Sulphide in Waters and Effluents 1983, Tentative Methods

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £2.75 net

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Contents

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Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct 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.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for 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.

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

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.

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. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

First published 1983

ISBN 0 11 751718 6

About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains 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 individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users — the senior analytical chemist, biologist, bacteriologist etc. 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 one of the joint technical committees of the Department of the Environment and the National Water Council. It has seven 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, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

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 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 the booklet.

L R PITTWELL
Secretary

31 August 1983

Introduction to the Sulphide Booklet

Sulphide levels are determined less regularly on a routine basis, than sulphate for example, but various methods are needed for the estimation of sulphide in different circumstances.

At low level hydrogen sulphide will taint potable water. At higher levels it is toxic and, according to pH, can accumulate markedly over waters containing only moderate amounts of sulphide. This can happen for example in sewers, where the oxidation of the hydrogen sulphide eventually to sulphuric acid, causes the corrosion of concrete pipes.

Industrial processes use and make significant quantities of sulphide waste in coal and petroleum, steel manufacture, tanning and so on. It is often mixed with other sulphur containing species, such as sulphite, thiosulphate and dithionite, which can interfere with the analysis for sulphide. Different sulphur compounds vary markedly in their toxicity, with hydrogen sulphide being the most toxic. Hence it is important to distinguish between the different forms and particularly to be able to determine sulphide in trade effluents.

The sulphide should be "fixed" immediately on sampling on basic zinc carbonate formed in situ, because there is often a tendency for oxidation to occur in stored samples. Sample bottles should be completely filled to exclude air, for this reason. However, hydrogen sulphide also forms naturally, for example, reduction occurs from bacterial action on sulphate in brackish water in mud-flats at river estuaries. Checks should therefore be made to ensure that the sulphide content does not vary with sample storage time.

Two chemical methods are given here. The first is the well-tried iodometric method, which has been improved by a panel member and now avoids interference from significant amounts of sulphite by forming its unreactive adduct with formaldehyde. This method is suitable for referee analysis. In the second, the original methylene blue method has been replaced by the more sensitive one based on ethylene blue formation with the readily available reagent diethylphenylene diamine — This method can be adapted for automatic analysis.

There are several instrumental techniques for the measurement of sulphide, including the ion selective electrode, polarography and ion chromatography, but at this moment in time only the sulphide ion selective electrode has a general applicability and a note on its use is included here. This does not necessarily exclude the other techniques especially in the field of ion chromatography where in recent years rapid progress has shown that this technique is eminently suitable for sulphide measurement and will need to be fully appraised in the near future. See another booklet in this series on HPLC and Ion Chromatography.

Effects of Severe Hydrogen Sulphide Exposure in Man. (See Ref 9).

< 0.001 ppm	Normal concentration in clean air.	20–50 ppm	Gradual but temporary loss of sense of smell.
0.0005–0.13 ppm	Lower limit of detection of rotten egg smell.	50–100 ppm long term intermittent exposure	Vague symptoms.
7 ppm	WHO recommended time weighted average maximum exposure.	100–1000 ppm for hours	Eye irritation, conjunctivitis, respiratory tract irritation, and eventually palmonary oedema.
10 ppm	WHO, UK and USA recommended short term average maximum exposure.	Over 1000 ppm short term	Panting, suspension of breathing, then death. Survivors sometimes experience heart problems.
10–20 ppm long term	Lower threshold for eye irritation.		

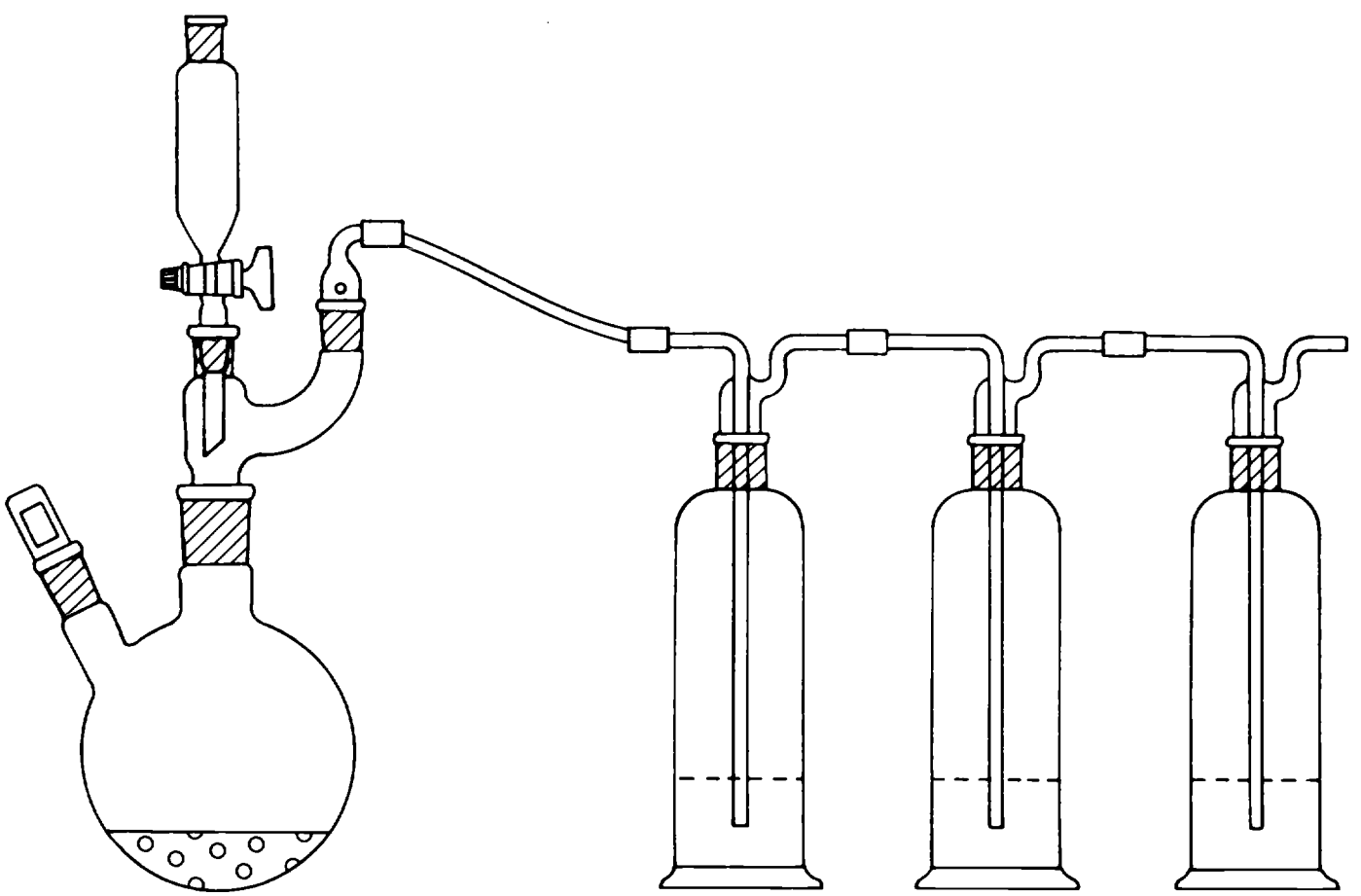


Figure 1. Apparatus for the determination of Sulphide by Gas Displacement.

A Determination of Sulphide by Iodometry (Tentative)

A1 Performance Characteristics (see Ref. 8)

A1.1	Substance Determined	Total hydrogen sulphide liberated by acidification of the sample.		
A1.2	Types of Sample	All types of water including sea water and most industrial wastes.		
A1.3	Basis of Method	Hydrogen sulphide liberated by acidification and carried in a stream of carbon dioxide, generated in situ, is absorbed into zinc acetate. Iodine is added to oxidize the zinc sulphide, the excess being back-titrated with sodium thiosulphate.		
A1.4	Range of Application	Up to 40 mg/l without the use of dilution or smaller aliquots.		
A1.5	Standard Deviation (c)(d)	Sulphide Concentration Standard mg/l	Standard Deviation	Degrees of Freedom
		Solutions:—		
		4.75	0.19(a)	8
		5.50	0.16(b)	5
		21.6	0.45(b)	8
		26.4	0.70(b)	9
		Trade Effluent:—		
		10.3	0.22(b)	8
A1.6	Limit of Detection (c)	0.26 mg/l (6 degrees of freedom).		
A1.7	Sensitivity	1 ml 0.00417M Iodate is equivalent to 2 mg/l sulphide (when using a 200 ml sample).		
A1.8	Bias	Not known but see Section A9.1.		
A1.9	Interference	See Section A3.		
A1.10	Time required for Analysis	About 1 hour for 1 sample:		

(a) Total Standard Deviation using Formaldehyde.

(b) Total Standard Deviation, without using Formaldehyde.

(c) Using 200 ml samples.

(d) For typical recovery data see Section A9.1.7.

These data were obtained by Chelsea College and North West Water Authority.

A2 Principle

A2.1 Hydrogen sulphide is liberated by acidification of the sample with hydrochloric acid. Calcium carbonate as marble chips, reacts with the acid and the carbon dioxide produced carries with it the hydrogen sulphide, which is absorbed in zinc acetate. The zinc sulphide produced is allowed to react with iodine formed when iodate-iodide is acidified and the excess iodine titrated with standard thiosulphate.

A2.2 The method described, which includes the use of formaldehyde to avoid interference by sulphur dioxide ([1]) has been developed by North West Water Authority from a method which has appeared in earlier editions of American Standard Methods ([2]).

A2.3 It has been found that carbon dioxide generated in situ provides more efficient scrubbing than carbon dioxide or nitrogen from an external source.

A3 Field of Application and Interferences

A3.1 The method is applicable to all types of waters, provided hydrogen sulphide can be liberated on acidification.

A3.2 The range can be varied by alteration of the volume and/or strength of the iodine in conjunction with the volume of sample taken.

A3.3 Those concerned with the discharge of trade effluents to sewer often require information on hydrogen sulphide generated by acidification and in these special circumstances the method will provide the necessary information.

A3.4 Anions such as sulphite, thiosulphate and dithionite can produce sulphur dioxide on acidification which if carried over into the Zinc Acetate, will react with iodine causing a positive bias. Formaldehyde forms an addition compound with sulphur dioxide which is unreactive towards iodine under the test conditions and its use in the procedure has been shown to be effective for up to at least 1000 mg/l sulphite as $SO_3^=$. Levels of sulphite below about 50 mg/l do not interfere and when it is known that the sample contains less than that amount, the use of formaldehyde is unnecessary.

A3.5 The sulphides of metals such as silver, mercury and copper are insoluble under the test conditions so that the presence of these compounds will not be detected. The sulphides of such metals as lead cadmium, nickel and cobalt, antimony and tin are insoluble in dilute acid, but the extent of their reactivity will depend on experimental conditions (see A9.3).

A3.6 Other volatile compounds which react with iodine will give high results. In many cases these will be soluble and so should be removed by separation of the mixed zinc precipitate. See Section A9.

A4 Hazards

A4.1 Formaldehyde is a suspected carcinogen and it should therefore be treated with extreme care ([3]). 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. Wastes containing formaldehyde should be disposed of with care, using copious amounts of water.

A4.2 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 ([4]), but, since chloro methyl ethers are known carcinogens, the obligatory operating conditions of paragraph A.4.1 should be followed.

A4.3 Hydrogen sulphide is a very toxic gas with a Threshold Limit Value similar to hydrogen cyanide (10 ppm). Care should be taken when sampling.

A4.4 Hydrochloric Acid is corrosive.

A5 Reagents

All reagents should be of analytical grade except where stated. Distilled or de-ionized water should be used throughout. Reagents are stable for at least two months except where stated otherwise.

A5.1 **Marble chips, native**

Approx 6 mm pieces.

A5.2 **Hydrochloric acid, 50% v/v**

Dilute the concentrated acid with an equal volume of distilled water.

A5.3 **Potassium Iodate-Iodine, 0.00417M**

Dissolve 0.8920 ± 0.0005 g potassium iodate (previously dried for 1 hour at 110°C), 8.7 ± 0.1 g potassium iodide and 0.6 + 0.1 g sodium bicarbonate in water and dilute to 1 litre.

A5.4 **Sodium thiosulphate 0.25M**

Dissolve 62.50 ± 0.01 g sodium thiosulphate pentahydrate in water and dilute to 1 litre. Preserve by adding 1 ml chloroform. Store in a dark glass bottle.

A5.5 **Sodium thiosulphate 0.0125M**

Dilute 50.00 ± 0.05 ml of the 0.25M Sodium thiosulphate to 1 litre with water. Add 1 ml chloroform as preservative and store in a dark glass bottle. This solution should be standardized against 0.00417M Potassium Iodate-Iodide.

A5.5.1 *Standardization*

Place 20.00 ± 0.05 ml potassium iodate-iodide in a conical flask, add 2.0 ± 0.2 ml 50% hydrochloric acid, mix. Dilute with water to 200 ml and titrate with sodium thiosulphate, adding 2 ml starch indicator when a pale straw colour is reached. Continue the titration until the blue colour just disappears. Note the titre (t mls) and calculate a factor

$$F = \frac{40.}{t}$$

Sodium thiosulphate may be adjusted to exactly 0.0125M (F = 1) for convenience of use but should be standardized daily, since the solution is not very stable.

A5.6 **Sodium Carbonate approximately 0.75M**

Dissolve 80 ± 5 g sodium carbonate, anhydrous, in water and dilute to 1 litre.

A5.7 **Zinc Acetate, approximately 0.5M**

Dissolve 110 ± 5 g zinc acetate dihydrate in water. Add 1.0 ml conc hydrochloric acid to prevent hydrolysis and dilute to 1 litre.

A5.8 **Starch Indicator.**

A5.9 **Formaldehyde, approx 40% solution.**

A6 Apparatus

Due to the tenacious nature of the zinc precipitate, all items of equipment in contact with the precipitate should first be rinsed in dilute hydrochloric acid.

In addition to normal laboratory glassware, the following are required.

A6.1 **500 ml flask.**

This can be either a 3-neck-parallel or a 2 neck fitted with a 2-neck-parallel adaptor. A dropping funnel, tubing adaptor and stopper should be fitted to either flask. (See Fig 1).

A6.2 **Three drechsel bottles with straight distribution tubes:**

Sintered ends must not be used. (See Fig 1). The bottles should be connected by plastic tubing and not rubber.

A6.3 **Centrifuge and appropriate tubes.**

A7 Sample Collection and Preservation

A7.1 See note under Section 4 regarding the toxicity of hydrogen sulphide.

A7.2 Samples taken for sulphide determination must always be fixed immediately after sampling. Any sized sample can be taken, but normally a 200 ml bottle will be found convenient. As the stabilized sample is a glutinous suspension and use of the whole sample is recommended, it is best to measure the volume of sample poured into the bottle. The bottle neck should be sufficiently wide to allow for adequate policing (not with rubber) if necessary. When stoppered, it should be airtight. If multiple determinations are made to

increase accuracy, the taking of several separate samples may be considered as an alternative to aliquotting. (See also section 8 note f). The fixing procedure is as follows:

A7.2.1 Place the sample carefully with a minimum of aeration, in a bottle until it is almost full. Add 2.0 + 0.2 ml Sodium Carbonate, mix, followed by 2.0 ± 0.2 ml Zinc Acetate, per 100 ml sample. Mix again.

A7.2.2 The whole sample is normally taken for analysis, but if volatile organic compounds are present, the sample can be centrifuged or filtered and the solid portion retained, see Section A.9.2.

A7.2.3 If only part of the sample is taken for analysis special attention must be paid to thorough mixing before removing the portion to be analysed. (See also Section 8 note c).

A7.3 It has been found that the presence of a large amount of suspended matter (10 mm on the bottom of the bottle) in the sample reduced the effectiveness of the preservatives. This was due to anaerobic bacterial action within the settled solid.

A7.4 The stabilized sample is stable for up to 5 days.

A8 Analytical Procedure

Step	Procedure	Notes
A8.1	Place 25 ± 5 g of marble chips in the reaction flask. Connect up the flask via the gas adaptor to 3 drechsel bottles connected in series.	
A8.2	Into each drechsel bottle put 5.0 ± 0.5 ml of zinc acetate and 50 ± 5 ml of water.	
A8.3	Place a measured volume of sample in the flask and dilute if necessary to 200 ml with distilled water. Place 100 ml ± 10 ml of 50% v/v hydrochloric acid in the funnel. (See notes a, b, and c, and also Section A7.2.3).	(a) The volume of the sample needed depends on the concentration of sulphide present, 200 ml will cover the range up to 40 mg/l sulphide. It is advisable to be aware of the approximate level in the sample. (b) Certain trade effluents may have a tendency to foam during the addition of the acid. In such cases 2–3 drops of silicone oil should be added at the beginning. (c) The zinc precipitate is very gelatinous and has a tendancy to adhere to surfaces. eg. measuring apparatus: when measuring aliquots, the device used should be rinsed out with water and the rinsings added to the sample aliquot in the flask.
A8.4	Add approximately 5 ml 50% v/v acid into the flask so as to dissolve the precipitate and generate a stream of carbon dioxide from the marble chips. The gas should bubble through at the rate of a few bubbles per second.	
A8.5	Continue to add acid in 5 ml portions to maintain the gas flow rate over a period of 1 hour ± 10 minutes.	
A8.6	Into a 500 ml conical flask place 20 ± 0.05 ml Iodate-Iodide solution, and 2.0 ± 0.2 ml 50% v/v hydrochloric acid, swirl to mix.	

A8.7 Combine the contents of the drechsel bottles into the first bottle together with 5.0 ± 0.5 ml formaldehyde, mix. Add slowly with mixing to the Iodine solution contained in the conical flask. (A.8.6.) Rinse out the drechsel bottles with the mixture and finally with water. Immerse the ends of the drechsel tubes in the mixture, if necessary, rinsing off afterwards with water (see notes d, e and f).

(d) If sulphite or other anions capable of producing sulphur dioxide on acidification are present below 50 mg/l the use of Formaldehyde is unnecessary and in this case the contents of the drechsel bottles are added in turn to the iodine solution slowly and with mixing.

(e) It is important to add the zinc sulphide to the iodine, otherwise losses can occur and side reactions may take effect. A small amount of zinc sulphide often forms on the ends of the distribution tubes, which must be dissolved in the iodine.

(f) Excess iodine must be present if not, the test should be repeated using less sample. Addition of more iodine will probably only give an approximate result.

A8.8 Titrate the excess iodine with sodium thiosulphate adding starch when the liquid becomes pale straw coloured and continuing until the blue colour just disappears: the solution may be slightly turbid due to precipitated sulphur. Record the titre B_1 ml.

Blank Determination

A8.9 Carry out the complete procedure, A8.1 to A8.8, but replace the sample in step A8.3 by 200 ml of distilled water. Record the titre B_2 ml (see note g).

(g) The difference between B_2 and direct titration of the iodide-iodate is normally about 0.2 ml and often arises from the zinc acetate used in Step 8.2.

Calculation

A8.10 Since 1 ml 0.00417M Iodate = 0.4 mg sulphide, as S.

Sulphide Concentration,

$$\text{as S, } = \frac{(B_2-B_1)\ F \times 200}{\text{Volume of Sample}} \text{ mg/l}$$

(For the determination of F see A5.51)

A9 Special Procedures and Sources of Error

A9.1 **Checking Recovery**

It may be considered necessary to check the recovery being obtained with the method. It is important that the initial level of sulphide in the standard be measured as accurately as possible otherwise apparently low recoveries may be recorded. Sulphide solutions are extremely unstable and it is very difficult to prepare and use standard solutions in the normal way. The following procedure should give accurate information.

A9.1.1 Wash crystals of sodium sulphide nona-hydrate, dry quickly on filter paper and quickly weigh 0.10 ± 0.01 g and dissolve in about 500 ml water contained in a 1 l standard flask, swirl gently. Solution occurs quickly and immediately the crystals disappear, add 20 ± 1 ml sodium carbonate solution, mix, followed by 20 ± 1 ml zinc acetate. Mix. Make up to volume.

This suspension should now contain approximately 10 mg/l sulphide as S and should be stable for at least 5 days.

A9.1.2 Thoroughly shake the flask, quickly pour off 200 ± 2 ml of the suspension into a 250 ml graduated cylinder. Pour into suitable centrifuge tubes. Efforts to pour directly 200 ml of the suspension into the centrifuge tubes may result in some settlement taking place. Centrifuge for 5 ± 1 mins at about 2000 rpm. Pour off the supernatant and mix the residues with a small amount of water to break up the lumps.

A9.1.3 Place 10.00 ± 0.02 ml potassium iodate/iodide solution in a conical flask, add 2.0 ± 0.2 ml 50% v/v hydrochloric acid. Wash the contents of the centrifuge tubes into the iodine solution, rinsing out the tubes with some of the mixture followed by water. Similarly wash out the graduated cylinder with the iodine solution and finally water.

Titrate the excess iodine with thiosulphate. Record titre T_1.

A9.1.4 Place 10.0 ± 0.2 ml 50% v/v hydrochloric acid in a conical flask. Titrate the iodine with thiosulphate. Record titre T_2 ml.

Sulphide concentration = $(T_2 - T_1)$ F mg/l as sulphide. (For F see A5.5.1).

A9.1.5 Direct titration of the suspension, without prior separation of the solid portion, will give incorrect results because of the iodine demand of the oxidation products arising from decomposition of the sodium sulphide.

A9.1.6 Establish the strength of the suspension and compare with the result obtained from Steps 8.1 to 8.9 using the suspension prepared in 10.1.1; hence calculate the recovery.

A9.1.7 Recoveries obtained in two laboratories were

96 ± 2% ± 30 mg/l level
93 ± 3% ± 5 mg/l level

A9.2 Interference of Volatile Compounds

Volatile compounds other than sulphur dioxide, which are capable of being carried over in the stream of carbon dioxide, and which react with iodine could cause problems. Two possibilities are suggested.

A9.2.1 If the offending components are contained in the soluble portion of the fixed sample, separation, either by filtration or centrifugation and analysis of the washed solid portion may be successful.

A9.2.2 The sample should be analysed, firstly in the normal way and secondly in the presence of an excess of copper to prevent the sulphide reacting; the success of this method will depend upon the copper ions not reacting with the interfering components.

A9.3 Heavy Metal "Insoluble" Sulphides

The method may not recover sulphide present as heavy metal sulphides, the amount recovered being dependent on which metals are present in the sample and the experimental conditions (see also Section A3.5).

More sulphide in this form can be recovered by filtering or centrifuging the fixed sample, transferring the suspended matter to the flask with a minimum amount of water, and using concentrated hydrochloric acid instead of the 50% v/v acid. Any heavy metal sulphides which are not decomposed by this modified procedure are probably of little environmental consequence, but the analyst should consider carefully the purpose of the analysis before using this modification. If necessary, analysis by X-ray Fluorescence should be considered (*12*). If insoluble sulphates are also present, X-ray Diffraction might be used to distinguish them (*13*).

B Spectrophotometric Determination of Sulphide, DPD Method (Tentative)

B1 Performance Characteristics (see Ref. 8)

B1.1	Substance Determined	Total available sulphide.		
B1.2	Types of Sample	Fresh water and lightly polluted effluents.		
B1.3	Basis of Method	N-N Diethyl-p-phenylenediamine (DPD) potassium dichromate and sulphide together form a blue colour which is measured spectrophotometrically.		
B1.4	Range of Application (C)	Up to 0.5 mg/l		
B1.5	Calibration Curve (c)	Linear up to 0.5 mg/l		
B1.6	Standard Deviation (c) (within batch)	Sulphide Concentration	Standard Deviation	Degrees of Freedom
	Standard Solutions	0.048	0.0023(b)	8
		0.05	0.0018(a)	11
		0.384	0.013 (b)	8
		0.40	0.0042(a)	11
B1.7	Limit of Detection (c)	0.0027 mg/l (5 degrees of freedom).		
B1.8	Sensitivity (c)	0.15 mg/l sulphide gives an absorbance of approximately 0.25		
B1.9	Bias	Not known		
B1.10	Interference	See Section 3.		
B1.11	Time required for Analysis	About 15 mins per sample.		

(a) Data obtained from the Laboratory of the Government Chemist.

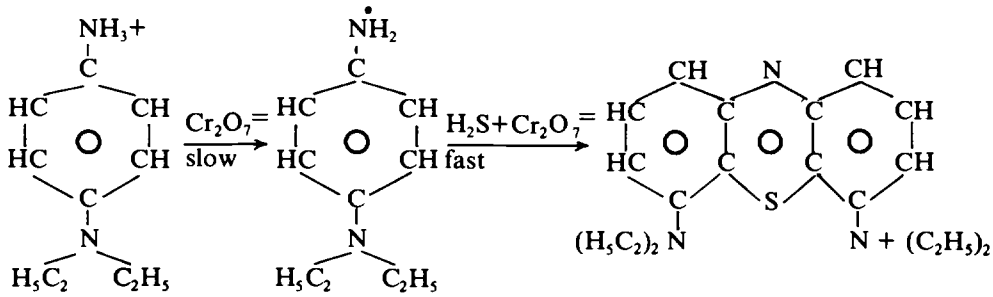
(b) Data obtained from British Leather Manufacturers' Research Association, Northampton.

(c) Using a 50ml sample.

B2 Principle

B2.1 Potassium Dichromate converts "DPD" (N-N-Diethyl-p-phenylene-diamine) to the free radical which reacts rapidly with sulphide to produce the coloured "DPD Blue" or "Ethylene Blue". This can then be measured at 670 nm using a suitable instrument. (5 and 6).

B2.2 The reaction is as follows:—



B3 Field of Application and Interferences

B3.1 The method is most applicable to fresh waters and lightly polluted effluents, particularly at the lower levels of concentration. Interferences may limit the analysis of more polluted samples.

B3.2 Highly coloured waters and those containing insoluble suspended matter may cause difficulties with the measurement of the colour. Some of these problems may be reduced by use of the fixing procedures (see Sections A7 and A8, B7 and B8). See also sections B8.10, B8.11 and B9.3.

B3.3 The sulphide present in the sample must be capable of liberation by acidification. Sulphide in heavy metal sulphides may be only partly recovered depending on which metals are present (see also Section A3.5).

B3.4 Thiosulphates when present at concentrations over 10 mg/l cause temporary loss of colour, the "clock reaction", depending on the concentration which is present.

B3.5 Sulphites at concentrations in excess of 2 mg/l cause progressive loss of colour.

B3.6 Zinc, if present at more than 0.5% w/v as zinc acetate, causes a progressively reduced colour formation.

B3.7 Sulphide ion itself in concentration of greater than about 100 mg/l inhibits colour formation, a situation which is easily corrected provided the analyst is aware of the level present.

B3.8 Iodides when present at greater than 2 mg/l cause reduced colour formation.

B3.9 Cyanides ions do not retard colour formation unless present at greater than 500 mg/l.

B4 Hazards

B4.1 Sulphuric acid is corrosive.

B4.2 Hydrogen sulphide is a very toxic gas, possessing the same Threshold Limit Value as hydrogen cyanide (10 ppm).

B4.3 DPD may cause dermatitis in some individuals.

B5 Reagents

All reagents should be of analytical grade except where stated. Reagents are stable for at least 2 months except where stated otherwise.

B5.1 **Sulphuric Acid, approx. 15% v/v**

Add 15.0 ± 0.5 ml concentrated sulphuric acid slowly and with stirring to 85 ± 1 ml distilled water and allow to cool.

B5.2 **DPD- Sulphuric Acid Reagent**

Dissolve 1.5 ± 0.1 g of N-N-Diethyl-p-phenylenediamine sulphate (or oxalate) in 100 ml dilute sulphuric acid 15% v/v (B5.1).

B5.3 **Potassium Dichromate**

Dissolve 0.20 ± 0.01 g potassium dichromate in 100 ± 1 ml distilled water.

B5.4 **Sodium Carbonate, approx 0.75 M**

Dissolve 80 ± 5 g Sodium Carbonate, anhydrous, in water, dilute in litre.

B5.5 **Zinc Acetate, approx 0.5M**

Dissolve 110 ± 5 g acetate dihydrate in water. Add 1.0 ml concentrated hydrochloric acid to prevent hydrolysis, dilute to 1 litre.

B5.6 **Potassium Iodate-Iodide 0.00417M**

Dissolve 0.8920 ± 0.0005 gas potassium iodate (Previously dried for 1 hour at 110°C), 8.7 ± 0.1 gas potassium iodide and 0.6 ± 0.1 g sodium bicarbonate in water and dilute to 1 litre.

B5.7 **Hydrochloric Acid, 50% v/v**

Dilute the concentrated acid with an equal volume of distilled water.

B5.8 **Starch Indicator**

B5.9 **Sodium Thiosulphate 0.25M**

Dissolve 62.50 ± 0.01 g sodium thiosulphate pentahydrate in water and dilute to 1 litre. Preserve by adding 1 ml chloroform. Store in a dark glass bottle.

B5.10 **Sodium Thiosulphate 0.0125M**

Dilute 50.00 ± 0.01 ml of the 0.25M Sodium Thiosulphate solution to 1 litre with water. Add 1 ml chloroform as preservative and store in a dark glass bottle. This solution should be standardized immediately before use against 0.00417 M Potassium Iodate as follows:—

B5.10.1 *Standardization*

Place 20.00 ± 0.05 ml potassium iodate-iodide solution in a conical flask, add 2.0 ± 0.2 ml 50% Hydrochloric Acid. Swirl and mix. Dilute with water to about 200 ml and titrate with sodium thiosulphate, adding 2 ml starch indicator when a pale yellow colour is reached. Continue the titration until the blue colour just disappears. Note the titre (t ml) and calculate a factor

$$(F = \frac{40}{t})$$

B5.11 **Standard Sulphide Suspension, approx 5 mg/l**

(For a 10 mg/l suspension see Section A9.1)

It is impracticable to prepare a sodium sulphide solution of exact strength, but this is unimportant provided the strength is known accurately.

Wash crystals of sodium sulphide nona-hydrate, dry quickly on filter paper, (avoid skin contact) and quickly weigh 0.040 ± 0.005 g and dissolve in about 500 ml distilled water, contained in a litre standard flask. Swirl very gently, solution will occur quickly and immediately the crystal(s) disappears, add 20 ± 1 ml sodium carbonate (B5.4) and mix. Add 20 ± 1 ml zinc acetate and mix. Make up to the mark with ordinary distilled water. This suspension should now be stable for at least 5 days.

B5.11.1 *The suspension is standardized in the following manner (Note 1)*

Thoroughly shake the flask, quickly pour off 200 ± 2 ml of the suspension into a 250 ml graduated cylinder. Pour into suitable centrifuge tubes (note 2). Centrifuge for 5 + 1 min at about 2000 rpm. Pour off the supernatant and mix the residues with a small amount of water to break up the lumps. Place 5.00 ± 0.02 ml potassium iodate-iodide solution in a conical flask. Add 2.0 ± 0.2 ml 50% v/v hydrochloric acid. Wash the contents of the centrifuge tubes into the iodine solution, rinsing out the tubes with some of the mixture

followed by water. Wash out the graduated cylinder with the iodine solution and finally water.

Titrate the excess iodine with the thiosulphate using a microburette. Record the titre T_1 and repeat with a second portion of the suspension. The two titrations should agree within 0.1 ml.

Place 5.00 ± 0.02 ml potassium iodate-iodide and 2.0 ± 0.2 ml 50% v/v hydrochloric acid in the conical flask. Titrate the iodine with thiosulphate, record Titre T_2.

Then mg/l S = in suspension = $(T_2 - T_1)$ F. (For F see B5.9.1).

Note 1 Direct titration of the suspension without separation of the solid portion will give an erroneous result because of the iodine demand of the decomposition products of sodium sulphide.

Note 2 The use of a graduated cylinder is recommended to minimize the taking of an unrepresentative portion from the flask.

B5.12 **Sulphide Suspension — Working Strength, approx 0.5 mg/l**

Dilute the suspension (5.10) 25 ml to 250 ml with distilled water.

B6 Apparatus

In addition to normal glassware, the following are required.

B6.1 **Spectrophotometer**

Capable of reading at 670 nm, and fitted with 10 mm glass cells.

B6.2 **10 ml microburette.**

B6.3 **Centrifuge and appropriate tubes.**

B7 Sample Collection and Preservation

B7.1 See note under section 4 regarding the toxicity of hydrogen sulphide.

B7.2 Samples taken for sulphide determination must always be fixed immediately after sampling.

Any sized sample can be taken but normally a 200 ml bottle will be found convenient. The procedure to be adopted is as follows:—

B7.2.1 Place the sample carefully, with a minimum of aeration in a bottle of known capacity such that the bottle is almost full. Add 2.0 ± 0.2 ml sodium carbonate, mix, followed by 2.0 ± 0.2 ml zinc acetate per 100 ml sample, mix again.

B7.2.2 Normally an aliquot of the well-shaken sample will be taken for analysis. (Alternatively see Section A7.2).

B7.2.3 If soluble interferences are present, the supernatant may be decanted and replaced with distilled water to the original mark. For very low levels of sulphide and particularly where large sampling bottles may have been used, a "concentration effect" can be attained by making up to a known fraction of the original volume with water.

B7.3 The presence of large amounts of suspended matter in the sample may reduce the effectiveness of the preservative.

B7.4 The preserved sample is stable for up to 5 days.

Step	Procedure	Notes
	Preparation of Calibration Curve	
B8.1	Into a series of 50 ml calibrated flasks place 0 (blank), 10, 20, 30, 40 and 50 ml of the well-shaken working strength sulphide suspension (B5.12) and make up to the mark with distilled water. These standards have nominal concentrations of 0 (blank) 0.1, 0.2, 0.3, 0.4, and 0.5 mg/l respectively.	
B8.2	To each flask add 1.00 ± 0.05 ml DPD Reagent and 1.0 ± 0.05 ml potassium dichromate solution. Mix immediately and keep out of direct sunlight for not less than 5 minutes (see note a).	(a) The colour is stable for several hours.
B8.3	Measure the absorbance of each solution in a 10 mm cell at 670 nm (see note b) using distilled water in the reference cell.	(b) 670 mm is the wavelength of maximum absorbance but this should be optimized on the instrument to allow for any error in wave-length calibration.
B8.4	Deduct the blank absorbance (B) from the absorbances of the standards and plot a graph of blank corrected absorbances against concentration (computed from the standardization in B5.11) (see note c).	(c) For guidance, in a 10 mm cell, an absorbance of 0.5 should correspond to not more than 0.3 mg/l sulphide. If this figure is exceeded, repeat and/or check the standardization and calibration.
	Analysis of Samples	
B8.5	Place a known volume, up to 50 ml of the sample in a 50 ml calibrated flask. Dilute to the mark with distilled water if necessary (see note d).	(d) It is helpful to know the approximate level of sulphide present. The maximum sample volume of 50 ml should contain not more than 0.5 mg/l sulphide.
B8.6	Prepare a blank using 50 ml distilled water in a 50 ml calibrated flask.	
B8.7	Carry out the procedure in Steps B8.2 and B8.3.	
B8.8	Deduct the blank absorbance (B) from the sample absorbances (S) and use this corrected absorbance (S-B) to read the concentration of sulphide from the calibration graph.	
	Calculation of Results	
B8.9	Allow for any dilution made in Step B8.5 as follows: Concentration of Sulphide as $S = \frac{R \times 50}{V}$ where R = mg/l sulphide read from the calibration graph, and V = volume of sample taken in ml	

Step	Procedure	Notes
	Compensation for Colour and Turbidity in Samples	
B8.10	Repeat the procedure in steps B8.5 and B8.7 but replace the DPD Reagent with 1.00 ± 0.05 ml dilute sulphuric acid (B5.1).	
B8.11	Deduct the absorbance (A) from the blank-corrected absorbance of the sample from Step B8.8. Use this absorbance (S-B-A) to read the concentration of sulphide from the calibration graph.	

B9 Sources of Error

B9.1 Measurement of Absorbance

The exact instrument setting for the wavelength of the absorption peak must be checked for each instrument and then used in all future work. The procedure used for measuring the absorbance should be rigorously controlled to ensure satisfactory precision. The same cells should always be used and should not be interchanged between the references and sample

They should always be placed in the same position in the cell-holder with the same face towards the light source. Before every set of measurements, the absorbance of the sample cell should be measured against the reference cell when both are filled with water. This will also enable the true absorbance of the blank to be determined.

B9.2 Preparation of Calibration Curve

The accuracy of this method depends on the successful preparation of the calibration curve. (See Section B8, Sections 8.1 to 8.4).

B9.3 Compensation for Colour and Turbidity

The use of the correction for colour and turbidity in the sample is an additional source of error in the final result and is therefore associated with a deterioration in performance characteristics, especially precision and limit of detection. For highly coloured or turbid samples, this additional error may be unacceptable and the method is not recommended for such samples.

C Note on the Sulphide Ion Selective Electrode

C1 Use

An ion selective electrode can be used for the selective analysis of sulphide especially in rivers and other relatively clean waters. It can be used as a direct measure of the sulphide ion activity or as an end point detector for potentiometric titration of sulphide with silver nitrate solutions.

There is only one type of sulphide ISE, based on a compressed disc of silver sulphide. It should be noted that under the correctly buffered operating conditions, the ISE will detect only the $S^{=}$ ion and does not respond to other sulphur ions or molecules eg HS^{-}, H_2S.

C2 Concentration Range

The electrode has a linear nernstian response between 0.1 – 300 ppm $S^{=}$ and can be used down to about 0.01 mg/l with additional calibration standards at closely spaced concentration intervals.

C3 Interferences and Poisons

Since the electrode has a compressed AgS disc membrane it also responds to Ag+ ions and can in fact be used to measure Ag+ ion activity. It also responds to a lesser extent to mercury ions and the electrode is poisoned if the level of Hg^{2+} ions exceeds 20 ppm.

In common with most ion selective electrodes the sulphide ISE is very dependent on pH and exhibits a linear dependence on pH over the range 9–12. To be operated successfully the electrode should be used only in samples buffered to pH 13.

C4 Analytical Procedure

The electrode is calibrated against standard solutions. Full calibration is only required if the electrode is used below the limit of nernstian response.

Since the response of the sulphide ion selective electrode is dependent of the $H_2S/HS^{-}/S^{=}$ equilibrium and in common with all ISE's is dependent on temperature, ionic strength and pH, standards used for calibration should have a similar temperature, ionic strength and pH. The usual way of achieving these conditions and preventing air oxidation at the same time is to use a sulphide anti-oxidant buffer. More information on the use of this buffer and ISE in general can be found in references 10 and 11.

Checking the Accuracy of Analytical Results

Once the methods have been put into normal 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 types of test are possible and they should be used as appropriate. As a minimum however, it is suggested that a standard suspension of sulphide (see A9 or B5.12) of suitable concentration be analysed at the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated. For more detailed information on the types of test available and the interpretation of their results, standard texts, such as those published by the Water Research Centre ([7]) and by the Standing Committee of Analysts ([8]) should be consulted.

References

1 Allcroft J B *3rd Report Standing Committee of Analysts*, DOE, London.

2 *Standard Methods for the Examination of Water and Waste Water*, APHA, AWWA and WPCF, Washington DC, 12th Edition, 1965, p 427–8.

3 *Environmental Science and Technology*, 1981, **15** (No 10) p.1116.

4 Tou J C and Kallos G J, *American Industrial Hygiene Association Journal*, July 1974, p. 419.

5 Rees T D, Gyllenpetz A B and Docherty A C, *Analyst* **96**, 201, (1971).

6 Koster M B and King M P, *Journal AWWA*, 1977 p. 544.

7 Cheeseman R V and Wilson A L, Water Research Centre, *Technical Report* TR66, Medmenham, 1978.

8 *"General Principles of Sampling and Accuracy of Results 1980"* Methods for the Examination of Waters and Associated Materials, HMSO, London.

9 Hydrogen Sulphide, *Environmental Health Criteria 19*, WHO Geneva 1981.

10 Midgeley D and Torrance K, *Potentiometric Water Analysis*, J Wiley and Sons, 1978.

11 Mosey F and Jago D A, Water Research Centre, *Technical Report* TR53, Medmenham, 1977.

12 *Emission Spectrophotometric Multielement Methods of Analysis for Waters, Sediments and other materials of interest to the Water Industry 1980*, Methods for the Examination of Waters and Associated Materials, HMSO, London.

13 *A Survey of Multielement and Related Methods of Analysis for Waters, Sediments and other materials of interest to the Water Industry 1980*, Methods for the Examination of Waters and Associated Materials, HMSO, London.

Estimation of the Accuracy of Analytical Results Using the Tentative Methods in this Booklet

Before firmly recommending the tentative methods for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of any of these methods could estimate the accuracy of its own analytical results and report the findings to the Technical Secretary of the General Non-Metallic Substances Working Group* of the Standing Committee of Analysts, together with full details of the precise method used.

The precision achieved is of particular interest. The value of this information would be greatly enhanced if it were obtained at the same determinand concentrations as those for which some information has already been gained, as set out in the Performance Characteristics sections of these methods.

Similar information at other determinand concentrations, and in sample types other than those already studied, would also be of great assistance. Detailed specifications for the tests to be carried out are beyond the scope of this booklet, but standard texts — such as those published by the Water Research Centre and by the Standing Committee of Analysts — provide guidelines from which precision tests may be designed. The same texts also provide guidelines for interference and recovery tests and any information on these matters would be gratefully received.

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*Results should be sent to:

The Secretary
The General Non-Metallic Substances Working Group
The Standing Committee of Analysts
The Department of the Environment
Romney House
43 Marsham Street
London SW1P 3PY
England

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
Romney House
43 Marsham Street
LONDON SW1P 3PY
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Dd 718529 C12 11/83

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