Environment Agency

The determination of easily liberated sulphide in soils and similar matrices (2010)

Methods for the Examination of Waters and Associated Materials

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Methods for the Examination of Waters and Associated Materials

This booklet contains guidance on the determination of sulphide in soils and similar matrices using a variety of techniques, and updates the earlier version published in 1983[(1)]. Using the procedures described in this booklet should enable laboratories to satisfy the relevant requirements of the Agency's Monitoring Certification Scheme (MCERTS) for laboratories undertaking chemical testing of soils[(2)]. However, if appropriate, laboratories should clearly demonstrate they are able to meet the MCERTS requirements. Each method has been validated in only one laboratory and consequently details are included for information purposes only as an example of the type of procedures that are available to analysts. Information on routine multi-laboratory use of these methods would be welcomed to assess their full capabilities. Each method has been accredited by UKAS and conforms to the MCERTS performance standard for laboratories undertaking chemical testing of soil, meeting the performance criteria prescribed therein.

Whilst this booklet may report details of the materials actually used, this does not constitute an endorsement of these products but serves only as illustrative examples. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate methods in their own laboratories.

Contents

About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments and biota.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

In the procedures described in each method any reference to the tolerances to be adopted with respect to, for example the amount or volume of reagents to be used is left to the discretion of the laboratory. These tolerances should be as low as possible in order to satisfy stringent performance criteria. Tolerances of between 1 - 5 % have been shown to be satisfactory for most purposes. Lower tolerances should result in improved precision.

In the methods described, for example for wavelengths, storage conditions, concentrations of the same or similar reagents, etc, differences may be noted. This information is provided by individual laboratories operating under their own management systems and is dependent on specific conditions pertaining to each laboratory. It is assumed this information is supported by sufficient data to justify its inclusion. Users intending to use or vary the quoted wavelengths, storage conditions, concentrations, etc, should ensure they are appropriate to their own laboratory and verify their application to demonstrate appropriate performance of the method. In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series “Methods for the Examination of Waters and Associated Materials” and their continuing revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is now managed by the Environment Agency.

Methods are produced by panels of experts in the appropriate field, often in co-operation with working groups and the main committee. The names of those members principally associated with these methods are listed at the back of this booklet. A report describing all SCA activities for the period 1 July to 30 June is produced annually and is available from the Agency’s web-page (www.environment-agency.gov.uk/nls).

Users should ensure they are aware of the most recent version of the draft they seek. If users wish to receive copies or advance notice of forthcoming publications, or obtain details of the index of methods then contact the Secretary on the Agency’s internet web-page or by post, see address listed at the back of this booklet.

Great efforts are made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

Dr D Westwood
Secretary
February 2010

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety. These should be consulted and be readily accessible to all analysts. Amongst such publications are; “Safe Practices in Chemical Laboratories” and “Hazards in the Chemical Laboratory”, 1992, produced by the Royal Society of Chemistry; “Guidelines for Microbiological Safety”, 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and “Safety Precautions, Notes for Guidance” produced by the Public Health Laboratory Service. Another useful publication is “Good Laboratory Practice” produced by the Department of Health.

The determination of easily liberated sulphide in soils and similar matrices

1 Introduction

Sulphur is a non-metal. Its most common valency states are -2, +4 and +6; the -2 reduction state is known as sulphide. Sulphide occurs naturally in mineral ores, oil and coal deposits, and from the natural anaerobic decomposition of organic matter containing sulphur-containing compounds. The average concentration of sulphur in the earth's crust is estimated to be in the approximate range of 260 - 520 mg/kg. Sulphides are widely used in the manufacture of pigments, dyes and cosmetics, as well as in tanning, pulp and chemical processes.

Hydrogen sulphide and sulphides of the alkali and alkaline earth metals are soluble in water and thus pose a threat to water resources. The odour threshold in water is about 0.05 mg/l as H_2S. A commonly used soil threshold value for sulphide, S^{2-}, is 25 mg/kg. This limit is based on dated ICRCL reference values.

Sulphide-rich ores or wastes can react with oxygen when exposed to atmospheric conditions to produce sulphuric acid. The presence of sulphuric acid increases the solubility and mobility of more sulphur species, along with any heavy metals present, and may cause serious problems such as acid mine drainage and the corrosion of concrete and steel products.

Anions such as sulphite, thiosulphate and dithionite can produce sulphur dioxide on the addition of acid to solutions containing these anions. Sulphur dioxide reacts with iodine causing a positive bias in sulphide determinations involving titrimetric determination involving iodine.

Thiosulphate, at concentrations exceeding 10 mg/l in the final distillate, results in temporary loss of colour using DPD. Sulphite, at concentrations in excess of 2 mg/l in the final distillate, results in colour loss. Iodide, when present at concentrations greater than 2 mg/l in the final distillate, results in loss of colour. Zinc, present at concentrations over 0.5 % w/v as zinc acetate, causes progressively reduced colour formation.

2 Analysis and reporting considerations

The following tables, Table I1 and Table I2 highlight the types of samples that are commonly analysed in laboratories.

Table I1 Sample description

Sample code	Sample type
A	"As received" in the laboratory
B	"As received" in the laboratory (but with inert material removed)
C	Inert material
D	Air-dried (i.e. sample A is air-dried)
E	Air-dried (i.e. sample B is air-dried)
F	Dry weight (i.e. sample A or D is dried)
G	Dry weight (i.e. sample B or E is dried)

Samples D and E when air-dried at temperatures, for example up to 30 °C, generally contain residual moisture in equilibrium with the matrix.
Samples F and G when dried at temperatures, for example at 105 °C, generally contain no moisture.

Table I2 Example sample composition

Sample code	Composition				Total sample	Result on sample analysed (mg/kg)
	Soil	Water	Residual moisture	Inert material		
A	780	150	20	50	1000	XA
B	780	150	20	0	950	XB
C	0	0	0	50	50	-
D	780	0	20	50	850	XD
E	780	0	20	0	800	XE
F	780	0	0	50	830	XF
G	780	0	0	0	780	XG

Figures represent amount of material present in grams

A typical soil sample submitted to a laboratory (i.e. the "as received" sample) comprises an amount of soil matter (including organic and inorganic fractions) mixed together with water (a small proportion of which may be bound to soil particles). A representative amount of the "as received" sample is usually taken for analysis. The result is then usually reported on the "as received" sample (i.e. sample A) but may be reported on another sample type, for example sample D, and expressed on an air-dried basis; less likely, is the report of this result expressed on sample type F, i.e. expressed on the dry weight basis. These results may be reported as moisture-corrected values.

Most of the water in the "as received" sample is lost during air-drying processes (usually at temperatures less than 30 °C) used to prepare an air-dried material for analysis. Residual moisture is usually present in equilibrium with the matrix. An homogeneous portion of the air-dried sample, sample D, is usually taken for analysis. The result is then reported on the air-dried sample, i.e. sample D; again less frequently, is the report of this result expressed on sample type F, i.e. expressed on the dry weight basis.

Only at elevated temperatures (for example at 105 °C) is all of the water driven off. This sample, sample F, is rarely analysed, but may be the basis on which results are

expressed, i.e. the result is expressed on a dry weight basis.

The sample may contain inert or extraneous material such as large stones, plant debris etc. This inert material may or may not be removed prior to drying or analysis. If inert material is removed prior to drying or analysis, this should be reported and the amount removed recorded.

How the sample is pre-treated and prepared will depend on individual laboratory practices and procedures. The fact that different practices and procedures are used is not an issue provided all information is available to establish exactly what has occurred, so that when inter-laboratory comparisons are made, “like-for-like” comparisons are made.

In many laboratories, the “as received” sample is analysed. Usually, a representative portion of the sample submitted to the laboratory is taken and analysed. Results are then expressed on the “as received” basis. Alternatively, results may be expressed on an air-dried basis (i.e. sample type D, with no material removed) or on a dry weight basis (i.e. sample type F, again with no material removed).

In some laboratories, the “as received” sample is analysed after having its extraneous material such as large stones etc removed. However, it is not always clear how the result is expressed. The result may be expressed on the “as received” basis (i.e. sample type A, or as sample type B (i.e. on the “as received” sample taking into account removal of the extraneous material). Alternatively, the result may be reported on an air-dried basis (i.e. sample type D, with no extraneous material removed) or on a dry weight basis (i.e. sample type F, again with no extraneous material removed). Also, results may be expressed on an air-dried basis (i.e. sample type E, with extraneous material removed) or on a dry weight basis (i.e. sample type G, again with extraneous material removed).

In some laboratories, sample D is analysed (i.e. the air-dried sample with no extraneous material removed) and result expressed on an air-dried basis. In some laboratories, sample E is analysed (i.e. the air-dried sample with extraneous material removed) and result expressed on an air-dried basis, but not making it clear whether removal of extraneous material has been taken into account or not.

Few laboratories analyse sample F or G and report result expressed on sample F or G. In addition, even fewer laboratories analyse the extraneous material removed, i.e. sample C.

Unless sufficient information is made available, it is impossible to make direct like-for-like inter-laboratory comparison of results provided by different laboratories undertaking different practices.

Table I3 highlights the calculations (based on the example composition values given in Table I2) used to express the results of the types of samples that can be analysed. For inter-laboratory comparisons it is essential to know what type of sample has been analysed and how, and on what sample type, the result is expressed.

Table I3 Sample analysed and expression of result

Sample analysed	Result of sample analysed (mg/kg)	Result expressed on sample type	Calculation for how result is to be expressed* (mg/kg)
A	XA	A	XA
		B	(XA x 1000) / (1000-50)
		D	(XA x 1000) / (1000-150)
		E	(XA x 1000) / (1000-200)
		F	(XA x 1000) / (1000-170)
		G	(XA x 1000) / (1000-220)
B	XB	A	(XB x (1000-50)) / 1000
		B	XB
		D	(XB x (1000-50)) / (1000-150)
		E	(XB x (1000-50)) / (1000-200)
		F	(XB x (1000-50)) / (1000-170)
		G	(XB x (1000-50)) / (1000-220)
D	XD	A	(XD x (1000-150)) / 1000
		B	(XD x (1000-150)) / (1000-50)
		D	XD
		E	(XD x (1000-150)) / (1000-200)
		F	(XD x (1000-150)) / (1000-170)
		G	(XD x (1000-150)) / (1000-220)
E	XE	A	(XE x (1000-200)) / 1000
		B	(XE x (1000-200)) / (1000-50)
		D	(XE x (1000-200)) / (1000-150)
		E	XE
		F	(XE x (1000-200)) / (1000-170)
		G	(XE x (1000-200)) / (1000-220)
F	XF	A	(XF x (1000-170)) / 1000
		B	(XF x (1000-170)) / (1000-50)
		D	(XF x (1000-170)) / (1000-150)
		E	(XF x (1000-170)) / (1000-200)
		F	XF
		G	(XF x (1000-170)) / (1000-220)
G	XG	A	(XG x (1000-220)) / 1000
		B	(XG x (1000-220)) / (1000-50)
		D	(XG x (1000-220)) / (1000-150)
		E	(XG x (1000-220)) / (1000-200)
		F	(XG x (1000-220)) / (1000-170)
		G	XG

* These calculations are based on the example composition values given in Table I2.

A The determination of easily liberated sulphide in “as received” samples following phosphoric acid steam distillation and spectrophotometric determination using DPD

A1 Performance characteristics of the method

A1.1	Substances determined	Easily liberated sulphide.
A1.2	Type of sample	“As received” soil samples.
A1.3	Basis of method	The “as received” soil sample is treated with phosphoric acid and immediately steam-distilled into 20 ml of 0.1M sodium hydroxide solution. An aliquot of the distillate is treated with DPD-sulphuric acid reagent and, following addition of potassium dichromate solution, the absorbance of the resulting blue colour is measured spectrophotometrically at about 670 nm.
A1.4	Range of application	Typically, up to 25 µg of sulphide in the absorbance solution. This is equivalent to about up to 100 mg/kg in the “as received” soil. The range can be extended, see section A7.8, note k.
A1.5	Calibration curve	All calibrations are linear over the range of application of the method.
A1.6	Interferences	Any substance, which is co-distilled under the conditions used resulting in a coloured or turbid solution will interfere with the determination. Heavy metal sulphides may be only partially affected depending on the metal present. Sulphide in excess of 100 mg/kg inhibits colour formation. High levels of sulphide will inhibit any colour formation, potentially leading to a false-negative result being reported. If the colour development is automated, the inhibition is likely to go un-noticed. If high levels of sulphide are suspected but colouration doesn’t occur, a quick check can be carried out using lead acetate paper before the addition of reagents. In the presence of sulphide, lead acetate paper produces a black colouration. Dilution of a distillate that is high in sulphide should produce a colour within the calibrated range. Cyanide at concentrations greater than 500 mg/kg may retard colour formation.
A1.7	Standard deviation	See Table A1.

A1.8	Limit of detection	Approximately 0.5 µg of sulphide (as S^{2-}) can be detected in the absorbance solution. This equates to about 0.1 mg/kg of sulphide in the "as received" soil.
A1.9	Sensitivity	Approximately 5 µg of sulphide (as S^{2-}) typically gives an absorbance value of 0.20 units when measured in 10 mm cells. This equates to about 4 mg/kg of sulphide in the "as received" soil.
A1.10	Bias	See Table A1.

A2 Principle

The "as received" sample is well mixed and a representative portion taken for analysis. To this portion, phosphoric acid is added and the mixture immediately steam-distilled. The distillate is collected in 0.1M sodium hydroxide solution, and following distillation, made to a known volume with water. An aliquot of the distillate, typically 10 ml, is taken and the sulphide concentration determined spectrophotometrically, following addition of acidified DPD (N-N-diphenyl-p-phenylenediamine) and potassium dichromate solution. The absorbance is measured at about 670 nm.

A3 Hazards

Appropriate precautions should be taken when handling soils containing sulphide and other contaminants, especially when acid is added to these soils, as toxic gases may be released. Hydrogen sulphide is poisonous. Appropriate personal protective equipment should be worn where necessary and the analysis carried out in an appropriate fume cupboard.

A4 Reagents

All reagents should be of sufficient purity that they do not give rise to significant interferences. Purity should be checked for each batch of materials by running procedural blanks with each batch of samples analysed.

A4.1 Water. This should be distilled, deionised or of similar grade quality.

A4.2 Sodium hydroxide solution (0.1M). Add 4 g of sodium hydroxide to approximately 800 ml of water (A4.1). Cool and mix well. Make to 1000 ml with water. This solution may be stored at room temperature for up to one year.

A4.3 Concentrated orthophosphoric acid (85 %).

A4.4 Concentrated hydrochloric acid (SG 1.16).

A4.5 Hydrochloric acid (50 % v/v). Add 500 ml of concentrated hydrochloric acid (A4.4) to 500 ml of water (A4.1) and mix well. This solution may be stored at 20 °C for up to 12 months.

A4.6 Concentrated sulphuric acid (SG 1.84).

A4.7 Sulphuric acid (15 % v/v). Carefully, slowly add 150 ml of concentrated sulphuric acid (A4.6) to approximately 800 ml of water (A4.1) and mix well. Allow the solution to cool, make to 1000 ml with water, and again mix well. This solution may be stored at 20 °C for up to 12 months.

A4.8 Sodium carbonate solution. Add 80.0 g of anhydrous sodium carbonate to approximately 800 ml of water (A4.1) and mix well. Make to 1000 ml with water and mix again. This solution may be stored at 20 °C for up to 12 months.

A4.9 Zinc acetate solution. Add 110.0 g of zinc acetate dihydrate to approximately 800 ml of water (A4.1) and mix well. To this solution, and to prevent hydrolysis, add 1 ml of concentrated hydrochloric acid (A4.4). Mix well and make to 1000 ml with water. Mix well. This solution may be stored at 20 °C for up to 12 months.

A4.10 Potassium dichromate solution. Add 2.00 g of anhydrous potassium dichromate to a 1000-ml volumetric flask and dissolve in water (A4.1). Make to 1000 ml with water and mix well. This solution may be stored at 20 °C for up to 12 months.

A4.11 Acidified DPD solution. Add 7.5 g of N-N-diethyl-p-phenylenediamine sulphate (DPD) to approximately 450 ml of 15 % sulphuric acid (A4.7) and mix well. Make to 500 ml with 15 % sulphuric acid (A4.7). This solution may be stored at 20 °C for up to 12 months.

A4.12 Potassium iodate-iodide solution (0.00417M). Add 0.8920 g of potassium iodate (previously dried for approximately 1 hour at 110 °C) and 8.7 g of potassium iodide to approximately 500 ml of water (A4.1). Mix well. To this solution, add 0.6 g of sodium hydrogencarbonate and mix well. Make to 1000 ml with water and mix well. This solution may be stored at 20 °C for up to 2 months.

A4.13 Aqueous starch indicator solution (1 % m/m) containing mercury iodide (1 % m/m) preservative. This solution may be commercially available. This solution may be stored at 20 °C for up to 12 months.

A4.14 Sodium thiosulphate solution (0.25M / 0.25N). Add 62.50 g of sodium thiosulphate pentahydrate to approximately 950 ml of water (A4.1) and mix well. To preserve the solution, add 1 ml of chloroform and mix well. Make to 1000 ml with water and mix well. This solution may be commercially available. This solution may be stored at 20 °C for up to 2 months.

A4.15 Sodium thiosulphate solution (0.0125M / 0.0125N). Add 50.00 ml of sodium thiosulphate solution (A4.14) to a 1000-ml volumetric flask containing approximately 900 ml of water. To preserve the solution, add 1 ml of chloroform and mix well. Make to 1000 ml with water. Mix well. This solution should be prepared and standardised on the day of use, as the solution is not stable for long periods of time. This solution may be commercially available. The solution should be standardised using potassium iodate-iodide solution (A4.12).

A4.15.1 Standardisation of sodium thiosulphate solution (A4.15). To 20.00 ml of potassium iodate-iodide solution (A4.12) contained in a conical flask, add 2.0 ml of 50 % v/v hydrochloric acid (A4.5). Mix well. Dilute the solution to 200 ml with water (A4.1) and titrate using the sodium thiosulphate solution to be standardised (A4.15). When the colour of the solution becomes pale straw-coloured, add 2 ml of starch indicator solution

(A4.13). Continue titration until the blue colour just disappears. Note the volume required (V ml).

(20.00 ml of 0.00417M potassium iodate-iodide solution (A4.12) should require 40.00 ml of 0.0125M sodium thiosulphate solution).

If the sodium thiosulphate solution to be standardised is not exactly 0.0125M, a factor, F, can be calculated using

$$F = 40 / V$$

A4.16 Standard stock sulphide suspension (typically, 5 mg/l as S^{2-}). Wash several crystals of sodium sulphide nonahydrate with water (A4.1) and (avoiding skin contact) dry quickly on filter paper. Immediately after this, weigh quickly but accurately, approximately 0.040 g of the sulphide crystals into a 1000-ml volumetric flask and dissolve in about 500 ml of water (A4.1). Swirl the solution gently. Dissolution should occur quickly. Immediately the sulphide dissolves, add 20 ± 1 ml of sodium carbonate solution (4.8). Mix well and add to the solution 20 ± 1 ml of zinc acetate solution (4.9). Mix well and make to 1000 ml with water (A4.1). Standardise the gelatinous suspension of sulphide as described in sections A4.16.1 - A4.16.3.

A4.16.1 Standardisation of sulphide suspension. The standard stock sulphide suspension (A4.16) should be thoroughly shaken and 200.0 ml (i.e. typically, 1 mg of sulphide) transferred quickly to a 250 ml measuring cylinder. Attempts to transfer the suspension directly to the centrifuge tubes may result in some settlement of the suspension. In addition, the suspension of zinc sulphide is very gelatinous and exhibits a tendency to adhere to the surface of glassware. The volume of suspension should therefore be quantitatively transferred as quickly as possible into suitable centrifuge tubes, rinsing the cylinder, as necessary, with water and transferring the rinsings to the tubes. Centrifuge the tubes at approximately 2000 rpm for about 5 minutes. The supernatant liquid should be discarded and the residues mixed with a small amount of water to break up any lumps.

Into a conical flask, add 5.00 ml of potassium iodate-iodide solution (A4.12) and 2.0 ml of 50 % v/v hydrochloric acid (A4.5). Mix well. The contents of the centrifuge tubes should then be quantitatively transferred into the conical flask. It may be necessary to rinse out the centrifuge tubes with a little water, returning the water to the conical flask.

The iodine produced in the conical flask should be titrated with the standardised sodium thiosulphate solution (A4.15). When the colour of the solution becomes pale straw-coloured, add several drops (0.2 - 0.5 ml) of starch indicator solution (A4.13). Continue titration until the blue colour just disappears. Note the volume required (T1 ml)

A4.16.2 The procedure described in section A4.16.1 should be repeated and the volume of standardised sodium thiosulphate solution (A4.15) recorded (T2 ml). The two titrations (T1 and T2) should agree to within 0.1 ml. If not, the whole procedure should be repeated using two further aliquots. The mean titre, T3, should be calculated, i.e. T3 = (T1 + T2) / 2.

A4.16.3 To a conical flask, add 5.00 ml of potassium iodate-iodide solution (A4.12) and 2.0 ml of 50 % v/v hydrochloric acid (A4.5). Mix well. To this flask, add about 200 ml of water (A4.1). The iodine produced in the conical flask should be titrated with the standardised sodium thiosulphate solution (A4.15). When the colour of the solution

becomes pale straw-coloured, add several drops (0.2 - 0.5 ml) of starch indicator solution (A4.13). Continue titration until the blue colour just disappears. Note the volume required (T4 ml).

The concentration of sulphide, C_s, as S^{2-}, in the suspension is given by

$$C_s = (T4 - T3) \times F \quad \text{mg/l (as } S^{2-})$$

Where F is the factor given in section A4.15.1.

(1.00 ml of 0.00417M potassium iodate-iodide solution is equivalent to 0.40 mg of sulphide, as S^{2-}. Therefore, 2.5 ml of 0.00417M potassium iodate-iodide solution is equivalent to 200 ml of an 5 mg/l solution of sulphide, as S^{2-}.)

A4.16.4 Standard stock sulphide suspension (typically, 0.5 mg/l as S^{2-}). The standardised stock sulphide suspension (A4.16) should be thoroughly shaken and 100.0 ml transferred quickly to a 1000-ml volumetric flask. Make to 1000 ml with water and mix well. This suspension should be used on the day of preparation.

A5 Apparatus

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

A5.1 Analytical balance capable of weighing to 0.0001g.

A5.2 Steam distillation equipment.

A5.3 Spectrophotometer capable of measuring at about 670 nm.

A6 Sample collection, preservation and storage

Samples should be collected in glass or plastic containers and the container filled to the top to minimise any headspace. Samples should be analysed as soon as possible. If storage of samples is unavoidable, samples should be kept in a refrigerator at a temperature between 3 - 7 °C and may be stored for up to 7 days. Further guidance can be found elsewhere[3] in this series.

A7 Analytical procedure

Step	Procedure	Note
A7.1	Weigh out M g (typically, 5.0 g) of a representative amount of the “as received” soil sample, see notes a - c.	(a) The sample may be placed directly into the distillation equipment. (b) If the result is to be reported on a dry weight basis, rather than an “as received” basis, a portion of the same sample should be

taken and analysed for its dry matter content, %DM.

(c) If “as received” soil is analysed, it may be necessary to carry out replicate analysis to improve precision.

A7.2 To the sample, add 30.0 ml of phosphoric acid (A4.3). Immediately, connect the distillation equipment (note d) and steam distil the mixture into 20 ml of sodium hydroxide solution (A4.2) until nearly 180 ml of distillate has been collected. When sufficient distillate has been collected, stop the distillation process and remove the receiving flask. Make to volume, V_D ml, (typically, 200 ml) with water (A4.1). Mix well. The solution is now ready for sulphide determination.

(d) Apparatus are commercially available for generating steam and undertaking the determination automatically.

A7.3. Standard sulphide solutions are not taken through the distillation process, before being determined spectrophotometrically, but would need to be if recovery estimates were to be determined.

A7.4 With each batch of samples, a blank should be run, whereby the representative amount of soil is replaced with an equal mass of water (A4.1). See note e. Similarly, a soil reference matrix material may be used, whereby a soil is spiked with a known concentration of sulphide, ideally, at a level appropriate for the samples being analysed. Both spiked and un-spiked soil samples would need to be analysed. See note f.

(e) The blank is used to evaluate any contamination or memory effects.

(f) The use of a soil reference matrix material enables an estimate of the recovery to be made on a batch to batch basis.

A7.5 A calibration graph should be prepared, for example by adding 0.0, 10.0, 20.0, 30.0, 40.0 or 50.0 ml of the 0.5 mg/l standard sulphide suspension (A4.16.4) to separate 50 ml volumetric flasks. See notes g and h.

(g) This equates to 0, 5, 10.0, 15.0, 20.0 or 25.0 µg of sulphide (as S^{2-}) in each 50 ml flask.

(h) Commercial apparatus are available allowing these procedures to be carried out automatically, but usually on a reduced scale.

A7.6 To each 50 ml flask, add 1.0 ml of acidified DPD solution (A4.11) and 1.0 ml of potassium dichromate solution (A4.10). Make to 50 ml with water (A4.1). Mix well, and allow the solution to stand for 10 minutes, see note i. The absorbance

(i) It usually takes about 8 minutes for a stabilised colour to develop which is generally stable for up to about 2 hours.

	of the solution should be measured at the wavelength showing maximum absorbance, i.e. λ_{max}, see note j.	(j) The wavelength showing maximum absorbance is usually about 670 nm, but this should be checked to allow for any error in wavelength calibration of the instrument.
A7.7	Prepare a calibration graph of absorbance versus amount of sulphide in 50 ml of solution.	
A7.8	Repeat section A7.6 using an aliquot, V_A ml (typically, 10.0 ml) of the distillate from section A7.2. From the calibration graph, determine the amount, R, of sulphide in the absorbance solution. See note k.	(k) If the absorbance of the solution is greater than that shown for the highest standard sulphide concentration, consideration should be given to repeating the distillation using a smaller quantity of sample (A7.1) increasing the distillation volume (A7.2) or changing the volume of aliquot taken for the determination (A7.8).
A7.9	An AQC sample, at an appropriate level (see note l) prepared from a separate standardised sulphide stock suspension to that described in section A4.16.4 should be analysed at the end of each batch of analyses to provide an external check on the calibration.	(l) For example, 30 ml of a 0.5 mg/l standard sulphide suspension (i.e. 15 µg) treated as described in section A7.8.

A8 Calculation of results

The amount of sulphide, A mg/kg, in the “as received” soil analysed (expressed on an “as received” basis) is given by

$$A = (R \times V_D) / (V_A \times M) \quad \text{mg/kg}$$

Where A is the amount of sulphide in the “as received” soil (m/kg),
R is the amount (µg in 50 ml) from the calibration graph (section A7.8),
V_D is the volume (ml) of distillate (section A7.2, typically 200 ml) and
V_A is the aliquot volume (ml) of distillate (section A7.8, typically 10 ml) and
M is the amount of “as received” soil (section A7.1, typically 10 g).

The amount of sulphide, A_{DW} mg/kg, in the “as received” soil analysed (expressed on a dry weight basis) is given by

$$A_{DW} = (A \times 100) / DM$$

where

A_{DW} is the amount of sulphide in the "as received" soil (mg/kg) on a dry weight basis
A is the amount of sulphide in the "as received" soil (mg/kg) on an "as received" basis,
DM is the percentage dry matter content (note b, section A7.1)

Table A1 Performance data

These data are based on automated instrumental procedures[4] (notes d and g).

	Soil spiked at 2 mg/kg			Soil spiked at 8 mg/kg		
Soil type	Bias (%)	RSD (%)	SD (mg/kg)	Bias (%)	RSD (%)	SD (mg/kg)
Sand	-6.86	12.35	0.248	-3.32	5.14	0.415
Clay	-3.69	8.73	0.175	-1.33	4.94	0.399
Top soil	-6.08	6.22	0.125	-1.81	5.16	0.417

Analysis based on 11 batches, analysed in duplicate.
RSD is relative standard deviation
SD is standard deviation
Performance data provided by BAE SYSTEMS Environmental.

B The determination of easily liberated sulphide in air-dried samples following sulphuric acid steam distillation and spectrophotometric determination using DPD

B1 Performance characteristics of the method

B1.1	Substances determined	Easily liberated sulphide.
B1.2	Type of sample	Air-dried samples of soil and contaminated land.
B1.3	Basis of method	The air-dried soil sample is treated with sulphuric acid and immediately steam-distilled into 40 ml of 0.1M sodium hydroxide solution. An aliquot of the distillate is treated with DPD-sulphuric acid reagent, and following addition of potassium dichromate solution, the absorbance of the resulting blue colour is measured spectrophotometrically at about 664 nm.
B1.4	Range of application	Typically, up to 50 µg of sulphide in the absorbance solution. This is equivalent to a range covering 5 - 250 mg/kg in the air dried soil. The range may be extended, see section B8.10, note k.
B1.5	Calibration curve	Linear over the range of application.
B1.6	Standard deviation	See Table B1.
B1.7	Limit of detection	Approximately 0.5 µg of sulphide (as S^{2-}) can be detected in the absorbance solution. This equates to about 3 mg/kg of sulphide in the air-dried soil.
B1.8	Sensitivity	Approximately 2 µg of sulphide (as S^{2-}) typically gives an absorbance value of 0.060 units when measured in 10 mm cells. This equates to about 10 mg/kg of sulphide in the air-dried soil.
B1.10	Bias	See Table B1.

B2 Principle

The air-dried sample is well mixed and an homogenised portion taken for analysis. To this portion, sulphuric acid is added and the mixture immediately steam-distilled. The distillate is collected in 40 ml of 0.1M sodium hydroxide solution and following distillation made to a known volume with water. An aliquot of the distillate, typically 2.0 ml, is taken and the sulphide concentration determined spectrophotometrically, following addition of acidified DPD (N-N-diphenyl-p-phenylenediamine) and potassium dichromate solution. The absorbance is measured at about 664 nm.

B3 Interferences

Some sulphides, especially heavy metal sulphides, or polysulphides may be only partially affected, liberating a portion of the hydrogen sulphide theoretically expected under the conditions described. This will depend on the metal sulphides present in the sample. In addition, any substance, which is co-distilled under the conditions used and which results in the formation of a coloured or turbid solution will interfere with the determination. Sulphide in excess of 100 mg/kg inhibits colour formation. High levels of sulphide will inhibit any colour formation, potentially leading to a false-negative result being reported. If the colour development is automated, the inhibition is likely to go un-noticed. If high levels of sulphide are suspected but colouration doesn't occur, a quick check can be carried out using lead acetate paper before the addition of reagents. In the presence of sulphide, lead acetate paper produces a black colouration. Dilution of a distillate that is high in sulphide should produce a colour within the calibrated range.

Cyanide at concentrations greater than 500 mg/kg may retard colour formation.

At low concentrations of sulphide, a light pink colour may be observed when colour development is complete. With increasing sulphide concentrations, colour develops from pink to purple and finally to blue. If colours such as red, yellow or bright green are observed, these may be due to the formation of non-sulphide DPD-complexes. Although measurement at the specific wavelength (i.e. about 664 nm) should eliminate these interferences, their formation may inhibit the DPD reagent reacting with sulphide, or lead to insufficient quantities of DPD reagent being present in solution for complexing with sulphide. This will lead to incomplete reaction of DPD reagent with sulphide present in the distillate, and lead to the determination and subsequent reporting of falsely low sulphide concentrations.

B4 Hazards

Appropriate precautions should be taken when handling soils containing sulphide and other contaminants, especially when acid is added to these soils leading to the release of toxic gases. Hydrogen sulphide is poisonous. Appropriate personal protective equipment should be worn where necessary and the analysis carried out in an appropriate fume cupboard.

B5 Reagents

All reagents should be of sufficient purity that they do not give rise to significant interference. Purity should be checked for each batch of materials by running procedural blanks with each batch of samples analysed.

B5.1 Water. This should be deionised or distilled or of similar quality.

B5.2 Sodium hydroxide solution (2M). Add 80.0 g of sodium hydroxide to approximately 900 ml of water (B5.1). Cool the solution and mix well. Make to 1000 ml with water (B5.1). This solution may be stored at room temperature for up to one month.

B5.3 Sodium hydroxide solution (0.1M). Add 4.0 g of sodium hydroxide to approximately 900 ml of water (B5.1). Cool the solution and mix well. Make to 1000 ml with water (B5.1). This solution may be stored at room temperature for up to one month.

B5.4 Sodium hydroxide solution (0.05M). Add 4.0 g of sodium hydroxide to approximately 1900 ml of water (B5.1). Cool the solution and mix well. Make to 2000 ml with water (B5.1). This solution may be stored at room temperature for up to one month.

B5.5 Concentrated hydrochloric acid (SG 1.16).

B5.6 Hydrochloric acid (50 % v/v). Add 500 ml of concentrated hydrochloric acid (B5.5) to 500 ml of water (B5.1) and mix well. This solution may be stored at room temperature for up to 6 months.

B5.7 Concentrated sulphuric acid (SG 1.84).

B5.8 Sulphuric acid (15 % v/v). Cautiously and slowly, add 150 ml of concentrated sulphuric acid (B5.7) to 800 ml of water (B5.1) and mix well. Allow the solution to cool, make to 1000 ml with water (B5.1) and mix well. This solution may be stored at room temperature for up to 2 months.

B5.9 Sulphuric acid (10 % v/v). Cautiously and slowly, add 100 ml of concentrated sulphuric acid (B5.7) to 800 ml of water (B5.1) and mix well. Allow the solution to cool, make to 1000 ml with water (B5.1) and mix well. This solution may be stored at room temperature for up to 2 months.

B5.10 Sodium carbonate solution (8 % m/v). Add 8.0 g of anhydrous sodium carbonate to approximately 80 ml of water (B5.1) and mix well. Make to 100 ml with water and mix again. This solution may be stored at room temperature for up to one month.

B5.11 Potassium dichromate solution. Add 0.20 g of anhydrous potassium dichromate to a 100-ml volumetric flask and dissolve in water (B5.1). Make to 100 ml with water (B5.1) and mix well. This solution may be stored at 5 ± 3 °C for up to 2 months.

B5.12 Acidified DPD solution. Add 1.5 g of N-N-diethyl-p-phenylenediamine sulphate (DPD) to approximately 85 ml of 15 % sulphuric acid (B5.8) and mix well. Make to 100 ml with 15 % sulphuric acid (B5.8). This solution may be stored at 5 ± 3 °C for up to 2 months.

B5.13 Potassium iodate-iodide (0.00417M). Dissolve 8.70 ± 0.05 g of potassium iodide, 0.8920 ± 0.0005 g of potassium iodate (previously dried for 1 hour at 110 °C) and 0.60 ± 0.05 g of sodium bicarbonate in approximately 900 ml of water (B5.1). Mix well. Make to 1000 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to one month.

B5.14 Aqueous starch indicator. This is commercially available.

B5.15 Sodium thiosulphate solution (0.025M / 0.025N). Add 6.250 g of sodium thiosulphate pentahydrate to approximately 300 ml of water (B5.1) and mix well. Add 0.40 ± 0.01 g of sodium hydroxide and mix well. Make to 1000 ml with water (B5.1) and mix well. This solution may be stored at 5 ± 3 °C for up to one week. (This solution may be commercially available).

B5.15.1 Standardisation of sodium thiosulphate solution. Add 20.0 ± 0.05 ml of potassium iodate-iodide solution (B5.13) to a 250 ml conical flask. Add 5.0 ± 0.2 ml of hydrochloric acid (B5.6) and approximately 50 ml of water (B5.1). Mix well. Titrate the solution with sodium thiosulphate solution (B5.15) to be standardised until the colour of the

solution is pale yellow or straw-coloured. Add a small amount of iodine indicator (B5.14) and mix. Continue titration with drop-wise addition of the sodium thiosulphate solution (B5.15) mixing continuously, until the blue colour first disappears. Note the titration volume, t ml. Calculate a factor using the equation:

$$F = \frac{20}{t}$$

B5.16 Standard stock sulphide solution (nominally, 500 mg/l as S^{2-}). Wash several crystals of sodium sulphide nonahydrate with water (B5.1) and (avoiding skin contact) dry quickly on filter paper. Immediately after this, weigh quickly but accurately, approximately 2.0 g of the sulphide crystals into a 500-ml volumetric flask and dissolve in about 250 ml of water (B5.1). Swirl the solution gently. Dissolution of the crystals should occur quickly. Immediately the sulphide dissolves, add 50 ± 1 ml of sodium carbonate solution (B5.10). Mix well and make to 500 ml with water (B5.1). This solution may be stored at 5 ± 3 °C for up to one month and should be standardised before use (see sections B5.16.1 - B5.16.2).

B5.16.1 Standardisation of standard stock sulphide solution. Add 20.0 ± 0.05 ml of potassium iodate-iodide solution (B5.13) to a 250 ml conical flask. Add 5.0 ± 0.2 ml of 50 %hydrochloric acid solution (B5.6) and approximately 50 ml of water (B5.1). Mix the solution well. Add 5.00 ± 0.05 ml (i.e. 2.5 mg of sulphide) of the standard stock sulphide solution (B5.16) to be standardised and mix well. Titrate the solution with standardised sodium thiosulphate solution (B5.15) until the colour of the solution is pale yellow or straw-coloured. Add a small amount of iodine indicator (B5.14) and mix. Continue titration with drop-wise addition of the standardised sodium thiosulphate solution (B5.15) mixing continuously, until the blue colour first disappears. Note the titration volume, T1 ml.

B5.16.2 Blank titration. Add 20.0 ± 0.05 ml of potassium iodate-iodide solution (B5.13) to a 250 ml conical flask. Add 5.0 ± 0.2 ml of 50 % hydrochloric acid solution (B5.6) and approximately 50 ml of water. Mix well. Titrate the solution with standardised sodium thiosulphate solution (B5.15) until the colour of the solution is pale yellow or straw-coloured. Add a small amount of iodine indicator (B5.14) and mix. Continue titration with drop-wise addition of the standardised sodium thiosulphate solution (B5.15) mixing continuously, until the blue colour first disappears. Note the titration volume, T2 ml (theoretically, this volume is expected to be 20 ml).

The concentration, C, of the standardised stock sulphide solution (B5.16) is given by:

$$C = (T2 - T1) \times 80 \times F \quad \text{mg/l}$$

Where F is the thiosulphate concentration factor (B5.15.1).

B5.17 Standard working sulphide solutions. For example, calibration solutions at nominal concentrations of 5.0, 10.0, 15.0, 20.0 and 25.0 mg/l should be prepared in 100 ml volumetric flasks from the standardised stock sulphide solution (B5.16)

After the standard stock sulphide solution (B5.16) has been standardised, the volume of standardised stock sulphide solution (B5.16) required to make 100 ml of each standard working sulphide solution can be calculated using the following formula.

$$V = Vr \times (Cr / Cs)$$

Where V is the volume (ml) of standardised standard stock sulphide solution (B5.16);
Vr is the volume (ml) of standard working sulphide solution required;
Cr is the concentration (mg/l) of standard working sulphide solution required; and
Cs is the concentration (mg/l) of standardised stock sulphide solution (B5.16).

The volume of standardised working sulphide solution (B5.16) should be made to 100 ml with 0.05M sodium hydroxide solution (B5.4). These solutions should be prepared on the day of use.

If the concentration of the standardised stock sulphide solution (B5.16) is exactly 500 mg/l as S^{2-}, then 1.0, 2.0, 3.0, 4.0 and 5.0 ml volumes of standardised standard stock sulphide solution (B5.16) made to 100 ml with 0.05M sodium hydroxide solution (B5.4) will create standard working sulphide solutions of concentrations 5.0, 10.0, 15.0, 20.0 and 25.0 mg/l respectively. This is equivalent to 10, 20, 30, 40 and 50 µg of sulphide (as S^{2-}) contained in the 2 ml aliquots taken for calibration.

B6 Apparatus

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

B6.1 Analytical balance capable of weighing to 0.0001g.

B6.2 Steam distillation equipment, capable of producing 50 ml of distillate in 90 seconds.

B6.3 Spectrophotometer capable of measuring at about 664 nm.

B7 Sample collection, preservation and storage

This method has been performance tested using air-dried samples (i.e. air at less than 30 °C) and may not be suitable for samples containing significant amounts of water. Once dried, the sample is ground to a particle size less than 2 mm. The use of an air-dried and ground sample rather than an “as received” sample enables a more homogeneous sub-sample to be taken. When air-dried samples are stored below 20 °C for up to 21 days, significant loss of sulphide does not occur. However, the procedures used to prepare crushed, ground, sieved and/or air-dried samples may adversely affect easily liberated sulphide present within the original sample. If hydrogen sulphide is released from the sample (i.e. its odour can be detected) whilst these procedures are being carried out, alternative procedures should be used, or consideration given to analysing an “as received” sample. When “as received” samples are analysed, care should be taken to ensure that the sub-sample used for analysis is representative of the bulk material being sampled and is ideally, homogeneous. This is especially important when smaller quantities of samples are required, for example, for repeat analyses, where high concentrations are determined or suspected. “As received” samples should be stored below 10 °C. Further guidance can be found elsewhere[3] in this series.

B8 Analytical procedure

Step	Procedure	Note
B8.1	Add 40 ml of 0.1M sodium hydroxide solution (B5.3) to a receiving flask, V_D ml (typically, 100 ml) of the steam distillation apparatus (B6.2). See note a.	(a) Apparatus are commercially available for generating steam and undertaking the determination automatically.
B8.2	Weigh out M g (typically, 10.0 g) of an homogenised air-dried sample, see notes b and c.	(b) The sample may be placed directly into the distillation flask. (c) If the result is to be reported on a dry weight basis (at say 105 °C) rather than on an air-dried basis, a portion of the same sample should be taken and analysed for its dry matter content, % DM.
B8.3	To the sample, add 25 ml of 10 % sulphuric acid solution (B5.9). Immediately, connect the distillation equipment (note d) and steam distil the mixture until nearly 50 ml of distillate has been collected.	(d) Ensure losses of hydrogen sulphide are minimised.
B8.4	When sufficient distillate has collected, stop the distillation process and remove the receiving flask. Make to V_D ml (typically, 100 ml) with water (B5.1). The solution is now ready for sulphide determination.	
B8.5	Standard sulphide solutions are not taken through the distillation process, before being determined spectrophotometrically, but would need to be if recovery estimates were needed to be determined.	
B8.6	With each batch of samples, a blank should run, whereby the homogenised soil is replaced with an equal mass of water (B5.1). See note e. Similarly, a soil reference matrix material may be used, whereby a soil is spiked with a known concentration of sulphide, ideally, at a level appropriate for the samples being analysed. Both spiked and un-spiked soils would need to be analysed. See note f.	(e) The blank is used to evaluate any contamination or memory effects. (f) The use of a soil reference matrix material enables an estimate of the recovery to be made on a batch to batch basis.

B8.7 An aliquot, V_A ml, typically 2.0 ml, of the working sulphide standard solutions (B5.17) should be added to a series of 50 ml volumetric flasks, see notes g and h.

(g) Commercial apparatus are available allowing these procedures to be carried out automatically, but usually on a reduced scale.

(h) This volume equates to 10, 20, 30, 40 and 50 µg of sulphide (as S^{2-}) in the 50 ml flasks.

B8.8 To each 50 ml flask, add 3.0 ml of potassium dichromate solution (B5.11), swirl the contents and add 3.0 ml of acidified DPD solution (B5.12). Make to 50 ml with water (B5.1). Mix well, and allow the solution to stand for 10 minutes, see note i. Read the absorbance of the solution in a 10 mm path-length cell using water as blank solution. The absorbance of the solution should be measured at the wavelength showing maximum absorbance, i.e. λ_{max}, see note j.

(i) It usually takes about 8 minutes for a stabilised colour to develop which is generally stable for up to about 2 hours.

(j) The wavelength showing maximum absorbance is usually 664 nm, but this should be checked to allow for any error in wavelength calibration of the instrument.

B8.9 Prepare a calibration graph of absorbance versus amount of sulphide in 50 ml of solution.

B8.10 Repeat section B8.8 using an aliquot (V_A ml) , typically 2.0 ml, of the distillate from section B8.4. From the calibration graph, determine the amount, R, of sulphide in the absorbance solution. See note k.

(k) If the absorbance of the solution is greater than that shown for the highest standard sulphide concentration, consideration should be given to repeating the distillation using a smaller quantity of sample (B8.2) or increasing the distillation volume (B8.4) or reducing the volume of aliquot taken for the determination (B8.10).

B8.11 An AQC sample, at an appropriate level (see note l) prepared from a separate standardised sulphide stock solution to that described in section B5.16 should be analysed at the end of each batch of analyses to provide an external check on the calibration.

(l) For example, 2.0 ml of a 20 mg/l standard sulphide solution (i.e. 40 µg) treated as described in section B8.10.

B9 Calculation of results

The amount of sulphide, A mg kg^{-1}, in the air-dried soil analysed (expressed on an air-dried basis) is given by

$$A = (R \times V_D) / (V_A \times M) \quad \text{mg/kg}$$

Where A is the amount of sulphide in the air dried soil (mg/kg),
R is the amount of sulphide (µg) from the calibration graph (section B8.10),
V_D is the volume (ml) of distillate (section B8.4, typically 100 ml) and
V_A is the aliquot volume (ml) of distillate (section B8.10, typically 2.0 ml) and
M is the amount (g) of air-dried soil (section B8.2, typically 10 g).

To convert the result from an air-dried basis, A, to a dry weight basis, A_{DW}, the following equation can be used,

$$A_{DW} = (A \times 100) / DM$$

Where A_{DW} is the amount of sulphide in the soil (mg/kg) on a dry weight basis
A is the amount of sulphide in the soil (mg/kg) on an air-dried basis,
DM is the percentage dry matter content (note c, section B8.2) in the air-dried sample.

Table B1 Performance data

Performance data are based upon eleven duplicate batches of analysis, spread over 11 days, providing 22 individual results for each test sample. The data are based on automated instrumental procedures (notes a and g).

	% Recovery 5 mg/l S^{2-} spike	% Recovery 20 mg/l S^{2-} spike	Precision (%RSD)	Bias (%)
Clay soil	110.2	99.1	12.7	
Loam soil	71.5	80.0	15.1	
Sandy soil	100.8	106.7	11.6	
5 mg/l standard			8.0	-6.1
20 mg/l standard			2.5	-0.7

RSD is relative standard deviation
Data provided by Severn Trent Laboratories

C The determination of easily liberated sulphide in “as received” samples following phosphoric acid steam distillation

C1 Performance characteristics of the method

C1.1	Substances determined	Easily liberated sulphide.
C1.2	Type of sample	“As received” samples of soil and contaminated land.
C1.3	Basis of method	The “as received” soil sample is treated with phosphoric acid and immediately steam-distilled into 25 ml of 1M sodium hydroxide solution. An aliquot of the distillate is spectrophotometrically determined using procedures similar to those described in methods A or B.
C1.4	Range of application	Up to 375 mg/kg in the “as received” soil. The range can be extended.
C1.5	Calibration curve	Linear over the range of application.
C1.6	Standard deviation	See Table C1.
C1.7	Limit of detection	Typically, 10 mg/kg of sulphide in the “as received” soil.
C1.8	Bias	See Table C1.

C2 Principle

The ‘as received’ sample is well mixed and an homogenised portion taken for analysis. To this portion, phosphoric acid is added and the mixture immediately steam-distilled. The distillate is collected in 25 ml of 1M sodium hydroxide solution and made to 500 ml with water. An aliquot of the distillate, typically 4 ml, is taken and the sulphide concentration determined spectrophotometrically.

C3 Interferences

Some sulphides, especially heavy metal sulphides, or polysulphides may be only partially detected, liberating a portion of the hydrogen sulphide under the conditions described. This will depend on the metal sulphides present in the sample. In addition, any substance, which is co-distilled under the conditions used and which results in the formation of a coloured or turbid solution will interfere with the determination. Sulphide in excess of 100 mg/kg inhibits colour formation. High levels of sulphide will inhibit any colour formation, potentially leading to a false-negative result being reported. If the colour development is automated, the inhibition is likely to go un-noticed. If high levels of sulphide are suspected but colouration doesn’t occur, a quick check can be carried out using lead acetate paper before the addition of reagents. In the presence of sulphide, lead acetate

paper produces a black colouration. Dilution of a distillate that is high in sulphide should produce a colour within the calibrated range.

Cyanide at concentrations greater than 500 mg/kg may retard colour formation.

At low concentrations of sulphide, a light pink colour may be observed when colour development is complete. With increasing sulphide concentrations, colour develops from pink to purple and finally to blue. If colours such as red, yellow or bright green are observed, these may be due to the formation of non-sulphide DPD-complexes. Although measurement at the specific wavelength (i.e. about 660 nm) should eliminate these interferences, their formation may inhibit the DPD reagent reacting with sulphide, or lead to insufficient quantities of DPD reagent being present in solution for complexing with sulphide. This will lead to incomplete reaction of DPD reagent with sulphide present in the distillate, and lead to the determination and subsequent reporting of falsely low sulphide concentrations.

C4 Hazards

Appropriate precautions should be taken when handling soils containing sulphide and other contaminants, especially when acid is added to these soils leading to the release of toxic gases. Hydrogen sulphide is poisonous. Appropriate personal protective equipment should be worn where necessary and the analysis carried out in an appropriate fume cupboard.

C5 Reagents

All reagents should be of sufficient purity that they do not give rise to significant interferes. Purity should be checked for each batch of materials by running procedural blanks with each batch of samples analysed.

C5.1 Water. This should be deionised or distilled or of similar quality.

C5.2 Sodium hydroxide solution (1M). Add 40.0 g of sodium hydroxide to approximately 900 ml of water (C5.1). Cool the solution and mix well. Make to 1000 ml with water (C5.1). This solution may be stored at room temperature for up to one month.

C5.3 Orthophosphoric acid (25 % m/v). Carefully, add 250 ml of concentrated orthophosphoric acid (85 %) to approximately 700 ml of water (C5.1) and mix well. Make to 1000 ml with water (C5.1) and mix well. This solution may be stored at room temperature for up to six months.

C5.4 Concentrated sulphuric acid (SG 1.84).

C5.5 Sulphuric acid (50 % v/v). Cautiously and slowly, add 500 ml of concentrated sulphuric acid (C5.7) to 500 ml of water (C5.1) and mix well. Allow the solution to cool. This solution may be stored at room temperature for up to 2 months.

C5.6 Potassium iodate solution (0.002M). Dry approximately 0.6 g of potassium iodate at 120 ± 5 °C for 60 ± 5 minutes. Add 0.428 ± 0.100 g of dried potassium iodate to approximately 900 ml of water (C5.1). Mix well. Make to 1000 ml with water (C5.1) and mix well. This solution may be stored at 5 ± 3 °C for up to 3 months.

C5.7 Aqueous starch indicator. Add 0.50 ± 0.1 g of soluble starch to a small beaker. Add 5 ml of water and make into a smooth paste. Carefully, add the paste to 90 ± 10 ml of boiling water. Mix well. Boil the mixture for a further 5 minutes and then cool the mixture to room temperature. This mixture may be stored at 5 ± 3 °C for up to 3 months. This mixture may be commercially available.

C5.8 Sodium thiosulphate solution (0.01M / 0.01N). Add 2.5 ± 0.1 g of sodium thiosulphate pentahydrate to approximately 800 ml of water (C5.1) and mix well. Make to 1000 ml with water (C5.1) and mix well. This solution may be stored at 5 ± 3 °C for up to one month. (This solution may be commercially available). This solution should be standardised before use. See C5.8.1 - C5.8.2.

C5.8.1 Standardisation of thiosulphate solution (C5.8). Add 5.0 ± 0.5 ml of potassium iodate solution (C5.6) to a 250 ml conical flask. Add 25 ± 1 ml of water (C5.1) followed by 0.20 ± 0.01 g of potassium iodide and 0.5 ml of sulphuric acid solution (C5.5). Mix well. Titrate the solution with 0.01M sodium thiosulphate solution (C5.8) until the colour of the solution is pale yellow or straw-coloured. Add a small amount of iodine indicator solution (C5.7) and mix. Continue titration with drop-wise addition of the sodium thiosulphate solution (C5.8) mixing continuously, until the blue colour first disappears. Record the titration volume, T1 ml. The concentration of the sodium thiosulphate solution, A, is given by

$$A = 0.06 / T1$$

C5.8.2 Add 10.0 ± 0.05 ml of potassium iodate solution (C5.6) to a 250 ml conical flask. Add 0.20 ± 0.01 g of potassium iodide and 0.5 ml of sulphuric acid solution (C5.5). Mix well. Add 50.0 ± 0.1 ml of the working stock standard stock sulphide solution (C5.9.2) and mix well. (This equates to 500 µg of sulphide). Allow the mixture to stand for about 5 minutes. Titrate the solution with standardised 0.01M sodium thiosulphate solution (C5.8) until the colour of the solution is pale yellow or straw-coloured. Add a small amount of iodine indicator solution (C5.7) and mix. Continue titration with drop-wise addition of the sodium thiosulphate solution (C5.8) mixing continuously, until the blue colour first disappears. Note the titration volume, D ml. Repeat this procedure using 50 ml of water in place of the added sulphide solution. Note the titration volume, E ml.

The concentration, C, of the stock standard sulphide solution (C5.9) is given by:

$$C = 320 \times A \times F \times (E - D) \quad \text{mg/l}$$

Where F is the dilution of the stock standard sulphide solution (C5.9) used to make the working stock standard sulphide solution (C5.9.2) that is standardised.

C5.9 Stock standard sulphide solution (nominally, 1000 mg/l as S^{2-}). Wash several crystals of sodium sulphide nonahydrate with water (C5.1) and (avoiding skin contact) dry quickly on filter paper. Immediately after this, weigh quickly but accurately, approximately 3.75 g of the sulphide crystals into a 500-ml volumetric flask and dissolve in about 250 ml of water (C5.1). Swirl the solution gently. Dissolution of the crystals should occur quickly. Mix well and make to 500 ml with water (C5.1). This solution may be stored (with minimum headspace above the solution) at 5 ± 3 °C for up to one week.

C5.9.1 Intermediate stock standard sulphide solution (nominally, 100 mg/l as S^{2-}). Add 100.0 ± 0.1 ml of standard stock sulphide solution (C5.9) to approximately 850 ml of water (C5.1). Mix well. Make to 1000 ml with water and mix well again. This solution should be used on the day of preparation.

C5.9.2 Working stock standard sulphide solution (nominally, 10 mg/l as S^{2-}). Add 100.0 ± 0.1 ml of standard stock sulphide solution (C5.9.1) to approximately 850 ml of water (C5.1). Mix well. Make to 1000 ml with water and mix well again. This solution should be used on the day of preparation, and should be used in the standardisation procedure (see sections C5.8.1 - C5.8.2).

C5.9.3 Standard working sulphide solutions. For example, calibration solutions at nominal concentrations of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mg/l should be prepared in 100 ml volumetric flasks from the intermediate stock standard sulphide solution (C5.9.1). Into a series of 100 ml volumetric flasks, add 0.5, 1.0, 1.50, 2.0, 2.50 or 3.0 ml of intermediate stock standard sulphide solution (C5.9.1). To each flask, add 1 ml of 1M sodium hydroxide solution (C5.2) and make to 100 ml with water. Mix well. These solutions should be used on the day of preparation.

C6 Apparatus

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

C6.1 Analytical balance capable of weighing to 0.0001g.

C6.2 Steam distillation equipment

C7 Sample collection, preservation and storage

This method has been performance tested using air-dried samples (i.e. air at less than 30 °C) and may not be suitable for samples containing significant amounts of water. Once dried, the sample is ground to a particle size less than 2 mm. The use of an air-dried and ground sample rather than an “as received” sample enables a more homogeneous sub-sample to be taken. When air-dried samples are stored below 20 °C for up to 21 days, significant loss of sulphide does not occur. However, the procedures used to prepare crushed, ground, sieved and/or air-dried samples may adversely affect easily liberated sulphide present within the original sample. If hydrogen sulphide is released from the sample (i.e. its odour can be detected) whilst these procedures are being carried out, alternative procedures should be used, or consideration given to analysing an “as received” sample. When “as received” samples are analysed, care should be taken to ensure that the sub-sample used for analysis is representative of the bulk material being sampled and is ideally, homogeneous. This is especially important when smaller quantities of samples are required, for example, for repeat analyses, where high concentrations are determined or suspected. “As received” samples should be stored below 10 °C. Further guidance can be found elsewhere[3] in this series.

C8 Analytical procedure

Step	Procedure	Note
C8.1	Add 25 ml of 1M sodium hydroxide solution (C5.2) to a receiving flask, V_D ml (typically 500 ml) of the steam distillation apparatus (C6.2). See note a.	(a) Apparatus are commercially available for generating steam and undertaking the determination automatically.
C8.2	Weigh out M g (typically, 10.0 g) of an homogenised “as received” sample, see notes b and c.	(b) The sample may be placed directly into the distillation flask. (c) If the result is to be reported on a dry weight basis (at say 105 °C) a portion of the same sample should be taken and analysed for its dry matter content, % DM.
C8.3	To the sample, add 5 ml of phosphoric acid solution (C5.3). Immediately, connect the distillation equipment (note d) and steam distil the mixture for 10 minutes.	(d) Ensure losses of hydrogen sulphide are minimised.
C8.4	After 10 minutes, stop the distillation process and remove the receiving flask. Make to V_D ml (typically, 500 ml) with water (C5.1). The solution is now ready for sulphide determination. Typically, 4 ml aliquots are used.	
C8.5	Standard sulphide solutions are not taken through the distillation process, before being determined spectrophotometrically, but would need to be if recovery estimates were needed to be determined.	
C8.6	With each batch of samples, a blank should run, whereby the homogenised soil is replaced with an equal mass of water (C5.1). See note e. Similarly, a soil reference matrix material may be used, whereby a soil is spiked with a known concentration of sulphide, ideally, at a level appropriate for the samples being analysed. Both spiked and un-spiked soils would need to be analysed. See note f.	(e) The blank is used to evaluate any contamination or memory effects. (f) The use of a soil reference matrix material enables an estimate of the recovery to be made on a batch to batch basis.

C8.7 An aliquot, V_A ml (typically, 10.0 ml) of the standard working sulphide solutions (see C5.9.3) should be added to a series of 100 ml volumetric flasks, see note g.

(g) This volume equates to 5, 10, 15, 20, 25 and 30 µg of sulphide (as S^{2-}) in the 100 ml flasks.

C8.8 The standards and samples are analysed using a discrete spectrophotometric analyser using procedures similar to those described in methods A or B.

C8.9 An AQC sample, at an appropriate level (see note l) prepared from a separate standard sulphide stock solution to that described in section C5.9.3 should be analysed at the end of each batch of analyses to provide an external check on the calibration.

(l) For example, 2.5 ml of a 3 mg/l standard sulphide solution treated as described in C8.7. (This equates to 7.5 µg in the 100-ml flask.

Table C1 Performance data

Performance data are based upon eleven duplicate batches of analysis, spread over 11 days, providing 22 individual results for each test sample. The data are based on automated instrumental procedures similar to those described in methods A and B

Matrix	Nominal value (mg/kg)	Mean value (mg/kg)	LOD (mg/kg)	Precision (% RSD)	Bias (%)
Loamy sand	0	8.248	9.91		
	30	35.445		11.49	90.66
	120	122.400		10.76	95.14
Silt loam	0	14.809	12.46		
	30	46.505		15.36	105.66
	120	130.380		12.21	96.32
Sandy clay	0	5.180	2.77		
	30	37.745		11.21	108.56
	120	129.448		12.53	103.57
Sediment	0	7.133	7.62		
	30	29.771		10.54	75.46
	120	103.090		9.89	79.97
Waste	0	2.401	2.84		
	30	30.940		9.41	95.13
	120	120.523		6.95	98.45
AQC	80	83.252		11.14	

RSD is relative standard deviation
LOD limit of detection
Data provided by Environment Agency, National Laboratory Service

D The determination of easily liberated sulphide in as received or air-dried samples following phosphoric acid steam distillation with iodometric titration

D1 Performance characteristics of the method

D1.1	Substances determined	Easily liberated sulphide.
D1.2	Type of sample	“As received” or air-dried and ground soil samples.
D1.3	Basis of method	The soil sample is treated with phosphoric acid and immediately steam-distilled into alkaline zinc acetate solution. A solution of iodate-iodide is added to oxidise the zinc sulphide, and excess iodine is back-titrated with sodium thiosulphate solution.
D1.4	Range of application	Typically, 10 - 300 mg/kg in the soil analysed.
D1.5	Standard deviation	See Table D1.
D1.6	Limit of detection	Typically, about 10 mg/kg in soils.
D1.7	Sensitivity	1 ml 0.00417M iodate is equivalent to 40 mg/kg sulphide (when using a 5 g sample).
D1.8	Bias	See Table D1.

D2 Principle

The sample is well mixed and a representative portion taken for analysis. Hydrogen sulphide is liberated by acidification of the sample with phosphoric acid in a steam distillation unit. The hydrogen sulphide produced is distilled over and is absorbed in alkaline 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.

D3 Interferences

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. This causes a positive bias in the result reported. Formaldehyde forms an addition compound with sulphur dioxide which does not react with iodine under the conditions used. Its use in the procedure has been shown to be effective for up to at least 1000 mg/kg as sulphite, $[SO_3]^{2-}$. Levels of sulphite below about 50 mg/kg do not interfere and when it is known that the sample contains less than this amount, the use of formaldehyde may not be necessary.

Depending on the metal present, heavy metal sulphides may not quantitatively liberate sulphide on addition of acid.

Volatile compounds which react with iodine will give high results. In many cases, these may be soluble and should be removed by separation of the zinc sulphide precipitate, following distillation.

D4 Hazards

Appropriate precautions should be taken when handling soils contaminated with sulphide and other contaminants, especially when acid is added to soils, as toxic gases may be released. Hydrogen sulphide is a poisonous gas with a World Health Organisation recommended Time Weighted Average maximum exposure of 7 ppm, similar to that of hydrogen cyanide. Appropriate personal protective equipment should be worn where necessary and the analysis carried out in an appropriate fume cupboard.

Formaldehyde is a suspected carcinogen and should be treated with care. The use of a fume cupboard reduces possible inhalation of the vapour. Gloves should be used to avoid skin contact. Wastes containing formaldehyde should be disposed of with care.

Phosphoric acid and hydrochloric acid are corrosive.

D5 Reagents

All reagents should be of analytical grade except where stated. Distilled, de-ionised or water of similar quality should be used throughout. Reagents may be stored at room temperature for up to two months except where stated otherwise.

D5.1 Concentrated orthophosphoric acid (85 %)

D5.2 Hydrochloric acid solution (50% v/v). To water, add an equal volume of concentrated hydrochloric acid. Mix well.

D5.3 Potassium iodate-iodine solution (0.00417M). Dissolve 0.8920 ± 0.0005 g of potassium iodate (previously dried for 1 hour at 110 °C) 8.70 ± 0.05 g of potassium iodide and 0.60 ± 0.05 g of sodium bicarbonate in approximately 900 ml of water. Mix well and make to 1000 ml with water. Mix well. This solution may be stored at room temperature in a dark coloured bottle for up to one month.

D5.4 Sodium thiosulphate solution (0.25M). Dissolve 62.50 ± 0.01 g of sodium thiosulphate pentahydrate in approxiamtely 900 ml of water. Mix well and make to 1000 ml with water. Preserve the solution by adding 1 ml of chloroform. Mix well. This solution may be stored in a dark coloured bottle at room temperature for up to one month.

D5.5 Sodium thiosulphate solution (0.0125M). Add 50.00 ± 0.05 ml of the 0.25M sodium thiosulphate (D5.4) to approxiamtely 900 ml of water. Mix well and make to 1000 ml with water. Prepare this solution on the day of use, and standardize it against 0.00417M potassium iodate-iodide (D5.3) before use.

D5.5.1 Standardisation of sodium thiosulphate solution (0.0125M). Add 5.00 ± 0.02 ml of potassium iodate-iodide solution (D5.3) to a conical flask, add 5.0 ± 0.2 ml of 50 % hydrochloric acid solution (D5.2) and mix. Add approximately 90 ml of water and titrate the solution with sodium thiosulphate solution (D5.5). Add 2 ml of starch indicator solution (D5.7) when the solution becomes a pale straw colour. Continue the titration until

the blue colour just disappears. Carry out the standardisation in duplicate. Calculate the average titre (T ml) and determine the factor, F:

$$F = 10 / T$$

D5.6 Alkaline zinc acetate (approximately 0.5M). Dissolve 110 ± 5 g of zinc acetate dihydrate in approximately 800 ml of water. Mix well. Add 125 ± 1 g of sodium hydroxide to the solution and mix well to dissolve. Cool the solution and make to 1000 ± 10 ml with water.

D5.7 Starch indicator solution. Add 1.0 ± 0.1 g of starch to 100 ± 10 ml of water. Mix well and boil gently for approximately 5 minutes to faciliate dissolution. This solution may be stored at room temperature for up to one month.

D5.8 Formaldehyde (approximately 40 % solution).

D5.9 Standard suspension of zinc sulphide (nominally 100 mg/l). Add 10.0 ± 0.1 g of zinc acetate dihydrate to approximately 200 ml of water. Mix well. Add 16.0 ± 0.5 g of sodium carbonate to approximately 200 ml of water. Mix well. Wash several crystals of sodium sulphide nonahydrate with water and quickly dry on a filter paper. Add 1.00 ± 0.01 g the sulphide to approximately 200 ml of water. When dissolved, immediately, add the zinc acetate solution followed by the sodium carbonate solution. Mix well and make to 1000 ml with water. Mix well. This solution may be stored in a dark coloured bottle room temperature for up to one month. The suspension of zinc sulphide should always be standardised before use.

D5.9.1 Standardisation of sulphide suspension. The standard stock sulphide suspension (D5.9) should be thoroughly shaken. As the suspension of zinc sulphide is very gelatinous, care should be taken to eliminate any sulphide adhering to the surface of any glassware. Add 5.00 ± 0.02 ml of this well shaken sulphide suspension to a conical flask.

Into the flask, add approximately 90 ml of water followed by 5.00 ± 0.02 ml of potassium iodate-iodide solution (D5.3) and 5.0 ± 0.2 ml of 50 % hydrochloric acid solution (D5.2). Mix well. The iodine produced in the conical flask should be titrated with the standardised 0.0125M sodium thiosulphate solution (D5.5.1). When the solution becomes a pale straw colour, add several drops (0.2 - 0.5 ml) of starch indicator solution (D5.7). Continue titration until the blue colour just disappears. Record the volume required (T1 ml).

D5.9.2 The procedure described in section D5.9.1 should be repeated and the volume of sodium thiosulphate solution (D5.5.1) recorded (T2 ml). The two titrations (T1 and T2) should agree to within 0.1 ml. If not, the whole procedure should be repeated using two further aliquots. The mean titre, T3, should be calculated from $T3 = (T1 + T2) / 2$.

D5.9.3 Carry out a blank determination. To a conical flask, add approximately 90 ml of water followed by 5.00 ± 0.02 ml of potassium iodate-iodide solution (D5.3) and 5.0 ± 0.2 ml of 50 % hydrochloric acid solution (D5.2). Mix well. The iodine produced in the conical flask should be titrated with standardised 0.0125M sodium thiosulphate solution (D5.5.1). When the solution becomes a pale straw colour, add several drops (0.2 - 0.5 ml) of starch indicator solution (D5.7). Continue titration until the blue colour just disappears. Record the volume required (T4 ml).

The concentration, (C_s) as S^{2-}, of sulphide in the suspension is given by

$$C_s = (T4 - T3) \times F \times 40 \quad \text{mg/l}$$

Where F is the factor given in section D5.5.1.

D6 Apparatus

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

D6.1 Analytical balance capable of weighing to 0.0001g

D6.2 Analytical balance capable of weighing to 0.01g

D6.3 Steam distillation equipment

D7 Sample collection preservation and storage

Samples should be collected in glass or plastic containers and the container filled to the top to minimise any headspace. Samples should be analysed as soon as possible. If storage of samples is unavoidable, samples may be kept in a refrigerator at a temperature in the range 3 - 7 °C and may be stored for up to 7 days. Further guidance can be found elsewhere[3] in this series.

D8 Analytical procedure

Step	Procedure	Note
D8.1	**Sample pre-treatment**	
D8.1.1	Weigh out M g (typically, 5.0 ± 0.2 g) of a representative amount of the “as received”, or dried and ground, soil sample, see notes a - c.	(a) This may be placed directly into the distillation equipment. (b) If “as received” soil is analysed and the result is to be reported on a dry weight basis (for example at 105 °C) rather than on an “as received” basis, a portion of the same sample should be taken and analysed for its dry matter content, DM%. (c) If “as received” soil is analysed, it may be necessary to carry out the analysis in duplicate to improve precision.

D8.2 Distillation

D8.2.1 To the sample, add 20 ± 1 ml of phosphoric acid (D5.1). Immediately, connect the distillation equipment and steam-distil the mixture into 10 ± 1 ml of zinc acetate solution (D5.6) contained in a conical flask, ensuring that the delivery tip is immersed into the solution. When nearly 200 ml of distillate has been collected, remove the flask and mix well, see note d.

(d) A blank should be taken through the entire procedure.

D8.3 Determination

D8.3.1 Into the flask, add 5.00 ± 0.02 ml of potassium iodate-iodide solution (D5.3) and 5.0 ± 0.2ml of 50 % v/v hydrochloric acid (D5.2). Mix well. The iodine produced in the conical flask should be titrated with 0.0125M sodium thiosulphate solution (D5.5). When the colour of the solution becomes pale straw-coloured, add several drops (typically, 0.2 - 0.5 ml) of starch indicator solution (D5.7). Continue titration until the blue colour just disappears. Record the volume required (TS ml), see notes e and f.

(e) If on addition of potassium iodate-iodide solution (D5.3) and 50 % v/v hydrochloric acid (D5.2), no iodine is produced as indicated by an orange/yellow colour, consideration should be given to repeating the distillation using a smaller quantity of sample (D8.1.1) or increasing (to 10.00 ± 0.02 ml) the volume of potassium iodate-iodide solution (D8.3.1) added.

(f) Record the blank titre (see note d) as B ml.

D8.4 AQC

D8.4.1 A suitable soil sample (for example a certified reference matrix material) should be taken through the entire analytical procedure as described in sections D8.1 - D8.3. Alternatively, in order to determine recovery estimates, the sample being analysed (D8.1) may be spiked at an appropriate level (see note g) and the analysis repeated using the entire analytical procedure described in sections D8.1 - D8.3. Record the volumes required ($T_{unspiked}$ ml) and (T_{spiked} ml).

(g) For example, 5 ml of standard stock sulphide suspension (D5.9) may be used.

D9 Calculation of results

D9.1 The amount of sulphide, A_{DW} mg/kg, in the dried and ground soil sample analysed (on a dry weight basis) is given by:

$$A_{DW} = (B-TS)*F*200 / M \quad mg/kg$$

Where F is the factor (see section D5.5.1);
B is the titre for the blank (see section D8.2.1 and note d);
T5 is the titre for the sample (see section D8.3.1); and
M is the mass of dried and ground soil (see section D8.1.1).

D9.1 The amount of sulphide, A_{DW} mg/kg, in the "as received" soil sample analysed (on a dry weight basis) is given by:

$$A_{DW} = (B-TS)*F*200 / (M*DM/100) \quad mg/kg$$

Where F is the factor (see section D5.5.1);
B is the titre for the blank (see section D8.2.1 and note d);
TS is the titre for the sample (see section D8.3.1);
M is the mass of dried and ground soil (see section D8.1.1); and
DM is the percentage dry matter content (see section D8.1.1 and note b).

D9.3 The percentage recovery, % R, for the AQC spiked soil (using 5 ml of standard stock sulphide suspension (D5.9)) is given by:

$$\% R = ((T_{unspiked} - T_{spiked}) / (B - T3))*100$$

Where
$T_{unspiked}$ is the titre for the unspiked soil sample (see section D8.4.1);
T_{spiked} is the titre for the spiked soil sample (see section D8.4.1);
B is the titre for the blank (see section D8.2.1 and note d); and
T3 is the average titration for the standardisation of the sulphide suspension (section D5.9.1).

Table D1 Performance data

	Soil spiked at 50 mg/kg			Soil spiked at 200 mg/kg		
Soil type	Bias (%)	RSD (%)	SD (mg/kg)	Bias (%)	RSD (%)	SD (mg/kg)
Sand	-6.2	8.8	4.24	-5.4	5.1	9.71
Clay	-7.9	8.0	5.83	-11.2	5.5	11.25
Loam	-2.6	9.1	6.39	-10.1	5.6	11.32

Analysis based on 11 batches, analysed in duplicate.
RSD is the relative standard deviation.
SD is the standard deviation.
Performance data provided by Derwentside Environmental Testing Services Limited

E The determination of easily liberated sulphide in “as received” samples following sulphuric acid steam distillation with ion selective electrode detection

E1 Performance characteristics of the method

E1.1	Substances determined	Easily liberated sulphide.
E1.2	Type of sample	“As received” soil and environmental samples.
E1.3	Basis of method	The soil sample is treated with sulphuric acid and zinc powder and heated to release hydrogen sulphide which is absorbed into alkaline ascorbic acid solution. The hydrogen sulphide in the alkaline ascorbic acid solution is then determined by ion selective electrode (ISE).
E1.4	Range of application	Typically, up to 2000 mg/kg in the “as received” sample.
E1.5	Interferences	None known.
E1.6	Standard deviation	See Table E1.
E1.7	Limit of detection	Typically, about 15 mg/kg in “as received” soil.
E1.8	Sensitivity	28 - 32 millivolts per decade.
E1.9	Bias	See Table E1.

E2 Principle

The sample is well mixed and a representative portion taken for analysis. Hydrogen sulphide is liberated by heating the sample with sulphuric acid and zinc powder. The hydrogen sulphide released is absorbed in alkaline ascorbic acid solution. The sulphide in the alkaline ascorbic acid solution is then determined by an ISE procedure.

E3 Hazards

Appropriate precautions should be taken when handling soils contaminated with sulphide and other contaminants, especially when acid is added to soils, as toxic gases may be released. Appropriate personal protective equipment should be worn where necessary and the analysis carried out in an appropriate fume cupboard.

Concentrated sulphuric acid is corrosive.

E4 Reagents

All reagents should be of analytical grade except where stated. Distilled or de-ionised water should be used throughout. Reagents may be stored at 20 °C for up to 2 years, except where otherwise stated.

E4.1 Sulphuric acid (5M). To approximately 3500 ml of water, slowly and carefully add 1327 ± 5 ml of concentrated suphuric acid. Mix well and allow the solution to cool. Make to 5000 ml with water.

E4.2 Zinc Acetate, approximately (0.5M). Dissolve 110 ± 1 g of zinc acetate dihydrate in approximately 800 ml of watrer. Mix well and make to 1000 ml with water. This solution may be stored at 20 °C for up to 6 months.

E4.3 Zinc powder. If the powder is too coarse, the reaction may not proceed.

E4.4 Alkaline ascorbic acid solution. Carefully, dissolve 40.0 $\pm$ 0.1 g of sodium hydroxide in approximately 300 ml of water. Mix well and allow the solution to cool. To the cooled solution, add 17.60 $\pm$ 0.01 g of L-ascorbic acid. Mix well and make to 1000 ml with water. Mix well. This solution should be prepared on the day of use.

E4.5 Concentrated hydrochloric acid (SG 1.16).

E4.6 Hydrochloric acid (50 % v/v). Add 500 ml of concentrated hydrochloric acid (E4.5) to 500 ml of water and mix well. This solution may be stored at room temperature for up to 6 months.

E4.7 Sodium hydroxide solution (1M). Add 40.0 g of sodium hydroxide to approximately 800 ml of water and mix well. Make to 1000 ml with water and mix again. This solution may be stored at room temperature for up to one month.

E4.8 Potassium iodate-iodide (0.00417M). Dissolve 8.70 ± 0.05 g of potassium iodide, 0.8920 ± 0.0005 g of potassium iodate (previously dried for 1 hour at 110 °C) and 0.60 ± 0.05 g of sodium bicarbonate in approximately 900 ml of water. Mix well. Make to 1000 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to one month.

E4.9 Aqueous starch indicator. This is commercially available.

E4.10 Sodium thiosulphate solution (0.0125M / 0.0125N). Add 3.125 g of sodium thiosulphate pentahydrate to approximately 300 ml of water and mix well. Add 0.40 ± 0.01 g of sodium hydroxide and mix well. Make to 1000 ml with water and mix well. This solution may be stored at 5 ± 3 °C for up to one week. (This solution may be commercially available).

E4.10.1 Standardisation of sodium thiosulphate solution. Add 100 ml of water into a conical flask, add 2.0 ± 0.1 ml of hydrochloric acid (E4.6) and 10.0 ± 0.2 ml of potassium iodate-iodide solution (E4.8) and mix well. Titrate the solution with sodium thiosulphate solution (E4.10) to be standardised until the colour of the solution is pale yellow or straw-coloured. Add a small amount of iodine indicator (E4.9) and mix. Continue titration with drop-wise addition of the sodium thiosulphate solution (E4.10) mixing continuously, until the blue colour first disappears. Note the titration volume, T ml. Calculate a factor using the equation:

$$F = \frac{60 \times 0.00417}{T}$$

E4.11 Standard stock sulphide solution (nominally, 3200 mg/l as S^{2-}). Wash 30 g of sodium sulphide nonahydrate with water and (avoiding skin contact) dry quickly on filter paper. Immediately after this, weigh quickly but accurately, approximately 24.0 g of the sulphide crystals into a 1000-ml volumetric flask and dissolve in about 500 ml of 1M sodium hydroxide solution (E4.7). Swirl the solution gently. Dissolution of the crystals should occur quickly. Mix well and make to 1000 ml with 1M sodium hydroxide solution (E4.7). This solution may be stored at 5 ± 3 °C for up to two months and should be standardised before use (see sections E4.11.1 - E4.11.2).

E4.11.1 Standardisation of standard stock sulphide solution. Add 2.00 ± 0.02 ml of standard stock solution (E4.11) into a 100 ml volumetric flask and dilute to 100 ml with water and mix well. Add 25.0 ± 0.2 ml of this solution, i.e. 1.6 mg of sulphide, into a conical flask and add 75 ml of water. Acidify with 2.0 ± 0.1 ml of hydrochloric acid (E4.6) and 10.0 ± 0.1 ml of potassium iodate-iodide solution (E4.8) and mix well. Titrate the solution with standardised sodium thiosulphate solution (E4.10) until the colour of the solution is pale yellow or straw-coloured. Add a small amount of iodine indicator (E4.9) and mix. Continue titration with drop-wise addition of the standardised sodium thiosulphate solution (E4.10) mixing continuously, until the blue colour first disappears. Note the titration volume, T1 ml.

E4.11.2 Blank titration. Add 100 ml of water into a conical flask, add 2.0 ± 0.1 ml of hydrochloric acid (E4.6) and 10.0 ± 0.2 ml of potassium iodate-iodide solution (E4.8) and mix well. Titrate the solution with standardised sodium thiosulphate solution (E4.10) until the colour of the solution is pale yellow or straw-coloured. Add a small amount of iodine indicator (E4.9) and mix. Continue titration with drop-wise addition of the standardised sodium thiosulphate solution (E4.10) mixing continuously, until the blue colour first disappears. Note the titration volume, T2 ml.

The concentration, C, of the standardised stock sulphide solution (E4.11) is given by:

$$C = \frac{(T2 - T1) \times 100000}{25} \quad \text{mg/l}$$

E4.12 Intermediate calibration sulphide solution (1000 mg/l). Add x ml of standard sulphide solution (E4.11) where

x = 10000 / concentration of standardised stock sulphide solution (E4.11)

to approximately 50 ml of alkaline ascorbic acid solution (E4.4). Mix well and make to 100 ml with alkaline ascorbic acid solution (E4.4). Mix well. This solution may be stored at 5 ± 3 °C for up to three days.

E4.13 Working calibration sulphide solution (100 mg/l). Add 10.0 ± 0.2 ml of intermediate calibration sulphide solution (E4.12) to approximately 70 ml of alkaline ascorbic acid solution (E4.4). Mix well and make to 100 ml with alkaline ascorbic acid solution (E4.4). Mix well. This solution should be prepared on the day of use.

E4.14 Working calibration sulphide solution (50 mg/l). Add 5.0 ± 0.2 ml of intermediate calibration sulphide solution (E4.12) to approximately 70 ml of alkaline ascorbic acid solution (E4.4). Mix well and make to 100 ml with alkaline ascorbic acid

solution (E4.4). Mix well. This solution should be prepared on the day of use.

E4.15 Working calibration sulphide solution (20 mg/l). Add 2.0 ± 0.1 ml of intermediate calibration sulphide solution (E4.12) to approximately 70 ml of alkaline ascorbic acid solution (E4.4). Mix well and make to 100 ml with alkaline ascorbic acid solution (E4.4). Mix well. This solution should be prepared on the day of use.

E4.16 Working calibration sulphide solution (10 mg/l). Add 1.0 ± 0.1 ml of working calibration sulphide solution (E4.12) to approximately 70 ml of alkaline ascorbic acid solution (E4.4). Mix well and make to 100 ml with alkaline ascorbic acid solution (E4.4). Mix well. This solution should be prepared on the day of use.

E4.17 Working calibration sulphide solution (1 mg/l). Add 100 ± 1 µl of intermediate calibration sulphide solution (E4.12) to approximately 70 ml of alkaline ascorbic acid solution (E4.4). Mix well and make to 100 ml with alkaline ascorbic acid solution (E4.4). Mix well. This solution should be prepared on the day of use.

E5 Apparatus

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

E5.1 Analytical balance capable of weighing to 0.01 g

E5.2 Glass bubbling equipment for collecting evolved gases. See Figure E1.

E5.3 Ion selective electrode meter (to read mV) with silver/sulphide ion selective electrode.

E5.4 Hot plate set at 180 ± 20 °C.

E6 Sample collection and storage

Samples should be collected in glass or plastic containers and the container filled to the top to minimise any headspace. Samples should be analysed as soon as possible. If storage of samples is unavoidable, samples should be kept in a refrigerator at a temperature in the range 3 - 7 °C and may be stored for up to 7 days. Further guidance can be found elsewhere[3] in this series.

E7 Analytical procedure

Step	Procedure	Note
E7.1	**Sample pre-treatment**	
E7.1.1	Weigh out M g (typically, 5.00 ± 0.05 g) of a representative amount of the “as received” soil sample (see notes a and b) into a conical flask.	(a) If “as received” soil is used and the result is to be reported on a dry weight basis, rather than an “as received” basis, a portion of the same sample should be

taken and analysed for its dry matter content, DM%.

(b) If “as received” soil is used, it may be necessary to carry out replicate analysis to improve precision.

E7.1.2 To the glass bubbling equipment (E5.2) add 5.0 ± 0.5 ml of alkaline ascorbic solution (E4.4).

E7.1.3 To the conical flask, add 0.75 ± 0.05 g of zinc powder (E4.3) followed by 20.0 ± 0.2 ml of 5M sulphuric acid (E4.1). Immediately and carefully connect the flask to the glass bubbling equipment (E5.2) to ensure an adequate seal and place the conical flask on a hot plate (E5.4). Carefully mix the contents of the flask. See note c. Leave the reaction to proceed for 10 ± 1 minutes.

(c) Ensure the sulphuric acid does not escape from the flask into the glass bubbling equipment. If this does happen, the analysis will need to be repeated, possibly using a smaller quantity of sample.

E7.1.4 Remove the flask from the hot plate and separate the flask from the glass bubbling equipment. Quantitatively transfer the alkaline ascorbic acid solution in the glass bubbling equipment to a suitable container (rinsing as necessary and combining the rinsings with the alkaline ascorbic acid solution in the container). Make to 100 ml with alkaline ascorbic acid solution (E4.4). See note d.

(d) A blank should be taken through the whole procedure and any hydrogen sulphide determined by ISE.

E7.2 Determination

E7.2.1 Following manufacturer’s instructions set up the ISE equipment. Using the calibration standard sulphide solutions (E4.13 - E4.17) calibrate the ISE equipment. See note e. Plot a graph of response of the ISE equipment versus amount of sulphide in 100 ml of calibration solution. See note f.

(e) This is equivalent to 0.1, 1, 2, 5 and 10 mg of sulphide in 100 ml.

(f) Ignore negative sign of mV reading and plot calibration standards as $\log_e$ functions.

E7.2.2 Record the response of the ISE equipment for the sample (E7.1.4) and blank (note d). From these responses, determine the amount of sulphide in the blank and sample analysed.

(g) If the response for the sample is greater than the response of the highest calibration standard, consideration should be given to repeating the analysis using a smaller quantity of sample (E7.1.1) or diluting (E7.1.4) the volume of alkaline ascorbic acid solution.

E7.3 AQC

E7.3.1 A suitable soil sample (for example a certified reference matrix material) should be taken through the entire analytical procedure as described in sections E7.1.1- E7.2.2. Alternatively, in order to determine recovery estimates, the sample being analysed (E7.1.1) may be spiked at an appropriate level (see note h) and the analysis repeated using the entire analytical procedure described in sections E7.1 - E7.2. Record the response of the spiked and un-spiked samples.

(h) For example, 1.0 ml of standard stock sulphide solution (E4.12) may be used. This equates to 1 mg of sulphide.

E8 Calculation of results

E8.1 The amount of sulphide, A_{AR} mg/kg, in the "as received" soil sample analysed (expressed on an "as received" basis) is given by:

$$A_{AR} = (Rs \times F) / M \quad \text{mg/kg}$$

Where F is the dilution factor, if appropriate (see section E7.2.2 and note g);
Rs is amount of sulphide in the alkaline ascorbic acid solution obtained from the graph (see section E 7.2.2 and note g); and
M is the mass of "as received" soil (see section E7.1.1).

E8.2 The amount of sulphide, A_{DW} mg/kg, in the "as received" soil sample analysed (expressed on a dry weight basis) is given by:

$$A_{DW} = (Rs \times F) / ((M \times DM) / 100) \quad \text{mg/kg}$$

Where DM is the percentage dry matter content (see section E7.1.1 and note b).

Table E1 Performance data

	Soil spiked at 200 mg/kg			Soil spiked at 800 mg/kg		
Soil type	Bias (%)	RSD (%)	SD (mg/kg)	Bias (%)	RSD (%)	SD (mg/kg)
Sandy loam	-14.9	13.5	23.03	-19.8	11.4	73.20

	Soil spiked at 200 mg/kg			Soil spiked at 800 mg/kg		
Soil type	Bias (%)	RSD (%)	SD (mg/kg)	Bias (%)	RSD (%)	SD (mg/kg)
Sludge	-25.2	13.6	20.38	-23.4	8.3	50.58

Analysis based on 11 batches, analysed in duplicate
RSD is relative standard deviation
SD is standard deviation
Performance data provided by Alcontrol Laboratories

Figure E1 Glass bubbling equipment for collecting evolved gases

References

1 Standing Committee of Analysts, “Sulphide in Waters and Effluents 1983 Tentative Methods”, *Methods for the Examination of Waters and Associated Materials,* ISBN 0117517186, in this series.

2 MCERTS Performance standard for laboratories undertaking chemical testing of soil, Environment Agency, Version 3. (www.mcerts.net).

3 Standing Committee of Analysts, “The preparation and pre-treatment of potentially contaminated soils prior to chemical analysis (2006)”, *Methods for the Examination of Waters and Associated Materials*, in this series, Environment Agency.

4 Sulphur and it inorganic derivatives in the Canadian Environment. National Research Council of Canada, No.15015, Associate Committee on Scientific Criteria for Environmental Quality, Ottawa (1977).

Address for correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts at the address given below. In addition, if users would like to receive advanced notice of forthcoming publications please contact the Secretary on the Agency's web-page.

Standing Committee of Analysts
Environment Agency (National Laboratory Service)
56 Town Green Street
Rothley
Leicestershire, LE7 7NW
http://www.environment-agency.gov.uk/nls

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CONTACTS:

ENVIRONMENT AGENCY HEAD OFFICE

Rio House, Waterside Drive, Aztec West, Almondsbury, Bristol BS32 4UD

www.environment-agency.gov.uk
www.environment-agency.wales.gov.uk

ENVIRONMENT AGENCY REGIONAL OFFICES

ANGLIAN
Kingfisher House
Goldhay Way
Orton Goldhay
Peterborough PE2 5ZR

MIDLANDS
Sapphire East
550 Streetsbrook Road
Solihull B91 1QT

NORTH EAST
Rivers House
21 Park Square South
Leeds LS1 2QG

NORTH WEST
PO Box 12
Richard Fairclough House
Knutsford Road
Warrington WA4 1HG

SOUTHERN
Guildbourne House
Chatsworth Road
Worthing
West Sussex BN11 1LD

SOUTH WEST
Manley House
Kestrel Way
Exeter EX2 7LQ

THAMES
Kings Meadow House
Kings Meadow Road
Reading RG1 8DQ

WALES
Cambria House
29 Newport Road
Cardiff CF24 0TP

ENVIRONMENT AGENCY
GENERAL ENQUIRY LINE
08708 506 506

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