatula

F6.2.2 Heating source for red heat

If a gas burner is used the gas must be sulphur free. Not all gas supplies can now achieve red heat.

F6.2.3 Standard Laboratory glassware

F6.3 Procedure

Wear safety goggles and if unsure of the sample reaction use a safety screen.

Step	Procedure	Notes
F6.3.1	Tare a crucible to ±0.001 g.	
F6.3.2	Accurately weigh out into the crucible about 1 to 2 g of sample (to ±0.001 g).	
F6.3.3	Cover the sample with about 5 g of solid sodium hydroxide. Heat gently until all the sodium hydroxide is molten. Ensure that the sample is completely immersed.	
F6.3.4	Slowly, not more than 0.1 g at a time, add 15 ± 1 g of sodium peroxide, always allowing for any reaction to subside before the next addition. Increase heat if necessary to maintain a clear melt.	
F6.3.5	Cool the crucible and sample.	
F6.3.6	When cold, put the crucible in a 250 ml beaker and cover with water. Warm to dissolve the melt. When the crucible is free of melt, remove it, rinsing it with water.	
F6.3.7	Cautiously add hydrochloric acid dropwise to the melt solution, with stirring until the solution is slightly acid. If necessary, add water and simmer to dissolve. If necessary filter through a fine sintered glass filter.	
F6.3.8	Use the solution for the determination of Sulphate Sulphur. If Ref 1, methods D or E are used, make up to a suitable volume in a calibrated flask with water.	

F7 Oxygen Flask Method

For organic combustible material. Inorganic materials tend to give very low results. Details are given in Emission Spectrophotometric Methods of Analysis etc 1980 (Ref 10), Section 1.1.1. Weigh a small gelatine or similar pill capsule, fill with sample to be analysed, close and reweigh. Wrap the capsule in the filter paper as directed in the reference and follow the instructions therein. Dissolve the burnt sample in 3% hydrogen peroxide, inserted into the flask prior to ignition. Run a blank using a second empty capsule and filter paper, both from the same batch as those used for the sample. Use the resultant solutions for sulphate determination and correct for the blank value. Alternatively, water and fluid samples may be absorbed into high purity cellulose, an equivalent amount of the same cellulose should be included in the blank. Viscous liquids may often be encapsulated without absorbant. As a safety precaution flasks should always be inside a reinforced wireglass screen when ignited.

F8 Other Combustion Analysers

These are of various types. In some the sample is injected as a liquid, in others it is loaded in a boat, but in all it is heated in a stream of oxygen, being burnt, usually to sulphur dioxide, rather than to sulphur trioxide. Commercial instruments come equipped with final quantification. In some instruments, the sample is carried by a stream of oxygen into a heated tube for combustion, finally passing over heated copper or cobalt oxides before absorption and measurement. Instruments of the Parr Bomb type may also be used, samples being absorbed in pure cellulose if necessary. Samples may also be entrained in a stream of hydrogen and burnt in air or oxygen using a Wickbold Burner, the exhaust from which passes over heated platinum or vanadium oxide catalyst and the resultant sulphur trioxide is absorbed in alkali for final determination as sulphate. Good blanks are essential for all these methods.

F9 Direct Spectrophotometric Methods for Total Sulphur

F9.1 X-ray fluorescence

Lower limit about 20ppmS.

By one means or another, including encapsulation, get the sample into a thin wafer or layer which will not volatilize appreciably in vacuum. Evaporation with added sodium hydroxide will suffice for most aqueous inorganic samples. Volatile organic substances are more difficult; but enclosure of liquids, including aqueous solutions in polycarbonate flat bottomed bottles is used with commercially available instruments. Then, carrying out the maker's instructions, analyse the sample for sulphur by X-ray fluorescence spectrophotometry. See Ref 19 chapter 4 and Ref 36 for outliine methods giving more detail.

F9.2 Ultra Violet DC Arc Emission Spectrophotometry

Sulphur does have a good emission line in the vacuum ultra violet region. The exact details of the analysis will be dependent on the nature of the sample and the equipment available. Solid samples and samples capable of transformation to a solid state can be analysed by DC arc emission using carbon electrodes. Metal samples are often analysed by point to plane DC spark emission, with a graphite counter electrode. For more details see Ref 19 Chapter 3.

The analytical wavelength for sulphur which is listed in Ref 19 table 5 is 180.73 nm. 182.03 nm, is alternative. The visible region line listed is rarely used because of its poor sensitivity.

F9.3 Inductively Coupled Plasma Emission Spectrophotometry

(see also Ref 35)
(A separate booklet of ICPS methods is in preparation.)

Determinand

Total Sulphur.

However, it is necessary either to separate the sample into volatile and non-volatile constituents by a distillation stage prior to separate analysis, or if oxidizable, to oxidize the volatile components (as in earlier sections) prior to making up to volume again.

Sample Type

Liquid or dissolvable samples.

Limit of Detection

80 µg/l to 500 µg/l (spectral line and instrument dependent); lower limits can be obtained by special techniques.

Interferences and Sources of Error

Volatile substances give an enhanced signal relative to non-volatile ones. Separate analytical working curves and separation are therefore needed if the volatile substances are not oxidized to non-volatile prior to analysis. If samples are preconcentrated, substances that precipitate sulphur compounds can cause losses. Volatile substances must be separated or oxidized prior to any concentration.

Calcium interferes slightly with 180.73 mm, but correction is possible, see Refs 35 and 19 Section 3.11.

Relative Standard Deviation

10% or better except close to the limit of detection where it approaches 30–50%.

Procedure

Use a vacuum region spectrophotometer at 180.73 nm (usually the most sensitive line), other possible lines are 182.04 nm or 182.62 nm. Separate or oxidize as required, correct for any volume change and follow the instrument manufacturer's instructions. Also measure the calcium concentration and correct for overlapping line interference as detailed in Refs 35 and 19, Section 3.11. If the 182 mm lines are used check for interference effects.

Standardization

Prepare an analytical working curve using standard solutions of either sodium sulphate, or sulphuric acid for non-volatile substances or a soluble mercaptan if a separate curve is prepared for volatile substances. To correct for calcium interference at 180.73 nm also prepare a series of standard calcium solutions free of sulphur compounds.

F9.3.1 Sulphate-sulphur or sulphur converted to sulphate is also determinable by a variant of the Barium–AAS method given in Ref 1 but using ICPS instead of AAS. A vacuum path spectrometer is not required.

F9.4 Flame photometry

Is used occasionally, the S_2 band spectrum head at 390 nm is measured (32). The method is too susceptible to interference effects to be used for all but simple samples.

F10 Sources of Error

There may be doubt whether some important sulphur compound has been oxidized completely by the above procedures, though this is unlikely. With suitable care it is possible to detect whether any volatile sulphur compounds have been lost, and in most cases to devise a procedure for trapping them. However, the two methods in section F9, if properly carried out, will give genuine total sulphur values provided the concentration is high enough; but the equipment is not always readily available. With ICPS, volatility needs to be considered when preparing standards, see text above.

G Other Techniques which have been used for Analysing Complex Mixtures of Sulphur Compounds

Other than the methods such as iodometry with and without formaldehyde etc already described, the following techniques and methods are in general use singly and in combination:

Methylene blue (bleach) colorimetric.
Reaction with cyanide and determination as thiocyanate.
Ion Chromatography and HPLC.
Potentiometry and Potentiometric Titration.
Polarography

For special purposes,

Electrophoresis.
Solvent extraction.
Simple Chromatography.
Gas Chromatography.
Direct Spectrophotometry.

G1 Methylene Blue Colorimetric (Ref 20).

Dithionite ions and other strong reducing agents such as Formaldehyde sulphoxylates can reduce dyestuffs such as methylene blue and indigo quantitatively. This can be used for their determination in the presence of other sulphur acids.

G2 Reaction with Cyanide (Ref 21)

Free sulphur and some polythioacids such as Tetrathionate and higher polythionates react with cyanide in the presence of sodium hydroxide to form thiocyanates, sulphate and thiosulphate.

$$S_4O_6^= + CN^- + 2OH^- \rightarrow SO_4^= + S_2O_3^= + SCN^- + H_2O$$

Higher polythionates produce proportionately more thiocyanate, so for a pure polythionate (separated by chromatography), the ratio of thiosulphate to thiocyanate identifies and quantifies the compound.

Trithionates only react on prolonged boiling. Under certain conditions free sulphur and some polysulphides will also react.

G3 Ion Chromatography (Refs 22–25) and High Performance Liquid Chromatography (Refs 25–27)

When examining a hitherto untested type of sample it is recommended that a cheap expendable guard column of the same type as the main column be used.

G3.1 Ion chromatography

This technique is very useful for most sulphur oxy anions including polythionates and also sulphide, especially if other anions are also determined. Mercaptans, polysulphides, thio-amino acids, pencillamines and the like can also be determined. Various detectors including potentiometric devices have been used. A booklet is in preparation.

G3.2 HPLC

Mixtures especially ones containing polythionates can also be analysed by HPLC using a variety of columns and detectors.

G4 Potentiometry

This and similar electrode methods are often used as detectors for Ion Chromatrography and HPLC. However simple mixtures of hydrosulphides and mercaptans can be titrated potentiometrically, giving similar stepped titration curves to those obtained when polybasic acids are titrated. Provided the mixtures are not too complex, the composition can be obtained using the points of inflection as end points.

G5 Polarography

Anode wave polarography can be used for the determination of sulphide, thiocyanate, thiosulphate and sulphite in the presence of hydroxide in solutions made 0.1 Molar in potassium nitrate. For more information on polarography see Ref 28 chapter 2. The half wave potentials are:

Sulphide	−0.76 volts
Thiosulphate	−0.15 volts
Hydroxide	−0.08 volts
Sulphite	− 0.007 volts
Thiocyanate	+ 0.18 volts

The potentials can be varied slightly by changing the supporting medium. See also Ref 32.

G6 Electrophoresis

This technique can be used for separating many soluble stable charged ions. The technique can therefore be used for both cationic and anionic forms of sulphur and also for sulphur compounds which have amino carboxylic or similar polar groups. Zwitterions such as betaine can be made to migrate by formation of a half salt such as the sodium salt or chloride (Ref 28 Chapter 8). The technique can be combined two dimensionally with paper chromatography.

G7 Packed Column and Thin Layer Liquid Chromatography and Gas Chromatography, with or without Solvent Extraction

Column and Thin Layer Chromatography have been used (Refs 25 and 28), and can be extended to neutral compounds.

For neutral compounds, extraction into a series of solvents of increasing polarity from solvents such as carbon tetrachloride, chloroform and hexane to ethanol and diethyl ether, followed, if volatile, by gas chromatography (Refs 29, 30 and 32) can also be useful, especially when coupled with mass spectrometry. If non volatile, derivatization may be used to improve volatility (Ref 31).

Note that Gas Chromatographs should not have metal or rubber parts exposed to the sample as these can decompose or absorb thio-compounds. Specific sulphur detectors are now available.

G8 Direct Spectrophotometry

Some compounds such as dithiocarbamates and dithiols give coloured complexes with metals soluble in solvents such as chloroform. Tetramethylthiuram disulphide and a few other sulphur compounds also have specific colorimetric reactions suitable for their analysis.

G9 Determination of Dithiocarbamates

A method for the determination of dithiocarbamates is given in Ref 37 in this series.

H Analytical Quality Control

Once the methods have been put into routine operation, many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check sources of inaccuracy should be made regularly. Many tests are possible and they should be used as appropriate. As a minimum, it is suggested that at least one sample of suitable concentration in each batch of samples be analysed at least in duplicate. Inclusion of a quality control standard of concentration unknown to the actual operator is also useful. Plots of the deviation between multiplicate samples, or of the control standard result, will facilitate detection of inadequate precision and allow the standard deviation of routine analytical results to be estimated. For further information see Refs 10, 11, 33 and 34.

Before placing reliance on any of the methods in this booklet, it is suggested that analysts test the method on their own samples and applications. Sections on method evaluation can be found in the back of most booklets containing Tentative Methods issued in this series. These can readily be adapted to the sulphur compounds concerned. At the same time it is suggested that interference effects be investigated using similar samples to which known amounts of suspect interferents have been added.

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