



ENVIRONMENT AGENCY

**The determination of cyanide and thiocyanate
in soils and similar matrices (2011)**

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 methods for the determination of cyanide and thiocyanate in soils. It should be read in conjunction with a previously published document in this series⁽¹⁾. Using the procedures described in this booklet should enable laboratories to satisfy the requirements of the Environment 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 examples 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.

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.

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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 cyanide in soils and similar matrices

1 Introduction

Several methods are described in this booklet for the determination of cyanide, in various forms, in soils and associated materials. Readers are directed to an earlier publication⁽¹⁾ in this series dealing with the determination of cyanide in waters.

In this booklet, cyanides are referred to in three distinct forms, namely:-

- (i) easily liberated cyanide (also commonly referred to as free cyanide);
- (ii) complex cyanide;
- (iii) total cyanide.

In practice, the free or easily liberated cyanide is defined by the analytical conditions under which hydrogen cyanide is liberated, for example from simple cyanide salts, and is typically determined at a specific pH.

Complex cyanide is usually defined (following the determination of easily liberated cyanide) as the hydrogen cyanide produced from complex cyanide compounds. Such complex cyanides in environmental samples include the iron cyanides, potassium ferricyanide ($K_3Fe(CN)_6$) and potassium ferrocyanide ($K_4Fe(CN)_6$) and complexes with mercury and cobalt. However, strongly complexed cyanide (see Table F1 in the earlier publication⁽¹⁾ in this series) may be incompletely determined.

Total cyanide is defined as the sum of the easily liberated cyanide and the complex cyanide.

Details are described for the determination of easily liberated cyanide and total cyanide following steam distillation of a buffered soil or alkaline soil extract under acidic condition. An aliquot of a pH-adjusted portion of the distillate is then spectrophotometrically determined at between 575 - 600 nm using chloramine-T, isonicotinic acid and generally, a barbituric acid derivative.

A method is also described for the determination of thiocyanate. Thiocyanate may be present in soils (such as contaminated land from gasworks or similar sites) that contain cyanide. The detection of high total cyanide concentrations may trigger the need for the analysis for thiocyanate. Thiocyanate is not broken down either in the easily liberated cyanide or total cyanide determinations, and consequently, potential cyanide from thiocyanate is not detected or included in these determinations. Details are described for the analysis of thiocyanate (on an alkaline soil extract) based on the addition of formaldehyde (to remove easily liberated cyanide) and spectrophotometric determination at 600 nm using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid.

Guidance on how results can be expressed is given in Appendix 1.

2 Methods

The following sections are divided into three parts, namely

- A methods for the determination of easily liberated cyanide;

- B methods for the determination of total cyanide; and
- C methods for the determination of thiocyanate.

Commercial apparatus are available allowing procedures to be carried out automatically, enabling easily liberated cyanide and total cyanide, and possibly thiocyanate to be determined simultaneously or sequentially. Usually, the spectrophotometric determination is carried out on a reduced scale.

Methods are either applicable to air-dried soils and similar matrices or to samples “as received” within the laboratory.

Where appropriate, each method contains details of performance, the distillation and spectrophotometric techniques and similar information to enable procedures to be undertaken. Standardisation of cyanide solutions can be undertaken using silver nitrate. However, the purity of potassium cyanide used as calibration standards is usually sufficient to negate the requirement to standardise cyanide solutions. It is for laboratories to decide whether standardisation of cyanide solutions is required. Since each method has been validated in only one laboratory details are included for information purposes only as examples 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.

3 Interferences

The addition of Cu(I) can act as a catalyst for the decomposition of complex cyanides, for example hexacyanoferrates. Laboratories should decide whether its addition is required for the matrices analysed. The addition of zinc sulphate, lead acetate, Sn(II) or Cu(II) reacts with sulphide to form acid insoluble sulphide removing the interference caused by sulphide. Laboratories should ascertain whether the presence of sulphide may be a cause for concern.

When hydrogen cyanide is liberated from the sample via the distillation process and then “fixed” in sodium hydroxide solution, this essentially eliminates many potential interferences. However, if the sample also contains water soluble monosulphide, hydrogen sulphide may also be liberated from the acidified sample and is also “fixed” in sodium hydroxide solution, and may therefore interfere with the cyanide determination, especially at sulphide concentrations greater than about 500 mg/kg. A 5 mg/l sulphide solution gives a response equivalent to 40 µg/l as cyanide. Dilution of the sample aliquot to below this level may reduce or eliminate this interference but this practice may need to be balanced against reducing the cyanide concentration to levels below those which can be adequately detected.

Samples that contain organic compounds, such as PAHs and petroleum hydrocarbon compounds, may produce a turbid solution following distillation of the acidified sample. The presence of turbidity in the spectrophotometric determination will interfere with the absorbance measurement. Methods that include alkaline extraction of the soil sample prior to distillation are less susceptible to this type of interference.

Any compound that possesses the potential to react with the reagents and develop a colour in the same spectral region, or affects the colour formation due to the presence of cyanide has the potential to cause an interference.

Interfering substances in the analysis of cyanide by spectrophotometric methods include, for example thiocyanate and iron, and nitrate and nitrite. The presence of thiocyanate and iron in spectrophotometric extracts leads to results that are lower than would normally be expected than if they were absent. The presence of nitrate and nitrite in spectrophotometric extracts leads to results that are higher than would normally be expected than if they were absent. In these cases, the steam distillation stage in the analytical procedure will effectively remove these interferences, as these substances do not tend to be labile under the conditions used.

4 Hazards

With only very few exceptions, cyanides are rapidly-acting poisons following ingestion, inhalation, or absorption through the skin. Cyanide solutions should not be pipetted by mouth and fumes should not be inhaled. Skin contact should be avoided and any splashes involving contact with cyanide solutions should be washed off immediately. Immediate first aid facilities should be available if poisoning is suspected. Provision of qualified personnel to administer first aid should be considered when cyanide is to be determined.

Hydrochloric acid and sodium hydroxide cause burns and are corrosive. Barbituric acid and tin(II) chloride are irritants. Pyridine is flammable and harmful. Formaldehyde is toxic. Thiocyanate, isonicotinic acid, 1,3-dimethylbarbituric acid, potassium hydrogen phthalate and chloramine-T are irritants.

5 Sample collection and preparation

Where performance testing has been carried out using “as received” samples the method may not be suitable for samples that are air-dried. It should be ensured that a representative sub-sample is taken for analysis. Repeat determination should improve the precision of the analysis if homogeneity of the sample is suspect.

Where performance testing has been carried out using air-dried samples the method may not be suitable for samples containing significant amounts of water. The use of an air-dried sample rather than an “as received” sample enables a more homogeneous sub-sample to be taken for analysis. The procedures used to prepare crushed, ground, sieved and/or air-dried samples may, however, adversely affect easily liberated cyanide present in the original sample prior to analysis. Analysts should, therefore, ascertain whether the procedures used to prepare crushed, ground, sieved and/or air-dried samples affect the resulting determination of easily liberated cyanide concentrations.

Care should be taken to ensure that the sub-sample used for analysis is homogeneous, and representative of the bulk material sampled, especially when smaller quantities are required for repeat analyses where high concentrations of cyanide are found or suspected. Further information can be found elsewhere in this series⁽³⁾.

6 References

1 Standing Committee of Analysts, “The determination of cyanide in waters and associated materials (2007)”, *Methods for the Examination of Waters and Associated Materials*, in this series, Environment Agency.

2 MCERTS performance standard for laboratories undertaking chemical testing of soil. Version 3. (see 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.

AA Determination of easily liberated cyanide by steam distillation of a buffered air-dried soil at a pH value of 4, followed by spectrophotometric determination using chloramine-T and barbituric acid

AA1 Performance characteristics of the method

| | |
|--------------------------------|--|
| AA1.1 Substance determined | Easily liberated cyanide in soil. |
| AA1.2 Type of sample | Air-dried samples of soil and contaminated land, ground to less than 2 mm. |
| AA1.3 Basis of method | Hydrogen cyanide (as easily liberated cyanide) is steam distilled from air-dried soil in the presence of zinc sulphate and pH 4 buffer. An alkaline aliquot of the distillate is determined spectrophotometrically using chloramine-T and barbituric acid at 575 nm. |
| AA1.4 Range of application | Typically, up to 100 mg/kg as cyanide, but can be extended, see section AA5.7, note i. |
| AA1.5 Calibration curve | Linear over the range of application. |
| AA1.6 Total standard deviation | See Table AA1. |
| AA1.7 Limit of detection | Typically, 0.05 µg of cyanide can be detected in the aliquot taken as described. This equates to about 0.5 mg/kg of cyanide in the air-dried soil. |
| AA1.8 Sensitivity | Typically, as described, 1 µg of cyanide (equivalent to 10 mg/kg cyanide in air-dried soil) gives an absorbance value of about 0.18. |
| AA1.9 Bias | See Table AA1. |

AA2 Principle

Hydrogen cyanide is liberated from soil at pH 4 in the presence of zinc sulphate and potassium hydrogen phthalate buffer. Zinc sulphate suppresses the release of hydrogen cyanide from complex cyanides. Following distillation, the liberated hydrogen cyanide from simple cyanide salts is absorbed into sodium hydroxide solution and determined spectrophotometrically at 575 nm using chloramine-T and barbituric acid. Complex cyanides possess greater stability and are not usually affected under the conditions described.

AA3 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

AA3.1 Zinc sulphate solution. Dissolve 100 ± 2 g of zinc(II) sulphate heptahydrate in approximately 750 ml of water. Quantitatively transfer the solution to a 1000 ml measuring cylinder and make to 1000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to six months.

AA3.2 Buffer solution (pH 4). Dissolve 51.0 ± 0.2 g of potassium hydrogen phthalate in approximately 900 ml of water. It may be necessary to heat the mixture to approximately $50\text{ }^{\circ}\text{C}$ to completely dissolve the salt. When dissolved, allow the solution to cool to ambient room temperature, and then quantitatively transfer to a 1000 ml measuring cylinder and make to 1000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to one month.

Using the quantities described has shown that for soils of pH values up to and equal to 12, there is sufficient buffering capacity to achieve acidification to a pH value of 4.

AA3.3 Sodium hydroxide solution (0.1 M). Dissolve 8.0 ± 0.1 g of sodium hydroxide in approximately 1800 ml of water. Transfer the solution to a 2000 ml measuring cylinder and make to 2000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to one month.

AA3.4 Sodium hydroxide solution (0.05M). Dissolve 4.0 ± 0.1 g of sodium hydroxide in approximately 1800 ml of water. Transfer the solution to a 2000 ml measuring cylinder and make to 2000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to one month.

AA3.5 Chloramine-T reagent. Dissolve 2.00 ± 0.01 g of chloramine-T in approximately 400 ml of water. Transfer the solution to a 500 ml volumetric flask and make to 500 ml with water. This solution should be prepared on the day of use.

AA3.6 Phosphate buffer solution. Dissolve 13.60 ± 0.01 g of potassium dihydrogen phosphate and 0.28 ± 0.01 g of sodium hydrogen phosphate in approximately 800 ml of water. Make to 1000 ml with water. This solution may be stored at $5 \pm 3^{\circ}\text{C}$ for up to one week.

AA3.7 Pyridine and barbituric acid reagent. To approximately 400 ml of water, add 37.5 ± 1 ml of pyridine and mix well. To this solution, add 7.5 ± 0.1 g of barbituric acid and mix well. To this solution, add 5 ± 1 ml of hydrochloric acid (AA3.11) and make to 500 ml with water. This solution may be stored at $5 \pm 3^{\circ}\text{C}$ for up to one week.

AA3.8 Cyanide stock standard solution (nominally 1000 mg/l). Dissolve 20.0 ± 0.1 g of sodium hydroxide in approximately 800 ml of water. Accurately, and as quickly as possible, weigh out approximately 2.5 g (typically between 2.4 - 2.6 g) of potassium cyanide and quantitatively transfer to the alkaline solution in a 1000 ml volumetric flask. Make to 1000 ml with water. Mix well. This solution may be stored at $5 \pm 3^{\circ}\text{C}$ for up to one month.

AA3.9 Cyanide standard solution (nominally 100 mg/l). Add 10.00 ± 0.05 ml of cyanide stock standard solution (AA3.8) to a 100 ml volumetric flask and make to 100 ml with 0.1M sodium hydroxide (AA3.3). This solution may be stored at $5 \pm 3^{\circ}\text{C}$ for up to one week.

AA3.10 Working cyanide standard solutions. For example, into a series of five 100 ml volumetric flasks, add 2.00, 4.00, 6.00, 8.00 or 10.00 ml of cyanide standard solution (AA3.9) to each flask. Make each flask to 100 ml with 0.05M sodium hydroxide solution (AA3.4). These solutions nominally contain 2.0, 4.0, 6.0, 8.0 and 10.0 mg/l of cyanide respectively. This is equivalent to 2, 4, 6, 8 and 10 µg of cyanide in the 1 ml (i.e. V1 ml) aliquot taken for the spectrophotometric determination (section AA5.5). These solutions may be stored at 5 ± 3 °C for up to one week.

AA3.11 Concentrated hydrochloric acid (SG 1.18).

AA4 Apparatus

In addition to normal laboratory glassware the following will be required.

AA4.1 Steam distillation apparatus capable of producing 50 ± 5 ml of distillate in about 150 seconds.

AA4.2 Spectrometer capable of measuring light absorbance at 575 nm with 10 mm path-length cells.

AA5 Analytical procedure

| Step | Procedure | Notes |
|-------|---|--|
| AA5.1 | Add 40 ml of sodium hydroxide solution (AA3.3) to a V-ml receiving flask (typically 100 ml) of the steam distillation apparatus (AA4.1). See note a. | (a) Commercial apparatus are available for generating steam and undertaking the determination automatically. |
| AA5.2 | Add M g (typically, 10.0 ± 0.1 g) of an homogenised air-dried ground sample (see section 6 and note b) to a distillation flask. To this flask, add 10.0 ± 0.2 ml of zinc sulphate solution (AA3.1) and 50 ± 1 ml of buffer solution (AA3.2) and mix well. Immediately set up the steam distillation apparatus (note c) and commence steam distillation (AA4.1). Continue the distillation until about 50 ml of distillate has collected in the receiving flask. | (b) If samples are to be reported on a dry weight basis (say at 105 °C) rather than on an air-dried basis, it will be necessary to carry out a dry solids content determination on a separate portion of the air-dried material. (c) Ensure losses of hydrogen cyanide are minimised. |
| AA5.3 | When sufficient distillate has been collected stop the distillation process and remove the receiving flask. Make the volume in the receiving flask to V ml (typically, 100 ml) with water. The solution is now ready for spectrophotometric determination but may be stored at 5 ± 3 °C for up to 24 hours before proceeding. | |

- AA5.4 Blank solutions and soil should be analysed with every batch of samples. For blank solutions, the sample is replaced with an equal mass of water. For soils, the sample should be a typical soil analysed in the laboratory containing negligible amounts of easily liberated cyanide and complex cyanide. The spiked soil should be spiked separately with appropriate levels of cyanide solutions. See note d.
- (d) Blanks may be used to evaluate equipment contamination and spiked soils to estimate batch to batch recoveries. Easily liberated cyanide should be added to assess the recovery of adequate amounts of easily liberated cyanide. Complex cyanide should be added to a separate sample to assess whether breakdown of complex cyanide contributes to the easily liberated cyanide determined.

Spectrophotometric determination

- AA5.5 To a V1 ml aliquot (typically, 1.0 ml) of the working cyanide standard solutions (AA3.10) see notes e and f, add 10 ml of water, 8 ml of phosphate buffer (AA3.6), quickly followed by 2 ml of chloramine-T reagent (AA3.5). Mix well and allow the solution to stand a short time, typically 5 minutes, see note g. To this solution, add 10 ml of pyridine and barbituric acid solution (AA3.7). Make the solution to V2 ml (typically 50 ml) with water. Mix well and allow the solution to stand for a short time, typically 1 hour, for the full colour to develop. Read the absorbance of the solution in a 10 mm path-length cell at 575 nm (note h) using water as a blank solution.
- (e) Standard cyanide solutions (AA3.10) are not taken through the distillation process before being determined spectrometrically, but would need to be if recovery estimates were needed to be determined.
- (f) Commercial apparatus are available allowing this procedure to be carried out automatically, but usually on a reduced scale.
- (g) Hydrogen cyanide reacts slowly with chloramine-T to form cyanogen chloride. Sufficient time should be allowed for this reaction to reach completion.
- (h) This wavelength may not be the wavelength of maximum absorption.
- AA5.6 Prepare a calibration graph of absorbance versus amount of cyanide in V1 ml of working cyanide standard solution.
- AA5.7 Repeat section AA5.5 using an aliquot, V1 ml, typically 1.0 ml, of the distillate from section AA5.3, in place of the volume of working cyanide standard solutions (AA3.10) see note i.
- (i) If the reading exceeds the calibration range, a smaller aliquot (V1 ml, AA8.7) may be taken and the spectrometric determination repeated, or the analysis repeated using a smaller quantity of sample (M g, AA8.2) or the distillate volume (V ml, AA8.3) increased

and suitable aliquot taken as appropriate.

AA5.8 From the calibration graph, obtain the amount (A μg) of cyanide in the aliquot (V1 ml, AA5.7) and determine the concentration of easily liberated cyanide, taking into account the volume (V1 ml, AA5.7) of aliquot, the distillate volume (V ml, AA5.3) and the amount (M g, AA5.2) of sample taken.

AA6 Calculations

The concentration, C, of easily liberated cyanide in the air-dried sample is given by

$$C = (A \times V) / (V1 \times M) \quad \text{mg/kg}$$

A is the amount (μg) of cyanide in the aliquot (V1 ml) taken and made to V2 ml and M is the amount (g) of air-dried soil distilled into V ml.

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed.

In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (say at 105 °C). See section 2.

Table AA1 Performance data for easily liberated cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| Low standard at 2 mg/kg as cyanide | | High standard at 8 mg/kg as cyanide | |
|------------------------------------|------|-------------------------------------|------|
| RSD | Bias | RSD | Bias |
| 17.1 | -8.3 | 13 | -8.3 |

| Soil spiked at 80 mg/kg as cyanide | | |
|------------------------------------|------|----------|
| | RSD | Recovery |
| Loam soil | 11.3 | 110.9 |
| Sandy soil | 16 | 112.2 |
| Clay soil | 12.6 | 111.4 |

All values are percentages

RSD is total standard deviation

Data for air-dried sample

Soil spiked with potassium cyanide solution (AA3.8) i.e. 800 µl to 10 g of soil.

Easily liberated cyanide blanks were also prepared containing an aqueous potassium ferrocyanide trihydrate solution ($[K_4(CN)_6] \cdot 3H_2O$) at 1000 mg/l, i.e. containing 2.705 g in 1000 ml, of which 800 µl was spiked to 10 g of soil, i.e. at

80 mg/kg.

Data provided by Severn Trent Laboratories

AB Determination of easily liberated cyanide by steam distillation of a buffered “as received” soil at a pH value of 4, followed by spectrophotometric determination using chloramine-T, sodium isonicotinate and sodium barbiturate

AB1 Performance characteristics of the method

| | |
|----------------------------|---|
| AB1.1 Substance determined | Easily liberated cyanide in soil. |
| AB1.2 Type of sample | “As received” samples of soil and contaminated land. |
| AB1.3 Basis of method | Hydrogen cyanide (as easily liberated cyanide) is steam distilled from an as received soil sample in the presence of zinc sulphate, lead acetate and pH 4 buffer. An alkaline aliquot of the distillate is determined spectrophotometrically using chloramine-T, sodium isonicotinate and sodium barbiturate at 600 nm. |
| AB1.4 Range of application | Typically, up to 120 mg/kg as cyanide but can be extended, see section AB5.7, note k. |
| AB1.5 Calibration curve | Linear over the range of application. |
| AB1.6 precision | See Table AB1. |
| AB1.7 Limit of detection | See Table AB1. Typically, 0.1 µg of cyanide can be detected in the aliquot taken as described. This equates to about 0.2 mg/kg of cyanide in the “as received” soil. |
| AB1.8 Sensitivity | Typically, as described, 1 µg of cyanide (equivalent to about 2 mg/kg cyanide in “as received” soil) gives an absorbance value of about 0.3. |
| AB1.9 Bias | See Table AB1. |

AB2 Principle

Hydrogen cyanide is liberated from an “as received” soil sample at pH 4 in the presence of zinc sulphate, lead acetate and potassium hydrogen phthalate buffer. Zinc sulphate suppresses the release of hydrogen cyanide from complex cyanides. Lead acetate suppresses the release of sulphide. Following distillation, the liberated hydrogen cyanide from simple cyanide salts is absorbed into sodium hydroxide solution and determined spectrophotometrically at 600 nm using chloramine-T, sodium isonicotinate and sodium barbiturate. Complex cyanides possess greater stability and are not usually affected under the conditions described.

AB3 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

AB3.1 Zinc sulphate solution. Dissolve 100.0 ± 0.1 g of zinc(II) sulphate heptahydrate in approximately 750 ml of water contained in a 1000 ml volumetric flask. Make to 1000 ml with water and mix well. This solution may be stored at room temperature for up to one year.

AB3.2 Buffer solution (pH 4). Dissolve 10.2 ± 0.1 g of potassium hydrogen phthalate in approximately 900 ml of water contained in a 1000 ml volumetric flask. It may be necessary to heat the mixture to approximately 40 - 50 °C to completely dissolve the salt. When dissolved, allow the solution to cool to ambient room temperature and make to 1000 ml with water. Mix well. This solution may be stored at room temperature for up to six months.

AB3.3 Sodium hydroxide solution (0.1 M). Dissolve 4.0 ± 0.1 g of sodium hydroxide in approximately 900 ml of water contained in a 1000 ml volumetric flask. Mix well and allow the solution to cool. Make to 1000 ml with water and mix well. This solution may be stored at room temperature for up to one month.

AB3.4 Chloramine-T reagent. Dissolve 1.00 ± 0.01 g of chloramine-T in approximately 90 ml of water contained in a 100 ml volumetric flask. Make to 100 ml with water and mix well. This solution may be stored at 5 ± 3 °C (in a refrigerator) for up to one month.

AB3.5 Cyanide stock standard solution (nominally 1000 mg/l). Dissolve 20.0 ± 0.1 g of sodium hydroxide in approximately 800 ml of water. Accurately, and as quickly as possible, weigh out approximately 2.5 g (typically between 2.4 - 2.6 g) of potassium cyanide and quantitatively transfer to the alkaline solution in a 1000 ml volumetric flask. Make to 1000 ml with water. Mix well. This solution may be stored at room temperature for up to one year.

AB3.6 Cyanide standard solution (nominally 10 mg/l). Add 1.00 ± 0.05 ml of cyanide stock standard solution (AB3.5) to a 100 ml volumetric flask containing 45 ml of sodium hydroxide solution (AB3.3). Mix well and make to 100 ml with water. This solution may be stored at room temperature for up to one month.

AB3.7 Working cyanide standard solutions. For example, into a series of five 100 ml volumetric flasks, add 0.125, 0.25, 0.50, 2.0 or 6.00 ml of cyanide standard solution (AB3.6) to each flask. To each flask, add 10 ml of sodium hydroxide solution (AB3.3). Make each flask to 100 ml with water. Mix well. These solutions nominally contain 0.0125, 0.025, 0.050, 0.20 and 0.60 mg/l of cyanide respectively. This is equivalent to 0.125, 0.25, 0.50, 2.0 and 6.0 µg of cyanide in the 10 ml (V1 ml) aliquot taken for the spectrophotometric determination (section AB5.6). These solutions may be stored at room temperature for up to one week.

AB3.8 Lead acetate solution. Dissolve 60.0 ± 0.1 g of lead acetate trihydrate in approximately 750 ml of water contained in a 1000 ml volumetric flask. Make to 1000 ml with water and mix well. This solution may be stored at room temperature for up to one year.

AB3.9 Sodium isonicotinate (recrystallised). Dissolve 3.30 ± 0.05 g of sodium hydroxide in 200 ± 5 ml of water. To this solution, add 10.00 ± 0.05 g of isonicotinic acid

and dissolve. Evaporate the solution to dryness. The solid may be stored at room temperature for up to six months.

AB3.10 Isonicotinate - barbiturate mixed reagent. Dissolve 2.00 ± 0.05 g of recrystallised sodium isonicotinate (AB3.9) and 2.00 ± 0.05 g of sodium barbiturate in 160 ± 5 ml of water. It may be necessary to heat the mixture to 65 ± 5 °C to facilitate dissolution. Allow the solution to cool, and make to 200 ml with water. The colour of the solution should be clear to pale yellow. This solution may be stored at room temperature for up to one month.

AB3.11 p-Nitrophenol solution (0.1 % m/v). Dissolve 0.10 ± 0.01 g of p-nitrophenol in approximately 70 ml of ethanol contained in a 100 ml volumetric flask. Make to 100 ml with ethanol and mix well. This solution may be stored at room temperature for up to one year.

AB3.12 Acetic acid solution (20 % v/v). Add 10.0 ± 0.1 ml of acetic acid to approximately 35 ml of water contained in a 50 ml volumetric flask. Mix well and make to 50 ml with water. This solution may be stored at room temperature for up to one year.

AB4 Apparatus

In addition to normal laboratory glassware the following will be required.

AB4.1 Steam distillation apparatus capable of producing about 180 ml of distillate in about 400 seconds.

AB4.2 Spectrometer capable of measuring light absorbance at 600 nm.

AB5 Analytical procedure

| Step | Procedure | Notes |
|-------|---|---|
| AB5.1 | Add 20 ml of sodium hydroxide solution (AB3.3) to a V-ml (typically 200 ml) receiving flask of the steam distillation apparatus (AB4.1). See note a. | (a) Commercial apparatus are available for generating steam and undertaking the determination automatically. |
| AB5.2 | A representative amount (M g, typically, 10.0 ± 0.1 g) of an "as received" soil sample (see section 6 and note b) should be added to a distillation flask. To this flask, add 10 - 20 ml of water, 10.0 ± 0.2 ml of zinc sulphate solution (AB3.1) and 3.0 ± 0.1 ml of lead acetate solution (AB3.8) followed by 30 ml of buffer solution (AB3.2) and mix well. Immediately set up the steam distillation apparatus (see note c) and commence steam distillation (AB4.1). Continue the distillation until about 180 ml of | (b) If samples are to be reported on a dry weight basis (at say 105 °C) rather than on an "as received" basis it will be necessary to carry out a dry solids content determination on a representative amount of the same "as received" sample. (c) Ensure losses of hydrogen cyanide are minimised. |

distillate has collected in the receiving flask.

AB5.3 When sufficient distillate has been collected, stop the distillation process and remove the receiving flask. Make to volume (V ml, typically 200 ml) in the receiving flask with water. The solution is now ready for spectrophotometric determination.

AB5.4 Blank solutions and soil should be analysed with every batch of samples. For blank solutions, the sample is replaced with an equal mass of water. For soils, the sample should be a typical soil analysed in the laboratory containing negligible amounts of easily liberated cyanide and complex cyanide. The spiked soil should be spiked separately with appropriate levels of cyanide solutions. See note d.

(d) Blanks may be used to evaluate equipment contamination and spiked soils to estimate batch to batch recoveries. Easily liberated cyanide should be added to assess the recovery of adequate amounts of easily liberated cyanide. Complex cyanide should be added to a separate sample to assess whether breakdown of complex cyanide contributes to the easily liberated cyanide determined.

Spectrophotometric determination

AB5.5 To an V1 ml aliquot, typically 10 ml of the working cyanide standard solutions (AB3.7) see notes e and f, add 2 drops (0.1 ml) of p-nitrophenol solution (AB3.11) and 2 drops (0.1 ml) of acetic acid solution (AB3.12). See note g. To the clear solution, add $200 \pm 5 \mu\text{l}$ of chloramine-T solution (AB3.5) and allow the solution to stand for several minutes, see note h. Add $5.0 \pm 0.1 \text{ ml}$ of isonicotinate - barbiturate mixed reagent (AB3.10) and allow the colour of the solution to fully develop, see note i. Read the absorbance of the solution in a 10 mm path-length cell at 600 nm (note j) using water as blank solution.

(e) Standard cyanide solutions (AB3.7) are not taken through the distillation process before being determined spectrometrically, but would need to be if recovery values were needed to be determined.

(f) Commercial apparatus are available allowing this procedure to be carried out automatically, but usually on a reduced scale.

(g) If the colour of the solution is not clear, add more acetic acid solution (AB3.12).

(h) Hydrogen cyanide reacts slowly with chloramine-T to form cyanogen chloride. Sufficient time should be allowed for this reaction to reach completion.

(i) This usually takes about 40 minutes.

(j) This wavelength may not be the wavelength of maximum absorption.

AB5.6 Prepare a calibration graph of absorbance versus amount of cyanide in V1 ml of working cyanide standard solution.

AB5.7 Repeat section AB5.5 using an aliquot, V1 ml, typically 10 ml, of the distillate from section AB5.3, in place of the volume of working cyanide standard solutions (AB3.7) see note k.

(k) If the reading exceeds the calibration range, a smaller aliquot (V1 ml, AB5.7) may be taken and the spectrometric determination repeated, or the analysis repeated using a smaller quantity of sample (M g, AB5.2) or the distillate volume (V ml, AB5.3) increased and suitable aliquot taken as appropriate.

AB5.8 From the calibration graph, obtain the amount (A µg) of cyanide in the aliquot (V1 ml, AB5.7) and determine the concentration of easily liberated cyanide, taking into account the volume of aliquot (V1 ml, AB5.7) the distillate volume (V ml, AB5.3) and the amount (M g, AB5.2) of sample taken.

AB6 Calculations

The concentration, C, of easily liberated cyanide in the “as received” sample is given by

$$C = (A \times V) / (V1 \times M) \quad \text{mg/kg}$$

A is the amount (µg) of cyanide in the aliquot (V1 ml) taken and
M is the amount (g) of “as received” soil distilled into V ml.

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed.

In addition, the reporting of results may also need to take into account whether results are calculated on an “as received” basis or on an air-dried basis (say at 30 °C) or on a dry weight basis (say at 105 °C). See section 2.

Table AB1 Performance data for easily liberated cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 2.4 mg/kg as cyanide | | Soil spiked at 9.6 mg/kg as cyanide | |
|------------|-------------------------------------|------|-------------------------------------|------|
| | Precision | Bias | Precision | Bias |
| Top soil | 2.4 | -2.2 | 3.7 | -1.6 |
| Sandy soil | 5.7 | -3.1 | 4.2 | -1.8 |
| Clay soil | 3.8 | -3.1 | 2.6 | -0.8 |

Values as percentages

Precision as total relative standard deviation

Data for "as received" sample

Spiked with potassium cyanide solution (AB3.5) i.e. 24 µl to 10 g of soil, and 96 µl to 10 g of soil.

| Soil type | Limit of detection** (mg/kg) |
|------------|------------------------------|
| Top soil | 0.1 |
| Sandy soil | 0.1 |
| Clay soil | 0.2 |

Data provided by BAE Systems

AC Determination of easily liberated cyanide by steam distillation of an alkaline extract of a sample of soil at a pH value of 3.8, followed by spectrophotometric determination using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid

Procedures are described whereby an alkaline extract of a sample of soil is treated with zinc sulphate. Following addition of citric acid and sodium hydroxide, the mixture is then steam distilled. A pH-adjusted portion of the distillate is then spectrophotometrically determined. For “as received” soils, a representative portion of the soil is taken. For air-dried samples, an homogeneous portion is taken. See section 6.

AC1 Performance characteristics of the method

| | |
|--------------------------------|--|
| AC1.1 Substance determined | Easily liberated cyanide in soil. |
| AC1.2 Type of sample | Samples of soil and contaminated land. |
| AC1.3 Basis of method | The sample of soil is extracted with sodium hydroxide solution. Zinc sulphate solution is added to an aliquot of this alkaline extract and the mixture steam distilled under acidic conditions at a pH value of 3.8 using a citric acid-sodium hydroxide buffer solution where hydrogen cyanide (as easily liberated cyanide) is liberated. A pH adjusted aliquot of the distillate is spectrophotometrically determined at 600 nm, using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid. |
| AC1.4 Range of application | Typically, up to 25 mg/kg as cyanide, but can be extended, see section AC5.9, note k. |
| AC1.5 Calibration curve | Linear over the range of application. |
| AC1.6 Total standard deviation | See Tables AC1 - AC3. |
| AC1.7 Limit of detection | Typically, 0.1 µg of cyanide can be detected in the aliquot taken as described. This equates to about 0.5 mg/kg of cyanide in the sample of soil analysed. |
| AC1.8 Sensitivity | Typically, as described, 0.1 µg of cyanide (equivalent to 0.5 mg/kg cyanide in the sample of soil analysed) gives an absorbance value of about 0.006. |
| AC1.9 Bias | See Tables AC1 - AC3. |

AC2 Principle

A representative or homogeneous portion of the sample of soil is extracted with 1M sodium hydroxide solution. Zinc sulphate solution is added to an aliquot of this extract and steam distilled under acidic conditions (at a pH value of 3.8) using a citric acid-sodium hydroxide buffer solution. (Zinc sulphate suppresses the release of hydrogen cyanide from complex cyanides). Following distillation, the liberated hydrogen cyanide from simple cyanide salts is absorbed into a pH 5.2 buffer solution containing chloramine-T and determined spectrophotometrically at 600 nm using isonicotinic acid and 1,3-dimethylbarbituric acid. Complex cyanides possess greater stability and are not usually affected under the conditions described.

AC3 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

AC3.1 Zinc sulphate solution. Dissolve 20.0 ± 0.2 g of zinc(II) sulphate heptahydrate in approximately 1200 ml of water. Quantitatively transfer the solution to a 2000 ml measuring cylinder and make to 2000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to 1 week.

AC3.2 Buffer solution (pH 5.2). Dissolve 41.0 ± 0.5 g of potassium hydrogen phthalate in approximately 1000 ml of water. Add 4.60 ± 0.05 g of sodium hydroxide and mix well. Add 6.0 ± 0.5 ml of 30% v/v polyethyleneglycol lauryl ether solution and mix well. Make to 2000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to 1 week.

AC3.3 Chloramine-T reagent. Dissolve 4.00 ± 0.1 g of chloramine-T in approximately 1000 ml of water, and make to 2000 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to 1 week.

AC3.4 Colour reagent. To approximately 1000 ml of water, dissolve 14.0 ± 0.2 g of sodium hydroxide. To this cooled solution, add 33.6 ± 0.3 g of 1,3-dimethylbarbituric acid and 27.2 ± 0.3 g of isonicotinic acid. Mix well. Add 6 ml of 30% v/v polyethyleneglycol lauryl ether solution and make to 2000 ml with water. Mix well. Filter (nominal pore size 0.45 µm) this solution. This solution may be stored at room temperature for up to 1 week.

AC3.5 Cyanide stock standard solution (nominally 100 mg/l). Dissolve 40.0 ± 0.5 g of sodium hydroxide in approximately 800 ml of water. Accurately, and as quickly as possible, weigh out 0.250 ± 0.001 g of potassium cyanide and quantitatively transfer to the alkaline solution in a 1000 ml volumetric flask. Make to 1000 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to one month.

AC3.6 Sodium hydroxide solution (1M). Dissolve 40.0 ± 0.1 g of sodium hydroxide in approximately 800 ml of water. Transfer the solution to a 1000 ml measuring cylinder and make to 1000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to 3 months.

AC3.7 Working cyanide standard solutions. For example, into a series of five 100 ml volumetric flasks, add 50 ml of 1M sodium hydroxide solution (AC3.6) followed by 1.0, 2.0, 3.0, 4.0 and 5.0 ml of cyanide standard solution (AC3.5) to each flask. Make each flask to

100 ml with 1M sodium hydroxide solution (AC3.6). These solutions nominally contain 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l of cyanide respectively. This is equivalent to 1, 2, 3, 4 and 5 µg of cyanide in the aliquot taken for the spectrophotometric determination (section AC5.5). These solutions should be used on the day of preparation.

AC3.8 Distillation reagent. Dissolve 100 ± 1 g of citric acid and 24.0 ± 0.2 g of sodium hydroxide in approximately 1000 ml of water. Mix well. Make to 2000 ml with water and mix well. This solution may be stored at room temperature for up to 1 week.

AC4 Apparatus

In addition to normal laboratory glassware the following will be required.

AC4.1 Steam distillation apparatus capable of producing 10 ml of distillate in about 15 minutes

AC4.2 Spectrometer capable of measuring light absorbance at 600 nm with 10 mm path-length cells.

AC5 Analytical procedure

| Step | Procedure | Notes |
|-------|--|---|
| AC5.1 | Add M g (typically, 8.0 ± 0.1 g) of a representative or homogeneous portion of the sample of soil (see section 6 and note a) to a flask. To this flask, add V ml, typically, 40.0 ± 0.5 ml of sodium hydroxide solution (AC3.6) and shake well for approximately 30 minutes. Filter the sample until at least 10 ml of filtrate are produced. See note b. | (a) If samples are to be reported on an air-dried basis (say at 30 °C) or a dry weight basis (say at 105 °C) rather than on an "as received" basis, it will be necessary to carry out a dry solids content determination on a separate portion of the "as received" material. (b) Centrifuging the mixture at 3000 rpm should speed up the filtration process. |
| AC5.2 | Transfer V1 ml (1.0 ml) of this clear alkaline extract to the steam distillation apparatus and dilute with 9.0 ml of water. To this flask, add 12.5 ml of zinc sulphate solution (AC3.1) see note c. To the receiving flask, typically 50 ml, (i.e.V2 ml) of the distillation apparatus (AC4.1) add 12.5 ml of pH 5.2 buffer solution (AC3.2) and 12.5 ml of chloramine-T solution (AC3.3) | (c) Commercial apparatus are available for generating steam and undertaking the determination automatically. |
| AC5.3 | To the diluted alkaline zinc sulphate mixture, add 4.2 ml of distillation reagent | (d) Ensure losses of hydrogen cyanide are minimised. |

(AC3.8) and immediately set up the steam distillation apparatus (note d) and commence steam distillation (AC4.1). Continue the distillation until about 10 ml of distillate has collected in the receiving flask.

AC5.4 When sufficient distillate has been collected stop the distillation process and remove the receiving flask. Mix well, then add 12.5 ml of colour reagent (AC3.4). Make the volume in the receiving flask to V2 ml (typically, 50 ml) with water. The solution is now ready for spectrophotometric determination.

AC5.5 Blank solutions and soil should be analysed with every batch of samples. For blank solutions, the sample is replaced with an equal mass of water. For soils, the sample should be a typical soil analysed in the laboratory containing negligible amounts of easily liberated cyanide and complex cyanide. The spiked soil should be spiked separately with appropriate levels of cyanide solutions. See notes e and f.

(e) Blanks may be used to evaluate equipment contamination and spiked soils to estimate batch to batch recoveries. Easily liberated cyanide should be added to assess the recovery of adequate amounts of easily liberated cyanide. Complex cyanide should be added to a separate sample to assess whether breakdown of complex cyanide contributes to the easily liberated cyanide determined.

(f) For example, 1 ml of cyanide stock standard solution (AC3.5) for the easily liberated cyanide, i.e. 100 µg of cyanide.

Spectrophotometric determination

AC5.6 To a V1 ml aliquot (typically, 1 ml) of the working cyanide standard solutions (AC3.7) see notes g and h, add 9 ml of water, 12.5 ml of buffer (AC3.2), quickly followed by 12.5 ml of chloramine-T reagent (AC3.3). Mix well and allow the solution to stand a short time, typically 5 minutes. To this solution, add 12.5 ml of colour reagent (AC3.4). Make the solution to V2 ml (typically 50 ml) with water. Mix well and allow the solution to stand at 37 °C for awhile, typically 30 - 60 minutes, for the full colour to develop, see note i. Read the absorbance of the solution in a 10 mm path-length cell at 600 nm (note j)

(g) Standard cyanide solutions (AC3.7) are not taken through the distillation process before being determined spectrometrically, but would need to be if recovery estimates were needed to be determined.

(h) Commercial apparatus are available allowing this procedure to be carried out automatically, but usually on a reduced scale. When using commercial automatic apparatus, the standard cyanide solutions are distilled.

using water as a blank solution.

(i) The reaction of hydrogen cyanide with chloramine-T to form cyanogen chloride and the subsequent colouration reaction are slow reactions. Sufficient time should be allowed for these reactions to reach completion.

(j) This wavelength may not be the wavelength of maximum absorption.

AC5.7 Prepare a calibration graph of absorbance versus mass of cyanide in V2 ml of mixed solution.

AC5.8 Repeat section AC5.6 using an aliquot, V1 ml, typically 10 ml, of the distillate from section AC5.4, in place of the volume of working cyanide standard solutions (AC3.7) and volume of water.

AC5.9 Read the absorbance of the sample solution in the same 10mm path length cell at 600 nm. see note k.

(k) If the reading exceeds the calibration range, a volumetric dilution may be prepared (using water) and the spectrophotometric determination repeated. If so, the maximum amount of cyanide that could be accommodated, and hence, the maximum dilution that could be tolerated, would need to be known, and whether the distillation process had adequately recovered all of the cyanide present in the sample. Alternatively, the analysis should be repeated using a smaller quantity of sample (M g, AC5.1) or the distillate volume (V2 ml, AC5.4) increased and suitable aliquot taken as appropriate.

AC5.10 From the calibration graph, obtain the mass (A μg) of cyanide in the sample solution (AC5.4) and determine the concentration of easily liberated cyanide in the "as received" soil, taking into account the extraction volume, V ml, (AC5.1) the volume distilled, V1 ml, (AC5.2) the distillate volume, V2 ml, (AC5.4) any

dilutions (note k) and the mass (M g, AC5.1) of sample taken.

AC6 Calculations

The concentration, C, of easily liberated cyanide in the sample of soil analysed is given by

$$C = D \times (A \times V) / (V1 \times M) \quad \text{mg/kg}$$

A is the mass (μg) of cyanide in the sample solution (AC5.7),

M is the mass (g) of soil extracted into V ml,

V1 is the volume of extracted sample that is distilled (AC5.2) and

D is the dilution factor, if appropriate

Any samples where the distillate volume, V2 ml, (AC5.4) is different to that described will need to take this into account.

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed.

In addition, the reporting of results may also need to take into account whether results are calculated on an "as received" basis, an air-dried basis (for example at 30 °C) or on a dry weight basis (say at 105 °C). See section 2.

Table AC1 Performance data for easily liberated cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 5 mg/kg as cyanide | | Soil spiked at 20 mg/kg as cyanide | |
|------------|-----------------------------------|-------|------------------------------------|-------|
| | RSD | Bias | RSD | Bias |
| Loam soil | 5.6 | -21.1 | 4.0 | -16.8 |
| Sandy soil | 3.6 | -14.5 | 2.7 | -12.1 |
| Clay soil | 6.4 | -28.5 | 4.5 | -20.3 |

All values are percentages

RSD is relative standard deviation

Data for "as received" sample

Spiked with potassium cyanide solution (AC3.5) i.e. 250 μl to 5 g of soil, and 1000 μl to 5 g of soil.

Data provided by Alcontrol Laboratories

Table AC2 Performance data for easily liberated cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 10 mg/kg as cyanide | | Soil spiked at 40 mg/kg as cyanide | |
|------------|------------------------------------|------|------------------------------------|-------|
| | RSD | Bias | RSD | Bias |
| Loam soil | 13.3 | -4.9 | 8.2 | -12.1 |
| Sandy soil | 5.0 | 0.4 | 2.9 | -3.3 |
| Clay soil | 7.2 | 3.6 | 3.3 | 3.0 |

All values are percentages

Precision is total standard deviation

Data for air-dried sample

Spiked with potassium cyanide solution (AC3.5) i.e. 500 µl to 5 g of soil, and 2000 µl to 5 g of soil.

The concentration range is up to 5.0 mg/l in solution, equivalent to 50 mg/kg in the air-dried soil.

Data provided by Chemtest

Table AC3 Performance data for easily liberated cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 10 mg/kg as cyanide | | Soil spiked at 40 mg/kg as cyanide | |
|-------------|------------------------------------|-------|------------------------------------|------|
| | Precision | Bias | Precision | Bias |
| Silt soil | 12.7 | -18.9 | 10.5 | -9.3 |
| Sandy soil | 4.8 | -0.9 | 4.7 | 0.9 |
| Clay soil | 7.3 | -3.8 | 5.7 | -1.2 |
| Made ground | 11.7 | -13.2 | 9.2 | -5.1 |

All values are percentages

Precision is total standard deviation

Data for "as received" sample

Soils were spiked with a solution containing 1000 mg/l potassium cyanide (2.5 g per 1000 ml) 1000 mg/l potassium hexacyanoferrate (2.12 g per 1000 ml) and 10000 mg/l potassium thiocyanate (16.7 g per 1000 ml) containing 40 g of sodium hydroxide per 1000 ml. To two 10 g portions of sample, 2.0 ml was added to one portion (i.e. 200 mg/kg) and 8.0 ml to another (i.e. 800 mg/kg).

The concentration range is up to 5.0 mg/l in solution, equivalent to 50 mg/kg in the "as received" soil.

Data provided by Scientifics

BA Determination of total cyanide by steam distillation of an acidified air-dried soil sample followed by spectrophotometric determination using chloramine-T and barbituric acid

BA1 Performance characteristics of the method

| | |
|--------------------------------|--|
| BA1.1 Substance determined | Total cyanide in soil. |
| BA1.2 Type of sample | Air-dried samples of soil and contaminated land, ground to less than 2 mm. |
| BA1.3 Basis of method | Hydrogen cyanide (as total cyanide) is steam distilled from air-dried soil sample in the presence of copper sulphate, tin(II) chloride and phosphoric acid. An alkaline aliquot of the distillate is determined spectrophotometrically using chloramine-T and barbituric acid at 575 nm. |
| BA1.4 Range of application | Typically, up to 100 mg/kg as cyanide but can be extended, see section BA5.7, note j. |
| BA1.5 Calibration curve | Linear over the range of application. |
| BA1.6 total standard deviation | See Table BA1. |
| BA1.7 Limit of detection | Typically, 0.05 µg of cyanide can be detected in the aliquot taken as described. This equates to about 0.5 mg/kg of cyanide in the air-dried soil. |
| BA1.8 Sensitivity | Typically, as described, 1 µg of cyanide (equivalent to 10 mg/kg cyanide in air-dried soil) gives an absorbance value of about 0.18. |
| BA1.9 Bias | See Table BA1. |

BA2 Principle

Hydrogen cyanide is liberated from soil in the presence of copper sulphate, tin(II) chloride and phosphoric acid. This usually occurs at a pH value of less than 1. Following distillation, the liberated hydrogen cyanide from simple cyanide salts and complex cyanide compounds is absorbed into sodium hydroxide solution and determined spectrophotometrically at 575 nm using chloramine-T and barbituric acid.

BA3 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

BA3.1 Ortho-phosphoric acid (SG 1.69).

BA3.2 Copper sulphate solution (approximately 20 % w/v). Dissolve 200 ± 5 g of copper(II) sulphate pentahydrate in approximately 750 ml of water. Make to 1000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to six months.

BA3.3 Concentrated hydrochloric acid (SG 1.18).

BA3.4 Tin(II) chloride solution. Dissolve 25 ± 1 g of tin(II) chloride dihydrate in 125 ± 5 ml of hydrochloric acid (BA3.3). When completely dissolved, quantitatively transfer to a 500 ml measuring cylinder and make to 500 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to six months.

BA3.5 Sodium hydroxide solution (0.1 M). Dissolve 8 ± 0.1 g of sodium hydroxide in approximately 1800 ml of water. Transfer the solution to a 2000 ml measuring cylinder and make to 2000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to one month.

BA3.6 Sodium hydroxide solution (0.05M). Dissolve 4 ± 0.1 g of sodium hydroxide in approximately 1800 ml of water. Transfer the solution to a 2000 ml measuring cylinder and make to 2000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to one month.

BA3.7 Chloramine-T reagent. Dissolve 2.00 ± 0.01 g of chloramine-T in approximately 400 ml of water. Transfer the solution to a 500 ml volumetric flask and make to 500 ml with water. This solution should be prepared on the day of use.

BA3.8 Phosphate buffer solution. Dissolve 13.60 ± 0.01 g of potassium dihydrogen phosphate and 0.28 ± 0.01 g of sodium hydrogen phosphate in approximately 800 ml of water. Make to 1000 ml with water. This solution may be stored at $5 \pm 3^\circ\text{C}$ for up to one week.

BA3.9 Pyridine and barbituric acid reagent. To approximately 400 ml of water, add 37.5 ± 1 ml of pyridine and mix well. To this solution, add 7.5 ± 0.1 g of barbituric acid and mix well. To this solution, add 5 ± 1 ml of hydrochloric acid (BA3.3) and make to 500 ml with water. This solution may be stored at $5 \pm 3^\circ\text{C}$ for up to one week.

BA3.10 Cyanide stock standard solution (nominally 1000 mg/l). Dissolve 20.0 ± 0.1 g of sodium hydroxide in approximately 800 ml of water. Accurately, and as quickly as possible, weigh out approximately 2.5 g (typically between 2.4 - 2.6 g) of potassium cyanide and quantitatively transfer to the alkaline solution in a 1000 ml volumetric flask. Make to 1000 ml with water. Mix well. This solution may be stored at $5 \pm 3^\circ\text{C}$ for up to one month.

BA3.11 Cyanide standard solution (nominally 100 mg/l). Add 10.00 ± 0.05 ml of cyanide stock standard solution (BA3.10) to a 100 ml volumetric flask and make to 100 ml with 0.1M sodium hydroxide (BA3.5). This solution may be stored at $5 \pm 3^\circ\text{C}$ for up to one week.

BA3.12 Working cyanide standard solutions. For example, into a series of five 100 ml

volumetric flasks, add 2.00, 4.00, 6.00, 8.00 or 10.00 ml of cyanide standard solution (BA3.11) to each flask. Make each flask to 100 ml with 0.05M sodium hydroxide solution (BA3.6). These solutions nominally contain 2.0, 4.0, 6.0, 8.0 and 10.0 mg/l of cyanide respectively. This is equivalent to 2, 4, 6, 8 and 10 µg of cyanide in the 1.0 ml (V1 ml) aliquot taken for the spectrophotometric determination (section BA5.5). These solutions may be stored at $5 \pm 3^\circ\text{C}$ for up to one week.

BA4 Apparatus

In addition to normal laboratory glassware the following will be required.

BA4.1 Steam distillation apparatus capable of producing 50 ± 5 ml of distillate in about 150 seconds.

BA4.2 Spectrometer capable of measuring light absorbance at 575 nm with 10 mm path-length cells.

BA5 Analytical procedure

| Step | Procedure | Notes |
|-------|---|---|
| BA5.1 | Add 40 ml of 0.1M sodium hydroxide solution (BA3.5) to a V-ml, typically 100 ml, receiving flask of the steam distillation apparatus (BA4.1). See note a. | (a) Commercial apparatus are available for generating steam and undertaking the determination automatically. |
| BA5.2 | Add M g (typically, 10.0 ± 0.1 g) of an homogenised air-dried ground sample (see section 6 and note b) to a distillation flask. To this flask, add 10.0 ± 0.2 ml of copper sulphate solution (BA3.2) and 2.0 ± 0.1 ml of tin(II) chloride solution (BA3.4) and 50 ± 1 ml of phosphoric acid (BA3.1) and mix well, see note c. Immediately set up the steam distillation apparatus (note d) and commence steam distillation (BA4.1). Continue the distillation until about 50 ml of distillate has collected in the receiving flask. | (b) If samples are to be reported on a dry weight basis (say at 105°C) rather than on an air-dried basis, it will be necessary to carry out a dry solids content determination on a separate portion of the air-dried material. (c) The pH value of this suspension is usually less than 1. (d) Ensure losses of hydrogen cyanide are minimised. |
| BA5.3 | When sufficient distillate has been collected stop the distillation process and remove the receiving flask. Make the volume in the receiving flask to V ml (typically, 100 ml) with water. The solution is now ready for spectrophotometric determination but may be stored at $5 \pm 3^\circ\text{C}$ for up to 24 hours before proceeding | |

- BA5.4 Blank solutions and soil should be analysed with every batch of samples. For blank solutions, the sample should be replaced with an equal mass of water. For soils, the sample should be replaced with an equal mass of soil spiked with an appropriate level of complex cyanide solution. See note e.
- (e) Blanks may be used to evaluate equipment contamination and spiked soils to estimate batch to batch recoveries.

Spectrophotometric determination

- BA5.5 To a V_1 ml aliquot, typically 1.0 ml, of the working cyanide standard solutions (BA3.12) see notes f and g, add 10 ml of water and 8 ml of phosphate buffer (BA3.8) quickly followed by 2 ml of chloramine-T reagent (BA3.7). Mix well and allow the solution to stand a short time, typically 5 minutes, see note h. To this solution, add 10 ml of pyridine and barbituric acid solution (BA3.9). Make the solution to V_2 ml (typically 50 ml) with water. Mix well and allow the solution to stand for a short time, typically 1 hour, for the full colour to develop. Read the absorbance of the solution in a 10 mm path-length cell at 575 nm (note i) using water as a blank solution.
- (f) Standard cyanide solutions (BA3.12) are not taken through the distillation process before being determined spectrometrically, but would need to be if recovery values were needed to be determined.
- (g) Commercial apparatus are available allowing this procedure to be carried out automatically, but usually on a reduced scale.
- (h) Hydrogen cyanide reacts slowly with chloramine-T to form cyanogen chloride. Sufficient time should be allowed for this reaction to reach completion.
- (i) This wavelength may not be the wavelength of maximum absorption.
- BA5.6 Prepare a calibration graph of absorbance versus amount of cyanide in V_1 ml of working cyanide standard solution.
- BA5.7 Repeat section BA5.5 using an aliquot, V_1 ml, (typically 1.0 ml) of the distillate from section BA5.3, in place of the volume of working cyanide standard solutions (BA3.12) see note j.
- (j) If the reading exceeds the calibration range, a smaller aliquot (V_1 ml, BA5.8) may be taken and the spectrometric determination repeated, or the analysis repeated using a smaller quantity of sample (M g, BA5.2) or the distillate volume (V ml, BA5.3) increased and suitable aliquot taken as appropriate.
- BA5.8 From the calibration graph, obtain the amount ($A \mu\text{g}$) of cyanide in the aliquot (V_1 ml, BA5.8) and determine the

concentration of total cyanide, taking into account the volume of aliquot (V1 ml, BA5.7) the distillate volume (V ml, BA5.3) and amount (M g, BA5.2) of sample taken.

BA6 Calculations

The concentration, C, of total cyanide in the air-dried sample is given by

$$C = (A \times V) / (V1 \times M) \quad \text{mg/kg}$$

A is the amount (μg) of cyanide in the aliquot (V1 ml) taken and made to V2 ml and M is the amount (g) of air-dried soil distilled into V ml.

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed.

In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (say at 105 °C). See section 2.

Table BA1 Performance data for total cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| Low standard at 2 mg/kg as cyanide | | High standard at 8 mg/kg as cyanide | |
|------------------------------------|------|-------------------------------------|------|
| RSD | Bias | RSD | Bias |
| 14.3 | -1.7 | 10.1 | 7.5 |

| Soil spiked at 80 mg/kg as cyanide | | |
|------------------------------------|------|----------|
| | RSD | Recovery |
| Loam soil | 8.2 | 91.2 |
| Sandy soil | 7.2 | 101.6 |
| Clay soil | 10.8 | 104.4 |

All values are percentages

RSD is total standard deviation

Spiked with an aqueous potassium ferrocyanide trihydrate solution ($[\text{K}_4(\text{CN})_6]3\text{H}_2\text{O}$) at 1000 mg/l, i.e. containing 2.705 g in 1000 ml, of which 800 μl was spiked to 10 g of soil, i.e. at 80 mg/kg.

Data provided by Severn Trent Laboratories

BB Determination of total cyanide by steam distillation under acidic conditions of an alkaline extract of an “as received” soil sample, followed by spectrophotometric determination using chloramine-T, sodium isonicotinate and sodium barbiturate

BB1 Performance characteristics of the method

| | |
|----------------------------|--|
| BB1.1 Substance determined | Total cyanide in soil. |
| BB1.2 Type of sample | “As received” samples of soil and contaminated land. |
| BB1.3 Basis of method | Hydrogen cyanide (as total cyanide) is steam distilled from an “as received” soil sample in the presence of copper sulphate, tin(II) chloride and phosphoric acid. An alkaline aliquot of the distillate is determined spectrophotometrically using chloramine-T, sodium isonicotinate and sodium barbiturate at 600 nm. |
| B1.4 Range of application | Typically, up to 120 mg/kg as cyanide, but can be extended, see section BB5.9, note k. |
| BB1.5 Calibration curve | Linear over the range of application. |
| BB1.6 Precision | See Table BB1. |
| BB1.7 Limit of detection | See Table BB1. Typically, 0.1 µg of cyanide can be detected in the aliquot taken as described. This equates to about 0.2 mg/kg of cyanide in the “as received” soil. |
| BB1.8 Sensitivity | Typically, as described, 1 µg of cyanide (equivalent to about 2 mg/kg cyanide in “as received” soil) gives an absorbance value of about 0.3. |
| BB1.9 Bias | See Table BB1. |

BB2 Principle

Hydrogen cyanide is liberated from an “as received” soil sample acidified with phosphoric acid in the presence of copper sulphate and tin(II) chloride. This usually occurs at a pH value of less than 1. Following distillation, the liberated hydrogen cyanide from simple cyanide salts and complex cyanide compounds is absorbed into sodium hydroxide solution and determined spectrophotometrically at 600 nm using chloramine-T, sodium isonicotinate and sodium barbiturate.

BB3 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

BB3.1 Orthophosphoric acid (SG 1.69).

BB3.2 Concentrated hydrochloric acid (SG 1.18).

BB3.3 Tin(II) chloride solution. Add 4.0 ± 0.1 g of tin(II) chloride dihydrate to a 100 ml volumetric flask. Add 1.0 ± 0.1 ml of hydrochloric acid (BB3.2) and make to 100 ml with water. Mix well. This solution should be prepared on the day of use.

BB3.4 Copper sulphate solution. Dissolve 156.4 ± 0.1 g of copper(II) sulphate pentahydrate in approximately 750 ml of water contained in a 1000 ml volumetric flask. Make to 1000 ml with water and mix well. This solution may be stored at room temperature for up to one year.

BB3.5 Sodium hydroxide solution (0.1 M). Dissolve 4.0 ± 0.1 g of sodium hydroxide in approximately 900 ml of water contained in a 1000 ml volumetric flask. Mix well and allow the solution to cool. Make to 1000 ml with water and mix well. This solution may be stored at room temperature for up to one month.

BB3.6 Chloramine-T reagent. Dissolve 1.00 ± 0.01 g of chloramine-T in approximately 90 ml of water contained in a 100 ml volumetric flask. Make to 100 ml with water and mix well. This solution may be stored at $5 \pm 3^\circ\text{C}$ (in a refrigerator) for up to one month.

BB3.7 Cyanide stock standard solution (nominally 1000 mg/l). Dissolve 20.0 ± 0.1 g of sodium hydroxide in approximately 800 ml of water. Accurately, and as quickly as possible, weigh out approximately 2.5 g (typically between 2.4 - 2.6 g) of potassium cyanide and quantitatively transfer to the alkaline solution in a 1000 ml volumetric flask. Make to 1000 ml with water. Mix well. This solution may be stored at room temperature for up to one year.

BB3.8 Cyanide standard solution (nominally 10 mg/l). Add 1.00 ± 0.05 ml of cyanide stock standard solution (BB3.7) to a 100 ml volumetric flask containing 45 ml of sodium hydroxide solution (BB3.5). Mix well and make to 100 ml with water. This solution may be stored at room temperature for up to one month.

BB3.9 Working cyanide standard solutions. For example, into a series of five 100 ml volumetric flasks, add 0.125, 0.25, 0.50, 2.0 or 6.00 ml of cyanide standard solution (BB3.8) to each flask. To each flask, add 10 ml of sodium hydroxide solution (BB3.5). Make each flask to 100 ml with water. These solutions nominally contain 0.0125, 0.025, 0.050, 0.20 and 0.60 mg/l of cyanide respectively. This is equivalent to 0.125, 0.25, 0.50, 2.0 and 6.0 μg of cyanide in the 10 ml (V1 ml) aliquot taken for the spectrophotometric determination (section BB5.7). These solutions may be stored at room temperature for up to one week.

BB3.10 Sodium hydroxide solution (1 M). Dissolve 40.0 ± 0.1 g of sodium hydroxide in approximately 900 ml of water contained in a 1000 ml volumetric flask. Mix well and allow

the solution to cool. Make to 1000 ml with water and mix well. This solution may be stored at room temperature for up to one year.

BB3.11 Sodium isonicotinate (recrystallised). Dissolve 3.30 ± 0.05 g of sodium hydroxide in 200 ± 5 ml of water. To this solution, add 10.00 ± 0.05 g of isonicotinic acid and dissolve. Evaporate the solution to dryness. The solid may be stored at room temperature for up to six months.

BB3.12 Isonicotinate - barbiturate mixed reagent. Dissolve 2.00 ± 0.05 g of recrystallised sodium isonicotinate (BB3.11) and 2.00 ± 0.05 g of sodium barbiturate in 160 ± 5 ml of water. It may be necessary to heat the mixture to 65 ± 5 °C to facilitate dissolution. Allow the solution to cool, and make to 200 ml with water. The colour of the solution should be clear to pale yellow. This solution may be stored at room temperature for up to one month.

BB3.13 p-Nitrophenol solution (0.1 % m/v). Dissolve 0.10 ± 0.01 g of p-nitrophenol in approximately 70 ml of ethanol contained in a 100 ml volumetric flask. Make to 100 ml with ethanol and mix well. This solution may be stored at room temperature for up to six months.

BB3.14 Acetic acid solution (20 % v/v). Add 10.0 ± 0.1 ml of acetic acid to approximately 35 ml of water contained in a 50 ml volumetric flask. Mix well and make to 50 ml with water. This solution may be stored at room temperature for up to one year.

BB4 Apparatus

In addition to normal laboratory glassware the following will be required.

BB4.1 Steam distillation apparatus capable of producing about 90 ml of distillate in about 190 seconds.

BB4.2 Spectrometer capable of measuring light absorbance at 600 nm with 10 mm path-length cells.

BB5 Analytical procedure

| Step | Procedure | Notes |
|-------------|---|--|
| BB5.1 | Add 10 ml of sodium hydroxide solution (BB3.5) to a V-ml, typically 100 ml receiving flask of the steam distillation apparatus (BB4.1). See note a. | (a) Commercial apparatus are available for generating steam and undertaking the determination automatically. |
| BB5.2 | A representative amount, M g, typically, 10.0 ± 0.1 g of an "as received" soil sample (see section 6 and note b) should be added to a 175 ml extraction bottle. To the bottle, add V ml, typically 50 ± 1 ml of sodium hydroxide solution (BB3.10). Seal the bottle | (b) If samples are to be reported on a dry weight basis (at say 105 °C) rather than on an "as received" basis it will be necessary to carry out a dry solids content determination on a representative |

and shake for approximately 60 minutes. Allow the contents of the bottle to settle.

amount of the same "as received" sample.

BB5.3 To a distillation flask, add 10.0 ± 0.1 ml of copper sulphate solution (BB3.4) and 2.0 ± 0.1 ml of tin(II) chloride solution (BB3.3). To this flask, add V3 ml, typically 30.0 ± 0.1 ml of the sodium hydroxide extract (BB5.2) immediately followed by 30 ml of phosphoric acid (BB3.1) and mix well. Immediately set up the steam distillation apparatus (note c) and commence steam distillation (BB4.1). Continue distillation until approximately 90 ml of distillate is collected in about 190 seconds.

(c) Ensure losses of hydrogen cyanide are minimised.

BB5.4 When sufficient distillate has been collected, stop the distillation process and remove the receiving flask. Make to volume, V ml typically 100 ml, with water. The solution is now ready for spectrophotometric determination.

BB5.5 Blank solutions and soil can be analysed with every batch of samples. For blank solutions, the sample is replaced with an equal mass of water. For soils, the sample is replaced with an equal mass of soil spiked with an appropriate level of complex cyanide solution. See note d. Alternatively, certified reference materials can be used.

(d) Blanks may be used to evaluate equipment contamination and spiked soils to estimate batch to batch recoveries.

Spectrophotometric determination

BB5.6 To an V1 ml aliquot, typically 10.0 ml of the working cyanide standard solutions (BB3.9) see notes e and f, add 2 drops (0.1 ml) of p-nitrophenol solution (BB3.13) and 2 drops (0.1 ml) of acetic acid solution (BB3.14). See note g. To the clear solution, add 200 ± 5 μ l of chloramine-T solution (BB3.6) and allow the solution to stand for several minutes, see note h. Add 5.0 ± 0.1 ml of isonicotinate - barbiturate mixed reagent (BB3.12) and allow the colour of the solution to fully develop, see note i. Mix well. Read the absorbance of the solution in a 10 mm path-length cell at 600 nm (note j) using water as blank solution.

(e) Standard cyanide solutions (BB3.9) are not taken through the distillation process before being determined spectrometrically, but would need to be if recovery estimates were needed to be determined.

(f) Commercial apparatus are available allowing this procedure to be carried out automatically, but usually on a reduced scale.

(g) If the colour of the solution is not clear, add more acetic acid solution (BB3.14).

(h) Hydrogen cyanide reacts slowly with chloramine-T to form cyanogen chloride. Sufficient time should be allowed for this reaction to reach completion.

(i) This usually takes about 40 minutes.

(j) This wavelength may not be the wavelength of maximum absorption.

BB5.7 Prepare a calibration graph of absorbance versus amount of cyanide in V1 ml of working cyanide standard solution.

BB5.8 Repeat section BB5.6 using a V1 ml aliquot, typically 10.0 ml, of the distillate from section BB5.4, in place of the volume of working cyanide standard solutions (BB3.9) see note k.

(k) If the reading exceeds the calibration range, a smaller aliquot (V1 ml, BB5.8) may be taken and the spectrometric determination repeated, or the analysis repeated using a smaller quantity of sample (M g, BB5.2) or smaller volume of aliquot (V3 ml, BB5.3) or the distillate volume (V ml, BB5.4) or extraction volume (Ve ml, BB5.2) increased and suitable aliquots taken as appropriate.

BB5.9 From the calibration graph, obtain the amount (A µg) of cyanide in the aliquot (V1 ml, BB5.8) and determine the concentration of total cyanide, taking into account the extraction volume (Ve ml, BB5.2) the volume of aliquot (V1 ml, BB5.8) the distillate volume (V ml, BB5.4) and amount (M g, BB5.2) of sample taken.

BB6 Calculations

The concentration, C, of total cyanide in the “as received” sample is given by

$$C = (A \times V \times 60) / (V1 \times V3 \times M) \quad \text{mg/kg}$$

A is the amount (µg) of cyanide in the aliquot (V1 ml) taken and M is the amount (g) of “as received” soil extracted into Ve ml and distilled into V ml and V3 ml extract used. (This assumes the volume (Ve ml, typically 50 ml) of sodium hydroxide and amount (10 g) of soil exhibits a volume of 60 ml).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed.

In addition, the reporting of results may also need to take into account whether results are calculated on an “as received” basis or on an air-dried basis (say at 105 °C) or on a dry weight basis (say at 105 °C). see section 2.

Table BB1 Performance data for total cyanide

The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| Certified reference material* | Reference value (mg/kg) | Precision (%) | Bias (%) |
|-------------------------------|----------------------------|------------------|-------------|
| LGC 6144 (Gas work’s soil) | 1306 | 9.5 | 24.4 |
| RTC 015 (Sandy loam) | 6.04 | 11.6 | -1.5 |
| RTC 022 (Loam) | 26.6 | 7.0 | -22.3 |

| Soil type | Limit of detection** (mg/kg) |
|-----------|---------------------------------|
| Sand | 0.1 |
| Clay | 0.2 |
| Top soil | 0.4 |

* Determined over 11 days with 11 batches in duplicate
 ** Determined over 10 days with 10 batches in duplicate
 Precision as total relative standard deviation
 Data provided by BAE Systems

BC Determination of total cyanide by steam distillation of an alkaline extract of a sample of soil at a pH value of 3.8 after exposure to ultra violet radiation, followed by spectrophotometric determination using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid

Procedures are described whereby an alkaline extract of a sample of soil is treated with citric acid and sodium hydroxide, and then steam distilled. A pH-adjusted portion of the distillate is then spectrophotometrically determined. For “as received” soils, a representative portion of the soil is taken. For air-dried samples, an homogeneous portion is taken. See section 6.

BC1 Performance characteristics of the method

| | |
|--------------------------------|---|
| BC1.1 Substance determined | Total cyanide in soil. |
| BC1.2 Type of sample | Samples of soil and contaminated land. |
| BC1.3 Basis of method | The sample of soil is extracted with sodium hydroxide solution. An aliquot of this alkaline extract is steam distilled under acidic conditions at a pH value of 3.8 using citric acid/alkali solution after exposure to ultra violet radiation, where hydrogen cyanide is liberated. A pH adjusted aliquot of the distillate is spectrophotometrically determined at 600 nm, using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid. |
| BC1.4 Range of application | Typically, up to 25 mg/kg as cyanide, but can be extended, see section BC5.11, note m. |
| BC1.5 Calibration curve | Linear over the range of application. |
| BC1.6 Total standard deviation | See Tables BC1, BC2 and BC3. |
| BC1.7 Limit of detection | Typically, 0.1 µg of cyanide can be detected in the aliquot taken as described. This equates to about 0.5 mg/kg of cyanide in the sample of soil analysed. |
| BC1.8 Sensitivity | Typically, as described, 0.1 µg of cyanide (equivalent to 0.5mg/kg cyanide in the sample of soil analysed) gives an absorbance value of about 0.006 abs units over a 10 mm path length. |
| BC1.9 Bias | See Tables BC1, BC2 and BC3. |

BC2 Principle

A representative or homogeneous portion of the sample of soil is extracted with 1M sodium hydroxide solution. An aliquot of the extract is steam distilled under acidic conditions (at a pH value of 3.8) using citric acid and sodium hydroxide and simultaneously irradiated with ultra violet (UV) radiation at 312 nm, i.e. UVb range. Ultra violet radiation breaks down complex cyanide under acidic conditions, which then forms hydrogen cyanide. Conversion of thiocyanate into cyanide is also prevented. Following distillation, the easily liberated hydrogen cyanide and hydrogen cyanide from complex cyanide, is absorbed into a pH 5.2 buffer solution containing chloramine-T and then determined spectrophotometrically at 600 nm, using isonicotinic acid and 1,3-dimethylbarbituric acid.

BC3 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

BC3.1 Buffer solution (pH 5.2). Dissolve 41.0 ± 0.5 g of potassium hydrogen phthalate in approximately 1000 ml of water. Add 4.60 ± 0.05 g of sodium hydroxide and mix well. Add 6.0 ± 0.5 ml of 30 % v/v polyethyleneglycol lauryl ether solution and mix well. Make to 2000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to 1 week.

BC3.2 Chloramine-T reagent. Dissolve 4.00 ± 0.1 g of chloramine-T in approximately 1000 ml of water. Make to 2000 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to 1 week.

BC3.3 Colour reagent. To approximately 1000 ml of water, dissolve 14.0 ± 0.2 g of sodium hydroxide. To this cooled solution, add 33.6 ± 0.3 g of 1,3-dimethylbarbituric acid and 27.2 ± 0.3 g of isonicotinic acid and mix well. Add 6 ml of 30 % v/v polyethyleneglycol lauryl ether solution and make to 2000 ml with water. Filter (nominal pore size 0.45 µm) this solution. This solution may be stored at room temperature for up to 1 week.

BC3.4 Cyanide stock standard solution (nominally 100 mg/l). Dissolve 40.0 ± 0.5 g of sodium hydroxide in approximately 800 ml of water. Accurately, and as quickly as possible, weigh out 0.250 ± 0.001 g of potassium cyanide and quantitatively transfer to the alkaline solution in a 1000 ml volumetric flask. Make to 1000 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to one month.

BC3.5 Sodium hydroxide solution (1M). Dissolve 40.0 ± 0.1 g of sodium hydroxide in approximately 800 ml of water. Transfer the solution to a 1000 ml measuring cylinder and make to 1000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to 3 months.

BC3.6 Working cyanide standard solutions. For example, into a series of five 100 ml volumetric flasks, add 50 ml of 1M sodium hydroxide solution (BC3.5) followed by 1.0, 2.0, 3.0, 4.0 and 5.0 ml of cyanide standard solution (BC3.4) to each flask. Make each flask to 100 ml with 1M sodium hydroxide solution (BC3.5). These solutions nominally contain 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l of cyanide respectively. This is equivalent to 1.0, 2.0, 3.0, 4.0 and 5.0 µg of cyanide in the aliquot taken for the spectrophotometric determination (section BC5.7). These solutions should be used on the day of preparation.

BC3.7 Distillation reagent. Dissolve 100 ± 1 g of citric acid and 24.0 ± 0.2 g of sodium hydroxide in approximately 1800 ml of water. Mix well and adjust the pH to 3.8 with concentrated hydrochloric acid. Make to 2000 ml with water and mix well. This solution may be stored at room temperature for up to 1 week.

BC3.8 Complex cyanide stock standard solution (nominally 100 mg/l). Dissolve 20.0 ± 0.2 g of sodium hydroxide in approximately 300 ml of water. Accurately weigh 0.106 ± 0.001 g of potassium hexacyanoferrate ($K_3Fe(CN)_6$) and stir until dissolved. Make to 500 ml with water, mix thoroughly and transfer to an amber-coloured bottle. This solution may be stored at 5 ± 3 °C for up to a month.

BC3.9 Working complex cyanide ultra violet check solution (4 mg/l). For example, transfer 4.0 ml of complex cyanide stock standard solution (BC3.8) into a 100 ml volumetric flask and make to volume with 1M sodium hydroxide and mix thoroughly. This solution should be used on the day of preparation.

BC4 Apparatus

In addition to normal laboratory glassware the following are required.

BC4.1 Steam distillation apparatus capable of producing 10 ml of distillate in about 15 minutes

BC4.2 Spectrometer capable of holding 10 mm path-length cells and measuring light absorbance at 600 nm.

BC4.3 Ultra violet light source (at 312 nm, i.e. UVb range) and suitable housing to fit the distillation flask without emitting radiation to the immediate environment.

BC5 Analytical procedure

| Step | Procedure | Notes |
|-------|--|---|
| BC5.1 | Add M g (typically, 8.0 ± 0.1 g) of a representative or homogeneous portion of the sample of soil (see section 6 and note a) to a flask. To this flask, add V ml, typically, 40.0 ± 0.5 ml of sodium hydroxide solution (BC3.5) and shake well for approximately 30 minutes. Filter the sample until at least 10 ml of filtrate is produced. See note b. | (a) If samples are to be reported on an air-dried basis (say at 30 °C) or a dry weight basis (say at 105 °C) rather than on an “as received” basis, it will be necessary to carry out a dry solids content determination on a separate portion of the “as received” material. (b) Centrifuging the mixture at 3000 rpm should speed up the filtration process. |
| BC5.2 | Transfer V1 ml, typically, 1.00 ml of this clear alkaline extract (BC5.1) to the steam | (c) Commercial apparatus are available for generating steam and |

distillation apparatus and dilute with 19.0 ml of water. See note c. undertaking the determination automatically.

BC5.3 Add 12.5 ml of pH 5.2 buffer solution (BC3.1) and 12.5 ml of chloramine-T solution (BC3.2) to a V-ml receiving flask (typically 50 ml) of the steam distillation apparatus (BC4.1).

BC5.4 Add 4.2 ml of distillation reagent (BC3.7) and immediately set up the steam distillation apparatus (note d). Expose the sample to the ultra violet radiation source for a minimum of 5 minutes (note e) and then commence steam distillation (BC4.1). Continue the distillation until about 10 ml of distillate has collected in the receiving flask.

(d) Ensure losses of hydrogen cyanide are minimised.

(e) The time of exposure to ultra violet radiation should be sufficient to obtain adequate recovery of an aliquot of the working complex cyanide ultra violet check solution (BC3.9) taken through the whole procedure.

BC5.5 When sufficient distillate has been collected stop the distillation process and remove the receiving flask. Mix well, then add 12.5 ml of colour reagent (BC3.3) to the receiving flask. Make the volume in the receiving flask to V2 ml, typically, 50 ml with water. The solution is now ready for spectrophotometric determination.

BC5.6 Blank and spiked soils should be analysed with every batch of samples. The blank should be a clean, cyanide-free soil. The spiked soil should be spiked with an appropriate level of complex cyanide solution. See notes f and g.

(f) Blanks may be used to evaluate equipment contamination and spiked soils to estimate batch to batch recoveries.

(g) For example, 1 ml of complex cyanide stock standard solution (BC3.8) i.e. 100 µg of cyanide.

BC5.7 An aliquot of the working complex cyanide ultra violet check solution (BC3.9) should be taken through the whole procedure to check the efficiency of the ultra violet digestion process.

Spectrophotometric determination

BC5.8 To a V1 ml aliquot (typically, 1.0 ml) of the working cyanide standard solutions (BC3.6) see notes h and i, add 9 ml of water, 12.5 ml of buffer solution (BC3.1), quickly followed by 12.5 ml of chloramine-T reagent

(h) Standard cyanide solutions (BC3.6) are not taken through the distillation process before being determined spectrometrically, but would need to be if recovery

(BC3.2). Mix well and allow the solution to stand at 37 °C, for a short time, typically, 30 - 60 minutes, see note j. To this solution, add 12.5 ml of colour reagent (BC3.3). Make the solution to V2 ml (typically 50 ml) with water. Mix well and allow the solution to stand for a short time for the full colour to develop, see note k. Read the absorbance of the solution in a 10 mm path-length cell at 600 nm (see note l) using water as blank solution.

estimates were needed to be determined.

(i) Commercial apparatus is available allowing this procedure to be carried out automatically, but usually on a reduced scale. When using commercial automatic apparatus, the standards are taken through the distillation process.

(j) This usually takes 5 minutes. Hydrogen cyanide reacts slowly with chloramine-T to form cyanogen chloride. Sufficient time should be allowed for this reaction to reach completion.

(k) This usually takes 30 minutes.

(l) This wavelength may not be the wavelength of maximum absorption.

BC5.9 Prepare a calibration graph of absorbance versus mass of cyanide in V2 ml of solution. (BC5.8).

BC5.10 Repeat section BC5.8 using an aliquot, V1 ml, typically 10 ml, of the distillate from section BC5.5, in place of the volume of working complex cyanide standard solutions (BC3.6) and volume of water.

BC5.11 Read the absorbance of the sample solution in the same 10 mm path length cell at 600 nm, see note m.

(m) If the reading exceeds the calibration range, a volumetric dilution may be prepared using water and the spectrometric determination repeated. If so, the maximum amount of cyanide that could be accommodated, and hence, the maximum dilution that could be tolerated, would need to be known, and whether the distillation process had adequately recovered all of the cyanide present in the sample. Alternatively, the analysis should be repeated using a smaller quantity of sample (M g, BC5.1) or the distillate volume (V2 ml,

BC5.5) increased and a suitable aliquot taken as appropriate.

BC5.12 From the calibration graph, obtain the mass (A µg) of cyanide in the sample solution (BC5.5) and determine the concentration of total cyanide, taking into account the extraction volume (V ml, BC5.1), the volume distilled, V1 ml (BC5.2) the distillate volume, V2 ml (BC5.5) any dilutions (note n) and the mass (M g, BC5.1) of sample taken.

BC6 Calculations

The concentration, C, of total cyanide in the sample analysed is given by

$$C = D \times (A \times V) / (V1 \times M) \quad \text{mg/kg}$$

A is the mass (µg) of cyanide in the sample solution (BC5.11);

M is the mass (g) of sample extracted into V ml (BC5.1);

V1 is the volume of extract distilled (BC5.2)

D is the dilution factor used, if appropriate, see note m.

Any samples where the distillate volume (V2 ml, BC5.5) is different to that used for standard solutions will need to take this into account.

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed.

In addition, the reporting of results may also need to take into account whether results are calculated on an "as received" basis, an air-dried basis (for example at 30 °C) or on a dry weight basis (say at 105 °C). See section 2.

Table BC1 Performance data for total cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 5 mg/kg as cyanide | | Soil spiked at 20 mg/kg as cyanide | |
|------------|-----------------------------------|------|------------------------------------|-------|
| | RSD | Bias | RSD | Bias |
| Loam soil | 4.0 | -4.0 | 2.8 | -12.8 |
| Sandy soil | 4.1 | -2.5 | 3.0 | -12.1 |
| Clay soil | 4.9 | -4.9 | 3.1 | -12.4 |

All values are percentages

RSD is relative standard deviation

Data for "as received" sample.

Spiked with potassium hexacyanoferrate solution (BC3.8) i.e. 250 µl to 5 g of soil, and 1000 µl to 5 g of soil.

Data provided by Alcontrol Laboratories

Table BC2 Performance data for total cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 10 mg/kg as cyanide | | Soil spiked at 40 mg/kg as cyanide | |
|------------|------------------------------------|------|------------------------------------|-------|
| | Precision | Bias | Precision | Bias |
| Loam soil | 13.1 | -9.9 | 5.1 | -12.6 |
| Sandy soil | 5.6 | -4.8 | 5.5 | -11.8 |
| Clay soil | 5.6 | -4.4 | 4.5 | -10.9 |

All values are percentages.

Precision is total standard deviation.

Data for air-dried sample.

Spiked with potassium hexacyanoferrate solution (BC3.8) i.e. 500 µl to 5 g of soil, and 2000 µl to 5 g of soil.

The concentration range is up to 5.0 mg/l in solution, equivalent to 50.0 mg/kg in the air-dried soil.

Data provided by Chemtest

Table BC3 Performance data for total cyanide

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 400 mg/kg as cyanide | | Soil spiked at 1600 mg/kg as cyanide | |
|-------------|-------------------------------------|------|--------------------------------------|------|
| | Precision | Bias | Precision | Bias |
| Silt soil | 6.1 | -6.1 | 4.5 | -7.0 |
| Sandy soil | 2.7 | -5.7 | 3.3 | -7.1 |
| Clay soil | 5.8 | -8.0 | 3.6 | -8.1 |
| Made ground | 4.4 | -5.8 | 3.9 | -7.8 |

All values are percentages.

Precision is total standard deviation.

Data for "as received" sample.

Soils were spiked with a solution containing 1000 mg/l potassium cyanide (2.5 g per 1000 ml) 1000 mg/l potassium hexacyanoferrate (2.12 g per 1000 ml) and 10000 mg/l potassium thiocyanate (16.7 g per 1000 ml) containing 40 g of sodium hydroxide per 1000 ml. To two 10 g portions of sample, 2.0 ml was added to one portion (i.e. 400 mg/kg) and 8.0 ml to another (i.e. 1600 mg/kg).

The concentration range is up to 5.0 mg/l in solution, equivalent to 50 mg/kg in the "as received" soil.

Data provided by Scientifics

CA Determination of thiocyanate by alkaline extraction of a soil sample, followed by spectrophotometric determination using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid

Procedures are described whereby an alkaline extract of a sample of soil is treated with formaldehyde and then spectrophotometrically determined. For “as received” soils, a representative portion of the soil is taken. For air-dried samples, an homogeneous portion is taken. See section 6.

CA1 Performance characteristics of the method

| | | |
|-------|--------------------------|---|
| CA1.1 | Substance determined | Thiocyanate in soil. |
| CA1.2 | Type of sample | Samples of soil and contaminated land. |
| CA1.3 | Basis of method | The sample is extracted with sodium hydroxide solution. Formaldehyde is added to an aliquot of this extract and the pH of the resultant solution adjusted to 5.2 before being spectrophotometrically determined at 600 nm using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid. |
| CA1.4 | Range of application | Typically, up to 25 mg/kg as thiocyanate in the sample analysed, but can be extended, see section CA5.6, note i. |
| CA1.5 | Calibration curve | Linear over the range of application. |
| CA1.6 | Interferences | Since there is no distillation stage in this procedure, interferences such as excessive background colouration of the extract, and substances in the extracted sample that react with the spectrophotometric determination, may cause interference. Water soluble monosulphide and easily liberated cyanide in the extract produce a positive interference, causing a higher result to be determined. See also section 4. |
| CA1.7 | Total standard deviation | See Tables CA1, CA2 and CA3. |
| CA1.8 | Limit of detection | Typically, 0.1 µg of thiocyanate can be detected in the aliquot of extract taken as described. This equates to about 0.5 mg/kg of thiocyanate in the sample analysed. |
| CA1.9 | Sensitivity | Typically, as described, 0.1 µg of thiocyanate (equivalent to 0.5 mg/kg thiocyanate in the sample analysed) gives an absorbance value of about 0.005 units in a 50 mm path length cell. |

CA2 Principle

A representative or homogeneous portion of the sample of soil is extracted with 1M sodium hydroxide solution. Formaldehyde is added to an aliquot of this extract (to suppress any easily liberated cyanide present in the extract). This solution is then buffered to a pH value of 5.2 and then spectrophotometrically determined at 600 nm, using chloramine-T, isonicotinic acid and 1,3-dimethylbarbituric acid.

CA3 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

CA3.1 Sodium hydroxide solution (1M). Dissolve 40.0 ± 0.1 g of sodium hydroxide in approximately 800 ml of water. Transfer the solution to a 1000 ml measuring cylinder and make to 1000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to 3 months.

CA3.2 Formaldehyde solution. Dilute 10.0 ml of formaldehyde solution (37 m/m %) in approximately 1000 ml of water contained in a 2000 ml volumetric flask. Add 6.0 ml of 30 % v/v polyethyleneglycol lauryl ether solution and mix well. Make to volume with water and mix thoroughly. Transfer the solution to a suitable container. This solution may be stored at room temperature for up to 1 week.

CA3.3 Buffer solution (pH 5.2). Dissolve 41.0 ± 0.5 g of potassium hydrogen phthalate in approximately 1000 ml of water. Add 4.60 ± 0.05 g of sodium hydroxide and mix well. Add 6.0 ml of 30 % v/v polyethyleneglycol lauryl ether solution and mix well. Make to 2000 ml with water. Mix well and transfer the solution to a suitable container. This solution may be stored at room temperature for up to 1 week.

CA3.4 Chloramine-T reagent. Dissolve 4.00 ± 0.1 g of chloramine-T in approximately 1000 ml of water. Transfer the solution to a 2000 ml volumetric flask and make to 2000 ml with water. This solution may be stored at 5 ± 3 °C for up to 1 week.

CA3.5 Colour reagent. To approximately 1000 ml of water, dissolve 14.0 ± 0.2 g of sodium hydroxide. To this cooled solution, add 33.6 ± 0.3 g of 1,3-dimethylbarbituric acid and 27.2 ± 0.3 g of isonicotinic acid and mix well. Add 6 ml of 30 % v/v polyethyleneglycol lauryl ether solution and make to 2000 ml with water. Filter (nominal pore size 0.45 µm) this solution. This solution may be stored at room temperature for up to 1 week.

CA3.6 Thiocyanate stock standard solution (nominally 100 mg/l). Dissolve 40.0 ± 0.5 g of sodium hydroxide in approximately 800 ml of water. Accurately, and as quickly as possible, weigh out 0.167 ± 0.001 g of potassium thiocyanate and quantitatively transfer to the alkaline solution. Make to 1000 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to one month.

CA3.7 Working thiocyanate standard solutions. For example, into a series of five 100 ml volumetric flasks, add 50 ml of 1M sodium hydroxide solution (CA3.1) followed by 1.0, 2.0, 3.0, 4.0 and 5.0 ml of thiocyanate stock standard solution (CA3.6) to each flask.

Make each flask to 100 ml with 1M sodium hydroxide solution (CA3.1). These solutions nominally contain 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l of thiocyanate respectively. This is equivalent to 1.0, 2.0, 3.0, 4.0 and 5.0 µg of thiocyanate in the aliquot taken for the spectrophotometric determination (section CA5.7). These solutions should be used on the day of preparation.

CA4 Apparatus

In addition to normal laboratory glassware the following are required.

Spectrophotometer capable of holding a 50 mm path length cell and measuring at 600 nm.

CA5 Analytical procedure

| Step | Procedure | Notes |
|-------|--|---|
| CA5.1 | Add M g (typically, 8.0 ± 0.1 g) of a representative or homogeneous portion of the sample of soil (see section 6 and note a) to a flask. To this flask, add V ml, typically, 40.0 ± 0.5 ml, of sodium hydroxide solution (CA3.5) and shake well for approximately 30 minutes. See note b. | <p>(a) If samples are to be reported on an air-dried basis (say at 30 °C) or a dry weight basis (say at 105 °C) rather than on an “as received” basis, it will be necessary to carry out a dry solids content determination on a separate portion of the “as received” material.</p> <p>(b) The use of automatic apparatus may normally require the samples to be filtered after extraction to prevent subsequent blockage of instrumentation. Centrifuging the mixture at 3000 rpm should speed up the filtration process.</p> |
| CA5.2 | Transfer V1 ml (1.0 ml) of this alkaline extract to a 50 ml volumetric flask and add 15 ml of formaldehyde solution (CA3.2). Make to 50 ml with water and mix well. To 10 ml of this solution add 25 ml of pH 5.2 buffer solution (CA3.3) and 12.5 ml of chloramine-T solution (CA3.4). Mix well and allow time for the complexation reaction to reach completion, see note c. Add 12.5 ml of colour reagent (CA3.5), mix well and heat the solution at 37 °C until the colouration reaction reaches completion, see note d. Read the absorbance of the solution in a 50 mm path length cell at 600 nm (note e) using water as a blank solution. | <p>(c) This usually takes 5 minutes.</p> <p>(d) This usually takes 30 minutes.</p> <p>(e) This wavelength may not be the wavelength of maximum absorption.</p> |

CA5.3 Blank and spiked soils should be analysed with every batch of samples. The blank should be a clean, thiocyanate-free soil. The spiked soil should be spiked with an appropriate level of thiocyanate solution. See notes f and g.

(f) Blanks may be used to evaluate equipment contamination and spiked soils to estimate batch to batch recoveries.

(g) For example, 1 ml of thiocyanate stock standard solution (CA3.6) i.e. 100 µg of thiocyanate.

Spectrophotometric determination

CA5.4 Take V1 ml, typically, 1.0 ml of the working thiocyanate standard solutions (CA3.7) and treat similarly as described in section CA5.2, see note h. Read the absorbance of the solutions in a 50 mm path length cell at 600 nm (note e) using water as a blank solution.

(h) This equates to 1.0, 2.0, 3.0, 4.0 and 5.0 µg of thiocyanate.

CA5.5 Prepare a calibration graph of absorbance versus mass of thiocyanate in V1 ml of working thiocyanate standard solutions (CA3.7).

CA5.6 From the calibration graph, obtain the mass (A µg) of thiocyanate in the sample solution).

(i) If the reading exceeds the calibration range, a volumetric dilution may be prepared using water and the spectrometric determination repeated. If so, the maximum amount of thiocyanate that could be accommodated, and hence, the maximum dilution that could be tolerated, would need to be known. Alternatively, the analysis may be repeated using a smaller quantity of sample (M g, CA5.1), or a smaller volume of extract, V1 ml, (CA5.2).

CA5.7 Determine the concentration of thiocyanate, taking into account the extraction volume (V ml, CA5.1), the volume of extract used, V1 ml (CA5.2) any dilutions (note i) and the mass (M g, CA5.1) of sample taken.

CA6 Calculations

The concentration, C, of thiocyanate in the sample of soil analysed is given by

$$C = D \times (A \times V) / (V1 \times M) \quad \text{mg/kg}$$

A is the mass (μg) of thiocyanate in the sample solution (CA5.7);

M is the mass (g) of soil extracted into V ml (CA5.1);

V1 is the volume of extract used (CA5.2); and

D is the dilution factor, if appropriate, see note j.

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed.

In addition, the reporting of results may also need to take into account whether results are calculated on an "as received" basis, an air-dried basis (for example at 30 °C) or on a dry weight basis (say at 105 °C). See section 2.

Table CA1 Performance data for thiocyanate

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 5 mg/kg as thiocyanate | | Soil spiked at 20 mg/kg as thiocyanate | |
|------------|---------------------------------------|------|--|------|
| | RSD | Bias | RSD | Bias |
| Loam soil | 3.4 | -4.9 | 2.4 | -8.9 |
| Sandy soil | 3.0 | -3.3 | 2.3 | -6.2 |
| Clay soil | 3.4 | -8.4 | 2.5 | -9.5 |

All values are percentages.

RSD is relative standard deviation.

Data for "as received" sample.

Spiked with potassium thiocyanate solution (CA3.6) i.e. 250 μl to 5 g of soil, and 1000 μl to 5 g of soil.

Data provided by Alcontrol Laboratories

Table CA2 Performance data for thiocyanate

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 10 mg/kg as thiocyanate | | Soil spiked at 40 mg/kg as thiocyanate | |
|------------|--|------|--|------|
| | Precision | Bias | Precision | Bias |
| Loam soil | 7.2 | 8.1 | 5.8 | 4.2 |
| Sandy soil | 5.8 | 9.6 | 4.4 | 4.2 |
| Clay soil | 4.8 | 7.9 | 3.8 | 4.0 |

Values are percentages.

Precision is total standard deviation.

Data for air-dried sample.

Spiked with potassium thiocyanate solution (CA3.6) i.e. 500 µl to 5 g of soil, and 2000 µl to 5 g of soil.

The concentration range is up to 5.0 mg/l in solution, equivalent to 50.0 mg/kg in the air-dried soil.

Data provided by Chemtest

Table CA3 Performance data for thiocyanate

Performance data are based on 11 duplicate batches of analyses carried out over a period of 11 days, providing 22 results. The performance summary refers to data generated by an automated discrete spectrophotometer using much smaller volumes. Manual measurement of extracts or the use of different types of automated equipment may result in different performance data being generated.

| | Soil spiked at 2000 mg/kg as thiocyanate | | Soil spiked at 8000 mg/kg as thiocyanate | |
|-------------|--|------|--|------|
| | Precision | Bias | Precision | Bias |
| Silt soil | 14.2 | -7.3 | 7.7 | -3.4 |
| Sandy soil | 11.5 | -3.8 | 7.1 | -1.3 |
| Clay soil | 15.9 | -5.1 | 10.6 | -2.6 |
| Made ground | 15.6 | -6.2 | 11.4 | -4.7 |

Values are percentages.

Precision is total standard deviation.

Data for "as received" sample.

Soils were spiked with a solution containing 1000 mg/l potassium cyanide (2.5 g per 1000 ml) 1000 mg/l potassium hexacyanoferrate (2.12 g per 1000 ml) and 10000 mg/l potassium thiocyanate (16.7 g per 1000 ml) containing 40 g of sodium hydroxide per 1000 ml. To two 10 g portions of sample, 2.0 ml was added to one portion (i.e. 2000 mg/kg) and 8.0 ml to another (i.e. 8000 mg/kg).

The concentration range is up to 50.0 mg/l in solution, equivalent to 500 mg/kg in the "as received" soil.

Data provided by Scientifics

Appendix 1 Expression of results

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 | $(XA \times 1000) / (1000-50)$ |
| | | D | $(XA \times 1000) / (1000-150)$ |
| | | E | $(XA \times 1000) / (1000-200)$ |
| | | F | $(XA \times 1000) / (1000-170)$ |
| | | G | $(XA \times 1000) / (1000-220)$ |
| | | B | XB |
| B | XB | | |
| D | $(XB \times (1000-50)) / (1000-150)$ | | |
| E | $(XB \times (1000-50)) / (1000-200)$ | | |
| F | $(XB \times (1000-50)) / (1000-170)$ | | |
| G | $(XB \times (1000-50)) / (1000-220)$ | | |
| D | XD | | |
| | | B | $(XD \times (1000-150)) / (1000-50)$ |
| | | D | XD |
| | | E | $(XD \times (1000-150)) / (1000-200)$ |
| | | F | $(XD \times (1000-150)) / (1000-170)$ |
| | | G | $(XD \times (1000-150)) / (1000-220)$ |
| | | E | XE |
| B | $(XE \times (1000-200)) / (1000-50)$ | | |
| D | $(XE \times (1000-200)) / (1000-150)$ | | |
| E | XE | | |
| F | $(XE \times (1000-200)) / (1000-170)$ | | |
| G | $(XE \times (1000-200)) / (1000-220)$ | | |
| F | XF | | |
| | | B | $(XF \times (1000-170)) / (1000-50)$ |
| | | D | $(XF \times (1000-170)) / (1000-150)$ |
| | | E | $(XF \times (1000-170)) / (1000-200)$ |
| | | F | XF |
| | | G | $(XF \times (1000-170)) / (1000-220)$ |
| | | G | XG |
| B | $(XG \times (1000-220)) / (1000-50)$ | | |
| D | $(XG \times (1000-220)) / (1000-150)$ | | |
| E | $(XG \times (1000-220)) / (1000-200)$ | | |
| F | $(XG \times (1000-220)) / (1000-170)$ | | |
| G | XG | | |

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

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 wish to receive advance notice of forthcoming publications, please contact the Secretary.

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