ENVIRONMENT AGENCY

The determination of cyanide in waters and associated materials (2007)

Methods for the Examination of Waters and Associated Materials

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This booklet is an updated version of the document published in 1988 and gives guidance on de-chlorination prior to determining cyanide, and corrects an earlier equation for calculating cyanide concentrations. Only limited performance data are available. Notes for the determination of cyanide in sludges and soils (previously described in method F) have not been included. A separated document is being considered that should be appropriate for such determinations and which should satisfy the requirements of the MCERTS performance standard for laboratories undertaking chemical testing of soil (see www.mcerts.net).

Whilst specific commercial products may be referred to in this document, this does not constitute an endorsement of these products but serves only as an illustrative example of the type of products available. Equivalent products are available and it should be understood that the performance of the method might differ when other materials are used and all should be confirmed by validation of the method.

Contents

About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments, soils (including contaminated land) and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

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.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available.

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. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are

1 General principles of sampling and accuracy of results
2 Microbiological methods
3 Empirical and physical methods
4 Metals and metalloids
5 General non-metallic substances
6 Organic impurities
7 Biological methods
8 Biodegradability and inhibition methods
9 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will be notified to the technical press. If users wish to receive copies or advanced notice of forthcoming publications or obtain details of the index of methods then contact the Secretary on the Agency's web-page (www.environment-agency.gov.uk/nls) or by post.

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

Dr D Westwood
Secretary
April 2007

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 waters and associated materials

A General information

A1 Introduction to the methods

Several methods are described in this booklet for the determination of cyanide, in various forms, in water. Details are described for a reflux distillation method for the determination of “total” cyanide, i.e. easily liberated cyanide and cyanide in complexed forms. However, strongly complexed cyanide (see Table F1) may be incompletely determined. The determination of “easily liberated” hydrogen cyanide, after absorption in alkaline solution, can be determined by ion selective electrode potentiometry (method B) or determined spectrophotometrically at 600 nm (method C).

The use of method D enables “easily liberated” hydrogen cyanide to be determined by micro-diffusion from an aliquot adjusted to a pH value of 6. This method is for the determination of low levels of “easily liberated” hydrogen cyanide and cyanide in relatively weakly complexed forms which can be dissociated at a pH value of 6.

Method E describes an air segmented continuous flow automated procedure for the determination of “easily liberated” cyanide by passage of hydrogen cyanide from an acidified solution through a gas permeable membrane into the specified reagent stream. With the addition of ultra-violet irradiation, “total” cyanide (subject to certain restrictions similar to those described in method B) can be determined. For samples containing thiocyanate, which would interfere, a preliminary reflux distillation procedure is described.

Section F describes guidance on the determination of strongly complexed cyanide, using liquid chromatography or infra-red aborptiometry. However, stable complexes of this type are not frequently of interest.

In the procedures described in this booklet any reference to the tolerances to be adopted with respect to the amount or volume of reagents to be used is left to the discretion of the laboratory. These tolerances should be as appropriate in order to satisfy any performance criteria that may be prescribed.

A1.1 Cyanogen chloride

No information is provided in this booklet for the determination of cyanogen chloride. Cyanogen chloride is formed when cyanide compounds are chlorinated, a process often used for the destruction of cyanide-containing wastes. Cyanogen chloride is slightly soluble in water and is toxic at low concentrations.

A2 Hazards

With only very few exceptions, cyanides are rapidly-acting poisons following injestion, 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 avaliable if poisoniong is suspected. Provision of qualified personel to administer first aid should be considered in the event of cyanide poisoning.

Barbituric acid (pyrimidine trione or malonylurea) is poisonous.

A3 Sample collection and preservation

As soon as possible after sampling, sodium hydroxide solution should be added to all aqueous samples. The final concentration of alkali should be approximatley 0.05M. For the majority of samples, this may be achieved by collecting samples in plastic (for example polyethylene) bottles that contain the necessary amount of solid sodium hydroxide or concentrated sodium hydroxide solution. Typically, for 100 ml of sample, this will require about 0.2 g of sodium hydroxide.

The sodium hydroxide used for this purpose should contain neglegible amounts of cyanide and wherever possible, the same batch of analytical reagent grade material should be used for the preservation of samples and for the preparation of reagent solutions.

Samples that are strongly alkaline need not be preserved. However, analysts should ensure that the alkalinity of the sample does not cause problems with the determination.

Potable water, or other samples containing residual disinfectant should be de-chlorinated, for example using ascorbic acid, prior to addition of sodium hydroxide. Table A1 shows information on the concentration of cyanide in samples in the presence of residual disinfectant and sodium hydroxide.

Preserved samples should be stored in the dark at room temperature in order to avoid light-induced decomposition of cyanide. The sample should be analysed as soon as possible after collection.

A4 Standard solutions of cyanide

All standard solutions of cyanide should be prepared in dilute (approximately 0.1M) sodium hydroxide solution.

A4.1 Water. Water should be of distilled or deionised quality.

A4.2 Sodium hydroxide solution (0.1M). Dissolve 4.0 ± 0.2 g of sodium hydroxide in about 800 ml of water (A4.1). Mix well, cool the solution and make to 1000 ml with water (A4.1). Store the solution in a polyethylene bottle. This solution may be stored at room temperature for up to one week.

A4.3 Stock standard cyanide solution (100 mg as cyanide per litre). Dissolve 0.250 ± 0.005 g of potassium cyanide in 500 ± 5 ml of sodium hydroxide solution (A4.2). Make to 1000 ml with water (A4.1). Store the solution in a stoppered glass bottle appropriately labelled, for example marked ”toxic”. This solution may be stored at room temperature for up to one week. The concentration may be checked by titration with standardised silver nitrate solution (see section A5).

A4.4 Working standard cyanide solution (1 mg as cyanide per litre). Add 1.00 ± 0.01 ml of the stock standard cyanide solution (A4.3) to a 100 ml volumetric flask and add 50.0 ± 0.5 ml of sodium hydroxide solution (A4.2). Make to volume with water (A4.1). Prepare this solution on the day of use.

A5 Checking stock standard cyanide solutions

A5.1 Cyanide solutions may be checked by titrating against standardised silver nitrate solution. The end-point of the titration is reached when an excess of silver is indicated by the formation of a red complex with 5-(4-dimethylaminobenzylidene) rhodanine.

A5.1.1 Indicator solution. Dissolve 0.020 ± 0.002 g of 5-(4-dimethylamino-benzylidene) rhodanine in about 80 ml of acetone. Mix well and make to 100 ± 2 ml with acetone. Store the solution in an amber bottle. The solution may be stored at room temperature for up to one week.

A5.1.2 Silver nitrate solution (0.01M). Dissolve 1.699 ± 0.001 g of analytical grade silver nitrate (previously dried at 120 °C for about 2 hours) in water (A4.1). Mix well and make to 1000 ml with water (A4.1). If stored in the dark at room temperature, this solution may be stored for up to one week. If stored for a longer period of time, the solution should be standardised with sodium chloride before being used.

A5.1.3 Magnetic stirrer, with bar.

A5.1.4 Burette, 10 ml capacity.

A5.1.5 Conical flask, 50 ml capacity.

A5.2 Procedure

A5.2.1 Add 25.00 ml of the stock standard cyanide solution (A4.3) to a 50 ml conical flask (A5.1.5). Add 0.10 ± 0.02 ml of the indicator solution (A5.1.1). Mix well. Fill the burette (A5.1.4) with the silver nitrate solution (A5.1.2). Place a magnetic stirring bar into the conical flask and place the flask on the magnetic stirrer. Insert the tip of the burette just below the meniscus of the cyanide solution contained in the flask and turn on the magnetic stirrer.

A5.2.2 Titrate the cyanide solution (A4.3) in the flask with the silver nitrate solution (A5.1.2) from the burette until the colour changes from yellow to red. The colour is stable for only a short time. Record the volume, V ml of silver nitrate solution used. The titre should be approximately 5 ml.

A5.2.3 The concentration, C, (in mg of cyanide per litre) of the stock standard cyanide solution (A4.3) is given by:

$$C = (2 \times V \times 260.17) / 25 \quad \text{mg/l}$$

where V is the volume of 0.01M silver nitrate solution (A5.1.2) required for the titration of 25 ml of the stock standard cyanide solution (A4.2).

Table A1 Performance data

Analyte (all samples were spiked to a nominal cyanide concentration of 50 µg/l)	Number of days after spiking	Number of analyses	Result (µg/l)	Standard deviation
Easily liberated cyanide	0	2	52.78	0.304
Easily liberated cyanide	7	2	52.52	0.714
Complex cyanide	0	5	47.71	1.182
Complex cyanide	10	5	48.54	0.127
Easily liberated cyanide	0	5	40.19	0.219
Easily liberated cyanide	7	5	40.60	0.512
Complex cyanide	0	5	51.04	1.576
Complex cyanide	10	5	49.01	0.734
Easily liberated cyanide - free chlorine spike 0.2 mg/l	0	5	35.76	0.943
Easily liberated cyanide - free chlorine spike 0.2 mg/l	1	5	6.16	0.713
Easily liberated cyanide - free chlorine spike 0.2 mg/l	2	5	0.92	0.086
Complex cyanide - free chlorine spike 0.2 mg/l	0	5	50.28	0.991
Complex cyanide - free chlorine spike 0.2 mg/l	1	5	44.81	0.774
Complex cyanide - free chlorine spike 0.2 mg/l	2	5	48.32	1.121
Complex cyanide - free chlorine spike 0.2 mg/l	3	5	50.21	0.459
Complex cyanide - free chlorine spike 0.2 mg/l	6	5	45.84	0.640
Complex cyanide - free chlorine spike 0.2 mg/l	7	5	45.44	0.645
Easily liberated cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	0	5	48.13	0.212
Easily liberated cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	1	5	45.77	0.440
Easily liberated cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	2	5	47.82	0.545
Easily liberated cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	3	5	47.28	0.490
Easily liberated cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	6	5	46.19	0.618
Easily liberated cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	7	5	44.70	0.596
Complex cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	0	5	48.40	0.659
Complex cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	1	5	47.74	0.701
Complex cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	2	5	50.20	0.480
Complex cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	3	5	51.27	0.343
Complex cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	6	5	50.45	0.565
Complex cyanide - free chlorine spike 0.2 mg/l treated with thiosulphate	7	5	47.90	0.846

All samples were “final samples” from a Scottish Water treatment works, dosed with phosphate for lead remediation and ammonia for chloramination. For chlorine spiked samples, measured free chlorine was 0.19 mg/l and total chlorine 0.69 mg/l. For samples treated with thiosulphate, sufficient reagent was added to de-chlorinate the sample to the point where chlorine was no longer detectable by the colourimetric method used.

Data provided by Scottish Water.

In addition, it has been shown that sodium thiosulphate can have an adverse effect on the conversion of complex cyanide to free cyanide (by ultra violet digestion and distillation). A sodium thiosulphate concentration of 500 mg/l caused an apparent 30 % loss of complex cyanide, whereas a sodium thiosulphate concentration of 5 mg/l (whilst sufficient to destroy any free chlorine present) caused no apparent effect.

B Determination of “total” cyanide by reflux distillation followed by ion selective electrode potentiometry

B1 Performance characteristics of the method

B1.1	Substance determined	“Total” cyanide is defined as the sum of “easily liberated” and complex cyanides under the conditons used.
B1.2	Type of sample	Raw and potable waters, wastewaters and sludges.
B1.3	Basis of method	Following acidification of the sample, easily liberated and complex cyanides, are converted to hydrogen cyanide. Hydrogen cyanide is liberated from the sample solution by distillation and purging with nitrogen. The hydrogen cyanide is passed through an alkaline “trap” and collected. The cyanide concentration is determinted in the alkaline solution by ion selective electrode potentiometry.
B1.4	Range of application	Typically, for aqueous samples, 0.05 - 10 mg cyanide per litre. The range may be extended by dilution of the original sample.
B1.5	Calibration curve	A standard addition technique is used to determine the concentration of cyanide in the alkaline “trap”; the electrode produces a log-linear response, typically, within the range 0.05 to 20 mg cyanide per litre.
B1.6	Within-batch standard deviation	See Table B1.
B1.7	Limit of detection	Typically, 0.05 mg cyanide per litre in the alkaline “trap” solution, corresponding to 0.01 mg/l in the sample (using 500 ml of sample and 100 ml of alkaline “trap” solution.
B1.8	Sensitivity	Theoretically, the potential of a chemical sensor changes by 59.16 mV at 25 °C for each decade change in concentration. (The Nernstian constant for univalent ions). Practically, the change in emf per decade change in cyanide concentration above 0.05 mg/l may not be the theoretical value, but should not be less than 54 mV or as recommended by the electrode manufacturer.

B1.9 Bias	Typically, better than ± 5 % for easily liberated cyanide and most metallo-cyanide complexes; large negative bias for cobalticyanide complexes, see Table B2.

Data provided by Bostock Hill and Rigby Ltd: Consulting Scientists and Analysts, Birmingham.

B2 Principle

Easily liberated and most complex cyanides are decomposed following reflux distillation with a mixture of hydrochloric acid and hydroxylamine. The hydrogen cyanide liberated is purged with nitrogen into an akaline “trap” containing an absorbing solution of sodium hydroxide and cadmium chloride.

After filtration, cyanide is determined in the alkaline solution using an ion selective electrode together with a standard addition procedure.

B3 Interferences

The effects of the principal potentially interfering substances, for example sulphide, thiocyanate and thiosulphate are minimized and, in many cases, eliminated in this method, see Table B3. The effects of some potentially interfering substances have been tested and are shown in Table B3. Additionally, the presence of urea (expressed as nitrogen) at 10 mg/l has been shown not to produce any significant effect.

B4 Hazards

Cyanide and cadmium chloride present a serious risk of poisoning if swallowed, inhaled or absorbed through the skin. Hydrogen cyanide is a toxic gas. Sodium hydroxide in pellet form is corrosive. Concentrated hydrochloric acid is corrosive. Hydrogen cyanide is liberated during the distillation of acidified samples containing cyanide. This operation should be carried out in a fume cupboard and purged gas passed through an alkaline waste trap. Barbituric acid is an irritant. Skin contact with the solid and reagents incorporating barbituric acid should be avoided. See also A2.

B5 Reagents

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

B5.1 Sodium hydroxide solution 1 M. Dissolve 40.0 ± 0.1 g of sodium hydroxide in water, cool and make to 1000 ml with water. Store the solution in a polyethylene container. This solution may be stored at room temperature for up to one month.

B5.2 Hydrochloric acid-hydroxylamine hydrochloride mixed reagent. Dissolve 100.0 ± 0.1 g of hydroxylamine hydrochloride in approximately 400 ml of water. To the solution carefully add 500 ± 5 ml of concentrated hydrochloric acid (SG 1.18). Mix well, allow the solution to cool and make to 1000 ml with water. This mixed reagent may be stored in a polyethylene bottle at rooom temperature for up to one week.

B5.3 Cadmium chloride (powdered).

B5.4 Hydrochloric acid (25 % v/v). Dilute 250 ± 5 ml, of concentrated hydrochloric acid (SG 1.18) to 1000 ml with water. This solution may be stored at room temperature for up to one year.

B5.5 Sodium hydroxide solution (0.1M). Dissolve 4.0 ± 0.2 g of sodium hydroxide in about 800 ml of water. Mix well, cool the solution and make to 1000 ml with water. Store the solution in a polyethylene bottle. This solution may be stored at room temperature for up to one week.

B5.6 Stock standard cyanide solution (1000 mg as cyanide per litre). Dissolve 0.250 ± 0.005 g of potassium cyanide in 50.0 ± 0.5 ml of sodium hydroxide solution (B5.5). Make to 100 ml with water. Store the solution in a stoppered glass bottle appropriately labelled, for example marked ”toxic”. This solution may be stored at room temperature for up to one week.

B5.7 Stock standard cyanide solution (100 mg as cyanide per litre). Add 10.0 ± 0.1 ml of the stock standard cyanide solution (B5.6) to a 100 ml volumetric flask and add 45.0 ± 0.5 ml of 0.1M sodium hydroxide solution (B5.5). Make to 100 ml with water. Store the solution in a stoppered glass bottle appropriately labelled, for example marked ”toxic”. This solution may be stored at room temperature for up to one week. The concentration may be checked by titration with standardised silver nitrate solution (see section A5).

B5.8 Working standard cyanide solution (10 mg/l). Add 10.0 ± 0.1 ml of the stock standard cyanide solution (B5.7) to a 100 ml volumetric flask and add 45.0 ± 0.5 ml of 0.1M sodium hydroxide solution (B5.5). Make to 100 ml with water. Prepare this solution on the day of use.

B5.9 Working standard cyanide solution (1 mg/l). Add 10.0 ± 0.1 ml of the stock standard cyanide solution (B5.8) to a 100 ml volumetric flask and add 45.0 ± 0.5 ml of 0.1M sodium hydroxide solution (B5.5). Make to 100 ml with water. Prepare this solution on the day of use.

B5.10 Working standard cyanide solution (0.1 mg/l). Add 10.0 ± 0.1 ml of the working standard cyanide solution (B5.9) to a 100 ml volumetric flask and add 45.0 ± 0.5 ml of 0.1M sodium hydroxide solution (B5.5). Make to 1000 ml with water. Prepare this solution on the day of use.

B6 Apparatus

B6.1 A reflux distillation apparatus with an absorption trap.

B6.2 A nitrogen gas cylinder or supply with a regulator capable of providing a flow rate of up to 15 litres per minute at a pressure of up to 1.5 kg/cm^2.

B6.3 Two Dreschel gas washing bottles (nominal capacity 500 ml) and bottle heads with medium porosity sintered outlets for pre- and post-scrubbing of the nitrogen purge. Fill the bottles to about three-quarters capacity with soda lime granules (4 - 10 mesh).

B6.4 Whatman 40 filter papers, or equivalent, washed in 25 % v/v hydrochloric acid solution (B5.4) and rinsed with two portions of water, for filtration of the absorption tube contents.

B6.5 A millivolt meter incorporating an expanded scale or digital meter with impedance of not less than 1012 ohms capable of resolving potential changes to at least 0.1 mV.

B6.6 An ion-selective electrode is required. The emf response (on standard solutions) per decade change in cyanide concentration should not be less than 54 mV, or as recommended by the electrode manufacturer, over the range of cyanide concentrations 0.05 - 20 mg/l.

B6.7 A double-junction sleeve type reference electrode. Use according to manufacturer's instructions.

B7 Analytical procedure

Step	Procedure	Notes
B7.1	To a 1000 ml distillation flask (note a) add a sample aliquot (E ml) expected to contain no more than 1 mg of cyanide. The volume of sample should not exceed 500 ml. If less tha 500 ml of sample are used, add water to make the volume to 500 ml.	(a) The entire distillation system should be rinsed thoroughly between determinations using 25 % v/v hydrochloric acid (B5.4).
B7.2	Add 50.0 ± 0.5 ml of 1M sodium hydroxide solution (B5.1) and 0.25 ± 0.05 g of cadmium chloride (B5.3) to the absorption tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber (i.e. above the level of the frit).	
B7.3	Connect the distillation flask, condenser, absorber and trap.	
B7.4	Start a slow stream of nitrogen (B6.2) entering the distillation flask by adjusting the source. Adjust the gas flow so that approximately one bubble per second enters the distillation flask through the air inlet tube.	
B7.5	Slowly add 25 ± 0.5 ml of hydrochloric acid hydroxylamine hydrochloride mixed reagent (B5.2) through the gas inlet tube. Rinse the tube with water and reconnect the pre-scrubber tube. Allow the gas flow to mix the flask contents for 3 ± 1 minutes.	

B7.6 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the pre-scrubber tube, note b. Reflux for 45 ± 3 minutes, ensuring no more than 100 ml of distillate and absorption solution is collected. Turn off the heat and continue the gas flow for at least 15 minutes. After cooling the boiling flask disconnect and close off the gas flow.

(b) The bubbling rate will not remain constant after the regents have been added and while heat is being applied to the flask. It will therefore be necessary to readjust the purge rate occasionally to prevent the solution in the boiling flask from backing up into the nitrogen inlet tube.

B7.7 Quantitatively transfer the solution from the absorption tube into a 100 ml volumteric flask and make to 100 ml with water, using washings from the absorption tube as necessary, note c.

(c) Any sodium hydroxide solution trapped inside the sintered disc of the gas absorption tube should be transferred to the sodium hydroxide solution inside the bottle by washing with water.

B7.8 Filter the solution from the volumetric flask through acid-washed filter paper (B6.4).

B7.9 Ensure that the electrodes and meter are in good operating condition before proceeding with the calibration. Checks should be carried out in accordance with the manufacturer's instructions.

B7.10 Prepare the three working standard solutions (B5.8 - B5.10).

B7.11 Transfer 50.0 ± 0.5 ml of the lowest concentration (note d) working standard solution (B5.10) into a clean 100 ml plastic beaker, pre-rinsed with a small portion of the solution being tested.

(d) Always progress from the lowest concentration to the highest concentration of standard solution as equilibrium may be reached only slowly.

B7.12 Place a magnetic stirring bar in the plastic beaker and place on the platform of a magnetic stirrer (note e). Switch on the stirrer and adjust the stirring rate so the liquid is thoroughly mixed but at the same time no vortex or air bubbles are formed. Maintain the same stirring rate for both sample and standard solutions. Insert the electrode, note f.

(e) Some thermal insulation should be provided between sample beaker and magnetic stirrer.

(f) The electrode should be pre-rinsed with the solution being tested.

B7.13 After a steady reading is reached (between 5 - 10 minutes) record the potential (millivolt) reading.

B7.14 Remove the electrode from the solution and and wash with water. Remove the beaker from the stirrer, note g.

(g) Sample beakers should be washed thoroughly with water immediately after use.

B7.15 Repeat steps B7.11 - B7.14 with the other standard solutions (B5.9 and B5.8) in ascending order of concentration. Plot a graph on semi-log paper of emf in millivolts (linear scale) against cyanide concentration of the calibration standard solutions (logarithmetic scale). Measure the slope of the line obtained (millivolts/decade of concentration) note h.

(h) The slope may vary from the theoretical value of 59.16 mV/decade. This is due to manufacturing variation and reference electrode liquid junction potentials.

B7.16 Carry out the sample analysis using 50.00 ± 0.02 ml of the absorption solution (B7.8) (note i) by repeating the procedures described in sections B7.11 - B7.13.

(i) Greater precision for the volume of the absorption solution is required due to the impending standard addition technique to be followed.

B7.17 Record the potential reading (A mV).

B7.18 Remove the electrode from the solution and and wash with water. Remove the beaker from the stirrer, note g.

B7.19 Choose one of the three standard cyanide solutions (B5.6, B5.7 or B5.8) such that the concentration (expressed as mg/l) is between 100 and 1000 times the expected amount of cyanide in the sample aliquot (B7.1)

B7.20 Add 1.00 ± 0.01 ml of the chosen cyanide standard solution into the sample, see notes e and f. Allow sufficient time for equilibration (between 5 - 10 minutes) to occur and record the new potential reading (B mV).

B7.21 Calculate the cyanide concentration in the original sample using the equations described in B8.

B8 Calculations

The cyanide concentration in the original sample $= C_o \times D / E$ mg/l
where

$C_o = 0.02 \times C_s / 1.02 \times \text{antilog}[((A-B)^{-1}) / S]$

and

C_o is the cyanide concentration (mg/l) in sample used for potentiometric measurement,

D is the final volume (ml) of absorbing solution, typically 100 ml (B7.7),
E is the volume (ml) of sample distilled, typically 500 ml (B7.1),
A-B is the absolute value of potential change (mV),
C_s is the cyanide concentration (mg/l) of the standard solution added at step B7.20,
S is the electrode slope, mV/decade, measured at step B7.15.

Table B1 Performance data

Sample type	Concentration (mg/l)	Standard deviation (mg/l)	Degrees of freedom
Standard solution(1)	0.1	0.0045	4
Standard solution(2)	5.0	0.067	5
Effluent	7.75	0.007	4
Sludge(3)	555*	11.2*	5

(1) = potassium cyanide
(2) = potassium ferrocyanide ($K_4Fe(CN)_6.3H_20$)
(3) = mixed metal effluent and sludge from metal finishing industry
* results expressed as mg/kg on a dry weight basis.

Table B2 Recovery of cyanide from standard solutions

Solution	Cyanide concentration (mg/l)	Cyanide recovery (%)
Potassium cyanide	0.1	103
Potassium cyanide	5.0	100
Potassium ferricyanide, as $K_3Fe(CN)_6$	5.0	101
Potassium ferrocyanide, as $K_4Fe(CN)_6.3H_20$	5.0	101
Potassium cobalticyanide, as $K_3Co(CN)_6$	5.0	18
Potassium cobalticyanide, as $K_3Co(CN)_6$	5.0	33*

* reflux time increased to 90 minutes. Further increase of reflux time gives no significant further improvement in recovery.

Table B3 Interference effects

Other substance	Concentration of other substance (mg/l)	Effect in mg/l of other substance in the presence of potassium cyanide at a concentration of 0.1 mg/l*
Sulphide, as S	450	+ 0.02
Thiocyanate, as SCN	1000	0.00
Thiosulphate, as S_2O_3	250	+ 0.02

* The maximum effect (95% confidence limit) assuming no interference would be ± 0.09.

C Determination of “total” cyanide by reflux distillation followed by spectrophotometric detection

C1 Performance characteristics of the method

C1.1	Substance determined	“Total” cyanide is defined as the sum of “easily liberated” and complex cyanides under the conditons used.
C1.2	Type of sample	Raw and potable waters, wastewaters and sludges.
C1.3	Basis of method	Following acidification of the sample, easily liberated and complex cyanides, are converted to hydrogen cyanide. Hydrogen cyanide is liberated from the sample solution by distillation and purging with nitrogen. The hydrogen cyanide is passed through an alkaline “trap” and collected. The cyanide concentration is determinted in the alkaline solution by colourimetric detection.
C1.4	Range of application	Typically for aqueous samples, 0.01 - 1 mg cyanide per litre. The range may be extended by dilution.
C1.5	Calibration curve	Linear over the range 0.1 - 10 µg/l.
C1.6	Within-batch standard deviation	See Table C1.
C1.7	Limit of detection	Typically, 0.01 mg/l, based on 100 ml of sample. Lower limits can be achieved using larger sample aliquots.
C1.8	Sensitivity	A standard cyanide solution containing 1 mg in 25 ml of solution gives an absorbance change of approximately 0.125 absorbance units using a 10 mm path length cell.

Data provided by Wastewater Technology Centre, Environmental Protection Service, Burlington, Ontario, L7R 4A6, Canada.

C2 Principle

Easily liberated and most complex cyanides are decomposed following reflux distillation with a mixture of hydrochloric acid and hydroxylamine. The hydrogen cyanide liberated is purged with nitrogen into an akaline “trap” containing an absorbing solution of sodium hydroxide and cadmium chloride.

After filtration, cyanide ion is determined in the absorbing solution using a spectophotometric procedure.

C3 Interferences

The effects of the principal potentially interfering substances, for example sulphide, thiocyanate and thiosulphate are minimized and, in many cases, eliminated in this method, see Table C2. Additionally, the presence of urea (expressed as nitrogen) at 10 mg/l has been shown not to produce any significant effect.

C4 Hazards

Cyanide presents a serious risk of poisoning if swallowed or by skin contact. Hydrogen cyanide is a highly toxic gas. See also A1.2. Sodium hydroxide in pellet form is extremely corrosive. Cadmium chloride is toxic by inhalation, in contact with skin and if swallowed. Concentrated hydrochloric acid is extremely corrosive. Hydrogen cyanide gas is liberated during the distillation of samples containing cyanide. This operation should be carried out in a fume cupboard and purge gas exhaust emissions shall be passed through an alkaline waste trap. Barbituric acid is an irritant. Skin contact with the solid and reagents incorporating it must be avoided. See also A1.2.

C5 Reagents

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

C5.1 Sodium hydroxide solution 1 M. Dissolve 40.0 ± 0.1 g of sodium hydroxide in water, cool and make to 1000 ml with water. Store the solution in a polyethylene container. This solution may be stored at room temperature for up to one week.

C5.2 Hydrochloric acid-hydroxylamine hydrochloride mixed reagent. Dissolve 100.0 ± 0.1 g of hydroxylamine hydrochloride in approximately 400 ml of water. To the solution carefully add 500 ± 5 ml of concentrated hydrochloric acid (SG 1.18). Mix well, allow to cool and make to 1000 ml with water. This mixed reagent may be stored in a polyethylene bottle at rooom temperature for up to one week.

C5.3 Cadmium chloride (powdered).

C5.4 Sodium isonicotinate, recrystallised. Dissolve 3.30 ± 0.05 g of sodium hydroxide in 200 ± 5 ml of water. Add 10.00 ± 0.05 g of isonicotinic acid to the solution and dissolve. Evaporate the solution to dryness on a water bath and dry the crystals at 110 °C before further use.

C5.5 Sodium barbiturate, recrystallised. Dissolve 3.10 ± 0.05 g of sodium hydroxide in 200 ± 5 ml of water. Add 10.00 ± 0.05 g of barbituric acid and dissolve. Evaporate the solution to dryness on a water bath and dry the crystals in a desiccator. Drying at 110 °C should not be attempted as subsequent dissolution may be difficult.

C5.6 Isonicotinate-barbiturate mixed reagent. Dissolve, while stirring 1.00 ± 0.05 g of sodium isonicotinate (C5.4) and 1.00 ± 0.05 g of sodium barbiturate (C5.5) in 80 ± 10 ml of water at 65 ± 5 °C. Allow the solution to cool and then filter through filter paper (C6.5) into a 100 ml volumetric flask. Make to 100 ml with water. The solution should be clear, pale yellow and possess a pH value of 6.5 ± 0.3. If not, repeat the preparation. The solution may be stored at room temperature for up to one week. (This

reagent can be prepared from commercially available sodium isonicotinate and sodium barbiturate).

C5.7 Acetic acid solution, (20 % v/v). Mix 1 volume of glacial acetic acid with 4 volumes of water. This solution may be stored at room temperature for up to one month.

C5.8 p-nitrophenol indicator (0.1 % w/v in ethanol). This solution may be stored at room temperature for up to one month.

C5.9 Chloramine-T solution. Dissolve 1.0 ± 0.01 g chloramine-T (sodium p-toluene-sulphonchloramide) in 100 ml of water. This solution may be stored in a refridgerator for up to one week.

C5.10 Sodium hydroxide solution (0.1 M). Dissolve 4.0 ± 0.1 g of sodium hydroxide in water, cool and make to 1000 ml with water. Store the solution in a polyethylene container. This solution may be stored at room temperature for up to one week.

C5.11 Stock standard cyanide solution (100 mg as cyanide per litre). Dissolve 0.250 ± 0.005 g of potassium cyanide in 500 ± 5 ml of sodium hydroxide solution (C5.10). Make to 1000 ml with water. Store the solution in a stoppered glass bottle appropriately labelled, for example marked ”toxic”. This solution may be stored at room temperature for up to one week. The concentration may be checked by titration with standard silver nitrate solution (see section A5).

C5.12 Working standard cyanide solution (10 mg/l). Add 10.0 ± 0.1 ml of the stock standard cyanide solution (C5.11) to a 100 ml volumetric flask and add 45.0 ± 0.5 ml of 0.1M sodium hydroxide solution (C5.10). Make to 100 ml with water. Prepare this solution on the day of use.

C5.13 Working standard cyanide solution (1 mg/l). Add 10.0 ± 0.1 ml of the stock standard cyanide solution (C5.12) to a 100 ml volumetric flask and add 45.0 ± 0.5 ml of 0.1M sodium hydroxide solution (C5.10). Make to 100 ml with water. Prepare this solution on the day of use.

C5.14 Working standard cyanide solution (0.1 mg/l). Add 10.0 ± 0.1 ml of the working standard cyanide solution (C5.13) to a 100 ml volumetric flask and add 45.0 ± 0.5 ml of 0.1M sodium hydroxide solution (C5.10). Make to 1000 ml with water. Prepare this solution on the day of use.

C5.15 Hydrochloric acid (25 % v/v). Dilute 250 ± 5 ml, of concentrated hydrochloric acid (SG 1.18) to 1000 ml with water. This solution may be stored at room temperature for up to one year.

C6 Apparatus

C6.1 A reflux distillation apparatus with an absorption trap.

C6.2 A nitrogen gas cylinder or supply with a regulator capable of providing a flow rate of up to 15 litres per minute at a pressure of up to 1.5 kg/cm^2.

C6.3 Two Dreschel gas washing bottles (nominal capacity 500 ml) and bottle heads with medium porosity sintered outlets for pre- and post-scrubbing of the nitrogen purge. Fill the bottles to about three-quarters capacity with soda lime granules (4-10 mesh).

C6.4 Whatman 40 filter papers, or equivalent, washed in 25% v/v hydrochloric acid solution (C5.15) and rinsed with two portions of water, for filtration of the absorption tube contents.

C6.5 Whatman 42 filter papers, or equivalent.

C6.6 Spectrophotometer capable of operating at 600 nm and equipped with 10 mm pathlength cells.

C7 Analytical procedure

Step	Procedure	Notes
C7.1	To a 1000 ml distillation flask (note a) add a sample aliquot (C ml) expected to contain no more than 0.1 mg of cyanide. The volume of sample should not exceed 500 ml. If less than 500 ml of sample are used, add water to make the volume to 500 ml.	(a) The entire distillation system should be rinsed thoroughly between determinations using 25 % v/v hydrochloric acid (C5.15).
C7.2	Add 50.0 ± 0.5 ml of sodium hydroxide solution (C5.1) and 0.25 ± 0.05 g of cadmium chloride (C5.3) to the absorption tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber (i.e. above the level of the frit).	
C7.3	Connect the distillation flask, condenser, absorber and trap.	
C7.4	Start a slow stream of nitrogen (C6.2) entering the distillation flask by adjusting the source. Adjust the gas flow so that approximately one bubble per second enters the distillation flask through the air inlet tube.	
C7.5	Slowly add 25 ± 0.5 ml of hydrochloric acid hydroxylamine hydrochloride mixed reagent (C5.2) through the gas inlet tube. Rinse the tube with water and reconnect the pre-scrubber tube. Allow the gas flow to mix the flask contents for 3 ± 1 minutes.	

C7.6 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the pre-scrubber tube, note b. Reflux for 45 ± 3 minutes, ensuring no more than 100 ml of distillate and absorption solution is collected. Turn off the heat and continue the gas flow for at least 15 minutes. After cooling the boiling flask disconnect and close off the gas flow.

(b) The bubbling rate will not remain constant after the regents have been added and while heat is being applied to the flask. It will therefore be necessary to readjust the purge rate occasionally to prevent the solution in the boiling flask from backing up into the nitrogen inlet tube.

C7.7 Quantitatively transfer the solution from the absorption tube into a 100 ml volumteric flask and make to 100 ml with water, using washings, as necessary from the absorption tube, note c.

(c) Any sodium hydroxide solution trapped inside the sintered disc of the gas absorption tube should be transferred to the sodium hydroxide solution inside the bottle by washing with water.

C7.8 Filter the solution from step C7.7 through acid-washed filter paper (C6.4).

C7.9 Use up to 5 ml of the standard cyanide solutions (C5.13 or C5.14) to prepare a series of standard solutions containing 0.1 - 5 µg of cyanide in 25 ml volumetric flasks. Add 10 ml of sodium hydroxide solution (C5.1) and adjust the volume in each flask to approximately 15 ml with water. Mix well.

C7.10 Add two drops (0.1 ml) of p-nitrophenol indicator (C5.8) and neutralize the solution to a colourless end point using the acetic acid solution (C5.7).

C7.11 Add 0.200 ± 0.002 ml of the chloramine-T reagent (C5.9) mix well and allow the solution to stand for at least 2 minutes.

C7.12 Add 5.00 ± 0.05 ml of the sodium barbiturate-sodium isonicotinate mixed reagent (C5.6) and mix well. Make to 25.0 ml with water and mix well. Leave the solution to stand for at least 30 minutes at 20 - 25 °C (note d).

(d) The absorbance reading obtained after 30 minutes is very stable showing no significant change after standing a further period of 90 minutes.

C7.13 Prepare a blank solution by carrying out steps C7.9 to C7.12 using water in place of the cyanide solution.

C7.14 Measure the absorbance of the solutions at 600 nm (note e) in a 10 mm pathlength cell

(e) The exact wavelength of maximum absorption should be

using the blank solution (C7.13) as reference.

determined, used and reported.

C7.15 Plot a graph of the absorbance against amount of cyanide (µg of cyanide).

C7.16 Carry out sample analysis by repeating the procedures described in steps C7.9 - C7.12 adding 5.0 ± 0.1 ml of the filtered solution (C7.8) in place of the calibration standard solutions. (note f).

(f) A smaller volume of absorbing solution may be taken in order to accommodate higher concentrations.

C7.17 Calculate the cyanide concentration in the original sample using the equations described in section C8.

C8 Calculations

The cyanide concentration in the original sample = (A x B) / (C x D) mg/l

where:

A is the amount of cyanide (µg) from calibration curve (C7.15),
B is the volume (ml) of filtered solution, typically 100 ml (C7.8),
C is the volume (ml) of original sample used in the distillation, typically, 500 ml (C7.1),
D is the volume (ml) of filtered solution used in the spectrophotometric determination, typically 5 ml (C7.16).

Table C1 Performance data

(Information on degrees of freedom is lacking)

Sample type	Concentration (mg/l)	Standard deviation (mg/l)
Sodium cyanide standard	0.01	0.002
Sodium cyanide standard	0.05	0.005
Sodium cyanide standard	0.10	0.012
Sodium cyanide standard	1.00	0.045

Table C2 Interference effects

Interfering substances		Cyanide added (mg/l)	Cyanide measured (mg/l)*
Thiocyanate (mg/l)	Iron (mg/l)		
100	0	0	0.005
1000	0	0.50	0.51
1000	0	10	9.6
100	300	0	0.002
100	1000	0	0.043

Thiocyanate as CNS and iron as Fe.
* Information on maximum effect to be expected assuming no interference is lacking.

D Determination of easily liberated cyanide by microdiffusion

D1 Performance characteristics of the method

D1.1	Substance determined	Easily liberated cyanide.
D1.2	Type of sample	Raw, potable and waste waters.
D1.3	Basis of method	Diffusion of hydrogen cyanide released at pH 6 into dilute sodium hydroxide, and subsequent spectrophotometric determination.
D1.4	Range of application	Up to 160 µg cyanide per litre. The range can be extended by taking a smaller sample volume.
D1.5	Calibration curve	Linear to at least 160 µg/l.
D1.6	Total standard deviation	See Table D1.
D1.7	Limit of detection	3 mg/l (11 *degrees of* freedom).
D1.8	Sensitivity	120 µg/l gives an absorbance value of about 0.38 units.
D1.9	Bias	See Table D2.
D1.10	Time required for analysis	About 5 hours total analytical time, 1 hour operator time, for a batch of 8 determinations.

Data from Thames Water Authority, New River Head Laboratories.

D2 Principle

The method relies upon diffusion of hydrogen cyanide liberated at pH 6 into a dilute sodium hydroxide receiving solution. The diffusion process is carried out in Conway-type glass diffusion cells and determined spectrophotometrically involving the reaction of cyanogen chloride formed by reaction of cyanide with N-chlorosuccinimide and barbituric acid in a pyridine-containing solution to form a purple-coloured complex, the absorbance of which is measured at 580 nm.

Cyanide complexes that resist dissociation at pH 6 are not deermined and such complexes include the hexacyanoferrates complexes.

“Easily liberated” cyanide is therefore defined as hydrogen cyanide liberated from an acidified solution at pH 6, at room temperature.

D3 Interference

The addition of cadmium chloride to the sample before addition of pH 6 buffer solution serves as a precaution against interference from large concentrations of hexacyanoferrates by precipitating them as cadmium salts. Limited interference testing has been carried out, using a method similar in all essentials to this method. Table D3 shows these results, but no estimate of the significance of the effects is available.

D4 Hazards

Potassium cyanide and its solutions present a serious risk of poisoning if swallowed, or absorbed through the skin. Contact with acids will liberate hydrogen cyanide. See also section A1.2. Pyridine is highly flammable, and harmful by inhalation, ingestion or by skin contact. N-chlorosuccinimide reacts explosively with aliphatic alcohols. Cadmium chloride is toxic by inhalation, ingestion or by skin contact presenting the danger of cumulative, irreversible effects. Barbituric acid is an irritant and skin contact with the solid and its solutions should be avoided. See also section A1.2.

D5 Reagents

Analytical grade reagents should be used wherever possible. Distilled or deionised water should be used.

D5.1 Sodium hydroxide solution (2M). Carefully, dissolve 80 ± 1 g of sodium hydroxide in about 900 ml of water. Mix well and cool the solution. Make to 1000 ml with water. Store in a stoppered polyethylene bottle. This solution may be stored at room temperature for up to one month.

D5.2 Sodium hydroxide solution (0.1M). Add 50 ± 1 ml of 2M sodium hydroxide solution (D5.1) to about 900 ml of water. Mix well and cool the solution. Make to 1000 ml with water. Store in a stoppered polyethylene bottle. This solution may be stored at room temperature for up to one week.

D5.3 Potassium dihydrogen orthophosphate solution (19 % m/v). Add 14.5 ± 0.1 g of sodium hydroxide in about 400 ml of water. Add 190 ± 1 g of potassium dihydrogen orthophosphate and more water to make to approximately 950 ml. Adjust the pH value of this solution to pH 5.9 - 6.1 using dropwise addition of 2M sodium hydroxide solution (D5.1) monitoring the pH with a suitable pH electrode system. When the correct pH value is obtained, quantitatively transfer the solution to a 1000 ml volumetric flask. Make to 1000 ml with water. Store in a polyethylene container. This solution may be stored at room temperature for up to one month.

D5.4 Buffer solution. Mix together 8.0 ± 0.1 ml of phosphoric acid (SG1.70) and 100 ± 1 ml of 19% m/v potassium dihydrogenorthophosphate solution (D5.3). Store in a polyethylene bottle. This solution may be stored at room temperature for up to one month.

D5.5 Cadmium chloride solution (1% m/v). Add 10.0 ± 0.1 g of anhydrous cadmium chloride to about 900 ml of water. Mix well and make to 1000 ml with water. Store in a glass bottle labelled TOXIC. This solution may be stored at room temperature for up to one year.

D5.6 N-chlorosuccinimide/succinimide reagent. Add 10.0 ± 0.1 g of succinimide to about 900 ml of water. Add 1.00 ± 0.01 g of N-chlorosuccinimide, mix well and make to 1000 ml with water. Store in an amber glass bottle. This solution may be stored at room temperature for up to 2 months.

D5.7 Barbituric acid/pyridine reagent. Mix together 10 ± 5 ml of water, 7.5 ± 1 ml of pyridine and 1.50 ± 0.05 ml of concentrated hydrochloric acid (SG 1.18). To this mixture, add 1.50 ± 0.01 g of barbituric acid and 50 ± 5 ml of water. Mix well. Warm the mixture gently if necessary to achieve dissolution. Make to 100 ml with water. Store in an amber glass bottle labelled TOXIC. This solution may be stored at room temperature for up to 3 days.

D5.8 Stock standard cyanide solution (100 mg as cyanide per litre). Dissolve 0.250 ± 0.005 g of potassium cyanide in 500 ± 5 ml of sodium hydroxide solution (D5.2). Make to 1000 ml with water. Store the solution in a stoppered glass bottle appropriately labelled, for example marked ”toxic”. This solution may be stored at room temperature for up to one week. The concentration may be checked by titration with standardised silver nitrate solution (see section A5).

D5.9 Working standard cyanide solution (1 mg as cyanide per litre). Add 1.00 ± 0.01 ml of the stock standard cyanide solution (D5.8) to a 100 ml volumetric flask and add 50.0 ± 0.5 ml of sodium hydroxide solution (D5.2). Make to volume with water. Prepare this solution on the day of use.

D6 Apparatus

D6.1 Conway-type glass diffusion cells. An alternative arrangement, based on the use of Petri dishes may be used.

D6.2 Fume cupboard for handling pyridine.

D6.3 A spectrophotometer capable of operating at 580 mm and equipped with 10 mm path length cells.

D7 Analytical procedure

Step	Procedure	Notes
	Calibration	
D7.1	Into a series of 50 ml volumetric flasks add, 0.0, 1.0, 2.0, 4.0, 6.0 and 8.0 ml of working standard cyanide solution (D5.9). Add to each flask 25.0 ± 0.5 ml of 0.1M sodium hydroxide solution (D5.2) and make to volume with water. These flasks now contain 20, 40, 80, 120 and 160 µg cyanide per litre, respectively.	

D7.2 Into a series of glass diffusion cells (D6.2) add 10.0 ml of the standard cyanide solutions (D7.1) into the outer rings.

D7.3 Add 2 ml of 1 % m/v cadmium chloride solution (D5.5) into the outer ring of each diffusion cell (D6.2) and mix carefully, notes a and b.

(a) Gentle tilting of the cell will achieve mixing.

(b) Take care to avoid splashing any solution into the centre ring of the diffusion cell.

D7.4 Add 5 ml of 0.1M sodium hydroxide solution (D5.2) into the centre ring of each diffusion cell (D6.2).

D7.5 Add 4 ml of 19 % m/v potassium dihydrogen orthophosphate solution (D5.3) into the outer ring of each diffusion cell (D6.2) and immediately cover the cell (note c) with the lid. Carefully mix the contents of the outer ring (notes a and b). Place the diffusion cells (note b) in a dark cupboard at room temperature. After at least 4 hours (note d), remove the diffusion cells from the cupboard.

(c) Ensure the seal is air-tight. This is most easily achieved by smearing a small quantity of petroleum jelly on the ground glass joint surface.

(d) Tests have shown that the diffusion cell can be left in the cupboard for at least 16 hours without ill effect.

D7.6 Remove the lid and transfer 4.0 ml of the sodium hydroxide solution from the centre ring of each cell to separate 10 ml volumetric flasks. Replace the lid.

D7.7 To each volumetric flask, add 0.400 ± 0.004 ml of buffer solution (D5.4) and mix.

D7.8 To each flask, add 0.400 ± 0.004 m of N-chlorosuccinimide/succinimide reagent (D5.6) and mix. Allow the flasks to stand for at least 2 minutes.

D7.9 To each flask, add 0.400 ± 0.004 ml of barbituric acid/pyridine reagent (D5.7) and mix.

D7.10 Make each flask to 10.0 ml with water and mix well. After 10 ± 5 minutes measure the absorbance (note e) of each solution at 580 nm (note f) in 10 mm cells using water in the reference cell.

(e) The absorbance increases to a maximum value within this time interval. Beyond 15 minutes, the absorbance decreases at a rate of about 5 % in 35 minutes.

(f) The exact wavelength of

maximum absorbance should be determined, used and reported.

Blank determination

D7.11 Pipette 5 ml of 0.1M sodium hydroxide solution (D5.2) and 5 ml of water into the outer ring of a diffusion cell (D6.2) and mix. Proceed as described in steps D7.2 to D7.10.

D7.12 Subtract the absorbance of the blank solution (step D7.11) from the absorbance of each of the standard solutions (D7.10). Plot a graph of corrected absorbance against cyanide concentration (µg/l). This should be linear through the origin.

Analysis of samples

D7.13 Pipette 10 ml of the sample (note g) into the outer ring of a diffusion cell (D6.2) and proceed as described in steps D7.2 to D7.10. Subtract the absorbance of the blank solution (step D7.11) from the absorbance of the sample. From the calibration graph determine the concentration of cyanide in the sample, taking into account any dilutions or volumes changes.

(g) Samples preserved by the addition of sodium hydroxide can be analysed directly. However, for samples which before preservation are extremely alkaline, it is necessary to establish that a pH value of 6.0 ± 0.2 has been achieved after addition of the phosphate buffer solution at step D7.4. If this is not the case, the sample should first be partially neutralized. See also section D9.2.

D8 Sources of error

The pH value of the sample during diffusion is not critical from the point of view of efficiency; tests have shown that 100 % recovery is obtained in the pH range 6.5 - 3.5. However, any significant lowering of pH below 6.0 may increase the diffusion of potentially interfering acids.

While the method specifies a sodium hydroxide concentration of 0.05 ± 0.01 M in samples and standards, tests have shown that a four-fold increase in this concentration produces little effect on the cyanide determination.

The pH value of the diffusate should be in the range of 6.2 - 5.8 for maximum absorbance, although a range of 6.4 - 5.3 may be tolerable.

Between 5 - 31 °C, there is no significant effect of temperature on the efficiency of the diffusion process.

Table D1 Performance data

Sample Type	Concentration (mg/l)	Standard deviation (mg/l)	Degrees of freedom
Standard solution	40	1.60	14
Standard solution	120	5.02	9
Settled sewage	5	2.21	4
Spiked settled sewage	84	2.15	9
Spiked sewage effluent	39	2.28	9

Table D2 Performance data

Sample Type	Concentration (mg/l)	Bias (mg/l)	Significance (95% confidence level)
Standard solution	32	-1.9	NS
Standard solution	80	- 5.0	S
Standard solution	144	- 4.2	S
Spiked sample	32	- 4.0	NS
Spiked sample	80	- 7.5	S
Spiked sample	144	- 9.7	S

NS not significant; S significant.

Table D3 Interference effects

Other substance expressed in terms of substance in brackets)	Concentration of other substance (mg/l)	Effect in µg/l of other substance at a cyanide concentration of 0 µg/l	100 µg/l
Sulphite	250		- 2
(as Na_2SO_3)	330		- 10
	500		- 50
	1000		- 70
Cyanohydrin	117	<2	
(as $CH_2(OH)CN$)	234	4	
	467	8	
	700	11	
	1116	18	
Formaldehyde	200		- 6
(as HCHO)	500		- 16
	1000		- 27
	2000		- 35
Hexacyanoferrate			
(as $K_3Fe(CN)_6$)	50	1	
(as $K_3Fe(CN)_6$)	200	10	
(as $K_4Fe(CN)_6.3H_2O$)	50	2	
(as $K_4Fe(CN)_6.3H_2O$)	200	9	
Thiocyanate	350	1	
(as NaCNS)			

E Determination of cyanide using continuous flow measurement

A continuous flow method based on method D may also be used.

E1 Performance characteristics of the method

E1.1	Substance determined:	Most cyanide ions.
E1.2	Type of Sample:	Raw, potable and waste waters.
E1.3	Basis of Method:	Continuous flow colourimetry, using reactions described in section D. Ultra-violet radiation is used to release cyanide from complex cyanides.
E1.4	Range of application:	Up to 5 mg of cyanide per litre.
E1.5	Calibration curves:	Linear over range of application.
E1.6	Within-batch standard deviation	See Table E1.
E1.7	Limit of detection:	Typically, up to 0.4 mg/l.
E1.8	Bias	Cyanide is incompletely recovered from certain complexes. Interferences may arise. See section E3.
E1.9	Time required for analysis	The automated system described is capable of operating at up to 30 determinations per hour.

Data obtained by Yorkshire Water Authority, Sheffield Laboratory

E2 Principle

The sample is acidified with a mixture of phosphoric, hydrochloric and hypophosphorous acids. (Hypophosphorous acid acts as an oxygen scavenger and helps prevent oxidation of cyanide during ultra-violet irradiation). Hydrogen cyanide is separated from the reaction mixture by passing the gas through a permeable silicone rubber membrane into dilute sodium hydroxide solution and then converting to cyanogen chloride by reaction with chloramine-T. The cyanogen chloride is reacted with pyridine and barbituric acid to form a red-violet coloured complex which is measured spectrophotometrically at 520 nm.

All these reactions are carried out automatically using continuous flow techniques.

When the determination of “total” cyanide is required, the acidified sample is irradiated with ultra-violet light which converts complex cyanides into hydrogen cyanide prior to dialysis. Table E2 shows the recovery of cyanide from certain complexes when using ultra-violet irradiation. Stable nickel and cobalt complexes yield low recoveries of hydrogen cyanide.

Thiocyanate, if present in the sample will be quantitively converted to cyanide by ultra-violet irradiation at the intensity which is required for satisfactory recovery of cyanide from

iron complexes. Therefore, prior reflux distillation of the thiocyanate-containing sample with EDTA should be carried out in order to release cyanide from iron and other complexes as a result of preferential complexing by EDTA. The cyanide-containing distillate from this procedure is then analysed by the automated method. Table E3 shows the recovery of cyanide from certain compounds using this reflux distillation procedure.

E3 Interferences

The main interference arises from sulphide. A concentration of sulphide at 1 mg/l depresses results by about 13 %, and sulphide at 20 mg/l causes about 100 % depression. Thiocyanate interferes in the determination of “total” cyanide using ultra-violet irradiation. However, using the procedures described in sections E7.13 - E7.20 should remove this source of intereference.

E4 Hazards

Cyanide presents a serious risk of poisoning if swallowed, inhaled or absorbed by skin. Hydrogen cyanide is a toxic gas. See also A1.2. Pyridine is highly flammable and harmful by ingestion, inhalation, or via contact with skin. Barbituric acid is an irritant and skin contact with the solid and its reagents should be avoided. See also A1.2. When in use, the ultra-violet radiation unit presents a potential hazard to operators. During operation, ozone may be produced. See section E6.3.

E5 Reagents

E5.1 Phosphoric acid/hydrochloric acid solution. Carefully, stirring continuously, add 500 ± 5 ml of phosphoric acid (SG 1.70) to 200 ± 20 ml of water. Add 200 ± 20 ml of concentrated hydrochloric acid (SG 1.18). Mix well and dilute to 1000 ml with water. This solution may be stored at room temperature for up to one year.

E5.2 Hypophosphorous acid solution (5 % m/v). Add 100 ± 1 ml of hypophosphorous acid (SG 1.21) to approximately 800 ml of water. Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to one month.

E5.3 Mixed acid reagent 1. Mix together 200 ± 2 ml of phosphoric/hydrochloric acid solution (E5.1) and 200 ± 2 ml of hypophosphorous acid solution (E5.2). Add 0.5 ± 0.1 ml of detergent (for example Triton X-100 or equivalent wetting agent). This solution may be stored at room temperature for up to one month.

E5.4 Mixed acid reagent 2. Mix together 200 ± 2 ml of phosphoric/hydrochloric acid solution (E5.1) and 200 ± 2 ml of water. Add 0.5 ± 0.1 ml of detergent (for exampe Triton X-100 or equivalent wetting agent). This solution may be stored at room temperature for up to one month.

E5.5 Sodium hydroxide solution (1.25M). Dissolve 50 ± 1 g of sodium hydroxide in about 800 ml of water. Mix well and cool, and make to 1000 ml with water. Store in a plastic bottle. This solution may be stored at room temperature for up to one month.

E5.6 Sodium hydroxide solution (0.01M). Dilute 8.0 ± 0.1 ml of sodium hydroxide solution (E5.5) to 1000 ml with water. Add 0.5 ± 0.1 ml of detergent (for example Triton X-100 or equivalent wetting agent). Store in a plastic bottle at room temperature. This solution may be stored for up to 4 weeks.

E5.7 Chloramine-T solution. Dissolve 0.40 ± 0.01 g of chloramine-T in 200 ± 20 ml of water. Add 10.9 ± 0.1 g of potassium dihydrogen orthophosphate and 0.220 ± 0.005 g of disodium hydrogen orthophosphate. Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to one week. The pH value of this solution should be 5.2 ± 0.1. Adjust to this value with sodium hydroxide solution (E5.5) or phosphoric acid (E5.8) as appropriate.

E5.8 Phosphoric acid (SG 1.70).

E5.9 Pyridine/barbituric acid reagent. Mix together 10 ± 5 ml of water, 7.5 ± 1 ml of pyridine and 1.50 ± 0.05 ml of hydrochloric acid (SG 1.18). Mix well and add 1.50 ± 0.01 g of barbituric acid and 50 ± 5 ml of water. Mix well and warm the mixture gently, if necessary, to aid dissolution. Cool and make to 100 ml with water. Store the solution in an amber glass bottle, appropriately labelled, for example marked ”toxic”. This solution may be stored at room temperature for up to three days.

E5.10 Saturated disodium EDTA solution.

E5.11 Sodium acetate buffer solution (pH value 4.5). Dissolve 243 ± 1 g of sodium acetate trihydrate and 465 ± 5 ml of acetic acid (SG 1.05) in about 900 ml of water and make to 1000 ml with water. This solution may be stored at room temperature for up to 6 months, and may be available commercially.

E5.12 Hydrochloric acid solution (1M). Dilute 89 ± 1 ml of concentrated hydrochloric acid (SG 1.18) to 1000 ml with water. This solution may be stored at room temperature for up to one year.

E5.13 Indicator solution for pH 4.5. Suitable solutions are available commercially.

E5.14 Stock standard cyanide solution (100 mg as cyanide per litre). Dissolve 0.250 ± 0.005 g of potassium cyanide in 500 ± 5 ml of sodium hydroxide solution (E5.15). Make to 1000 ml with water. Store the solution in a stoppered glass bottle appropriately labelled, for example marked ”toxic”. This solution may be stored at room temperature for up to one week. The concentration may be checked by titration with standardised silver nitrate solution (see section A5).

E5.15 Sodium hydroxide solution (0.1 M). Dissolve 4.0 ± 0.1 g of sodium hydroxide in water, cool and make to 1000 ml with water. Store the solution in a polyethylene container. This solution may be stored at room temperature for up to one week.

E6 Apparatus

Suitable continuous flow apparatus is available commercially.

The design of the manifold depends on the concentration range of the method. A different mixed acid reagent is required when determining total cyanide.

All waste receptacles connected to the manifold should contain about 10 pellets of sodium hydroxide before starting the analysis. This is a precaution against the possible release of hydrogen cyanide from acidic waste solutions. The waste receptacles should be emptied at the end of each operating period.

The manifold may incorporate an ultra-violet radiation unit. The lamp should be switched on for “total” cyanide determinations but remains switched off for the determination of “easily liberated” cyanide.

A reflux distillation apparatus is required for the analysis of thiocyanate-containing samples.

E7 Analytical procedure

Step	Procedure	Notes
	“Easily liberated” cyanide and “total” cyanide in the absence of thiocyanate	
E7.1	Following the manufacturer's general operating instructions, set up the instrument ensuring all reagents are correctly connected in series, see note a.	(a) Ensure that there is available sufficient of each reagent to avoid having to replenish any reagent during one batch of analyses.
E7.2	With the sample probe at rest in the wash receptacle solution, start the pump and switch on detection and measurement units (note b). Switch on the UV radiation unit only if total cyanide determinations are required.	(b) Allow the system to equilibrate (20 minutes should be sufficient) and during this period check that the bubble pattern and hydraulic behaviour of the system is satisfactory. If not, eliminate difficulties before proceeding to step E7.3.
E7.3	Set the colourimeter control to suit the concentration range of the samples if the instrument has the facility to attenuate the absorbance range.	
E7 .4	When an acceptably smooth baseline trace is given at the measurement unit, adjust the baseline response to about 5 per cent of full scale (note c) with the zero control, and then transfer the sample probe into the highest concentration of standard solution (note d).	(c) An elevated setting of the baseline allows for any negative drift that may occur. (d) This is the largest concentration that the calibration is intended to cover.
E7.5	When there is a positive stable response at the measurement unit due to the colour produced from the standard solution (note e) adjust this response to read between 90 and 95 % of full scale (notes f and g).	(e) The sample probe need remain only in the standard solution for sufficient time to give a steady reading. (f) A setting of 5 to 10 % below full scale allows for any increase in sensitivity that may occur.

(g) This may be directly possible on some measurement units but others may require range expansion facilities.

E7.6 Return the sample probe to rest in the wash position (note h).

(h) First remove any traces of standard solution from the outside of the sample probe.

Analysis of solutions

E7.7 Load the turn-table with suitable calibration, blank and sample solutions, for example in the following order (notes i and j).

(i) The turn-table can be loaded during the initial stabilisation period (steps D7.2 to D7.4).

(j) Other loading patterns may be used.

Position number on turn-table	Solution
1-5	Calibration standard solutions in ascending order, see section E8.
6-9	Blank solutions (note k).
10-17	Samples.
8	Check calibration (note l).
19-22	Blank solutions (note k).
23-30	Samples.
31	Check calibration (note l).
32-35	Blank solutions (note k).
36-40	Calibration standards solutions in ascending order.

(k) Water.

(l) A different standard to those which occupy position numbers 1-5 should be used to check the calibration.

Repeat the sequence 6 - 40 until all the samples have been processed (note m).

(m) When cross contamination occurs between 2 samples (visible on the measurement unit trace as incomplete separation of consecutive sample responses) both samples should be re-analysed, separated by a blank solution.

E7.8 When a steady baseline is obtained on the measurement unit, re-adjust it to about 5% of full scale if necessary and start the sample unit.

E7.9 When all the system responses due to the processed solutions have appeared on the measurement unit and a final baseline has been obtained, the unit can be switched off.

Calculation of results

E7.10 Plot a calibration curve of measurement unit responses (y-axis) against concentration (x-axis) of standard solutions (note n).

(n) Ensure the blank corrected responses of the calibration standard analysed at the end of each group and those at the end of the turntable are all acceptably close to their respective initial blank corrected calibration standard response.

E7.11 Using the calibration curve convert the measurement unit response due to the samples into concentration in the samples (note o).

(o) The measurement unit response of the samples should be corrected for any baseline and sensitivity changes. The results are expressed as mg cyanide per litre.

Shut-down procedure

E7.12 Immerse the reagent lines in water and continue pumping for a further 20 minutes. Turn off the pump and release the pressure in the pump tubes. Carry out any necessary maintenance in preparation for the next run.

Total cyanide in the presence of thiocyanate

E7.13 Measure 200 ± 2 ml of sample into a 500 ml round-bottomed distillation flask, add one glass bead and 3 ± 1 drops of pH 4.5 indicator solution (E5.13).

E7.14 Assemble the distillation unit.

E7.15 Measure 20 ± 1 ml, of 1.25 M sodium hydroxide solution (E5.5) into a 150 ml beaker and place the beaker under the delivery adaptor, with the tip of the adaptor just below the meniscus of the solution.

E7.16 Through a dropping funnel, add 10.0 ± 0.5 ml of acetate buffer solution (E5.11) and 10.0 ± 0.5 ml of saturated EDTA solution (E5.10) to the sample in the distillation flask.

E7.17 Add 1M hydrochloric acid solution (E5.12) dropwise to the distillation flask through the dropping funnel until the colour change

(p) The colour change will depend on the nature of the commercial indicator used.

characteristic of the indicator just occurs (note p).

E7.18 Heat the distillation flask and distil until about 100 ml of distillate collects in the receiving beaker (note q).

(q) This usually takes about 30 minutes from the beginning of distillation.

E7.19 Quantitatively transfer the distillate to a 200 ml volumetric flask and make to volume with water.

E7.20 Determine cyanide in the distillate by the procedure described in steps E7.1 to E7.12. The UV radiation unit is not switched on for this determination.

E8 Preparation of calibration curve

As indicated in step E7.6, at least five calibration standards should be run at the beginning of and at intervals in each batch of samples. The concentrations of the standards should be selected having regard for the expected sample cyanide concentration and of the manifold configuration in use.

For the calibration, add to a series of 50 ml calibrated flasks, 0.5, 1,0, 1.5, 2.0 and 2.5 ml of stock standard cyanide solution (E5.14). Add to each flask 25.0 ± 0.5 ml of 0.1M sodium hydroxide solution (E5.15) and make to volume with water. These flasks now contain 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l of cyanide respectively. These solutions should be prepared freshly for each batch of determinations.

Calibration is carried out as described in step E7.10.

Table E1 Performance data

Sample Type	Concentration (mg/l)	Standard deviation (mg/l)	Degrees of freedom
Cyanide solution	1.00	0.012	9
Cyanide solution	2.50	0.006	9
Cyanide solution	5.00	0.007	9

Table E2 Recovery of cyanide from complexes

Solution	Cyanide concentration (mg/l)	Cyanide recovery (%)
Potassium ferricyanide	0.10	99
Potassium ferrocyanide	0.10	97
Sodium nitroprusside	0.10	91

Data from Yorkshire Water Authority, Sheffield Laboratory.

Table E3 Recovery of cyanide using the reflux distillation procedure

Solution	Cyanide concentration (mg/l)	Cyanide recovery (%)
Cyanide standard	0.1	98
Cyanide standard	0.2	103
Thiocyanate (10 mg/l)	-	1
Ferricyanide	0.1	95
Ferrocyanide	0.1	96
Cyanide standard + 20 mg/l CNS	0.2	106
Ferrocyanide + 20 mg/l CNS	0.2	119

Data from Yorkshire Water Authority, Sheffield Laboratory.

F Guidance on the determination of total cyanide in the presence of strongly interfering metals and similar substances

F1 Introduction

Cyanide co-ordinates to many metals. Some of these co-ordinate bonds are so strong that they do not break during normal analytical procedures, even those for complex cyanides. Hence, cyanide in such compounds may not be included in the analysis; but, unless there is a risk of eventual decomposition with liberation of hydrogen cyanide, or the complex cyanide is toxic, knowledge of the amount of such ultra-stable complexed cyanides may be unimportant or misleading. An example of such a complexed cyanide is cyanocobalamine-vitamin B12, which is not only essential for human and animal health, but is produced in some sewage treatment processes and in some rivers.

F2 Metals forming stable complex cyanides

Stable cyanides are shown in Table F1.

Table Fl Metals forming stable complex cyanides

Mn (2)6	Fe (2)6	Co (2)6	Ni (0)4	Cu (1)4	
Mn (3)6	Fe (3)6	Co (3)6	Ni (1)4	Cu (2)4	
Mo (3)8		Ru (2)6			
Mo (4)8	Tc (4)6	Ru (3)6	Rh (3)6	Pd (2)4	Ag (1)3
Mo (5)8					
W (4)8	Re (1)6			Pt (2)6	
W (5)8	Re (5)8	Os (4)6	Ir (3)6	Pt (4)6	Au (3)4
	Re (6)8				

The metals underlined form some of the strongest cyanide complexes. The number in brackets is the valance state of the metals forming complex cyanides. The number to the right of the brackets is the maximum number of cyanide groups which can be co-ordinated in that valence state. Groups (ligands) other than cyanide may also be co-ordinated to the metal.

Hence the following complexes may be formed.

$[Mn(CN)_6]^{4-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{4-}$	$[Ni(CN)_4]^{4-}$	$[Cu(CN)_4]^{3-}$	
$[Mn(CN)_6]^{3-}$	$[Fe(CN)_6]^{3-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{3-}$	$[Cu(CN)_4]^{2-}$	
$[Mo(CN)_8]^{5-}$		$[Ru(CN)_6]^{4-}$			
$[Mo(CN)_8]^{4-}$	$[Tc(CN)_6]^{2-}$	$[Ru(CN)_6]^{3-}$	$[Rh(CN)_6]^{3-}$	$[Pd(CN)_4]^{2-}$	$[Ag(CN)_3]^{2-}$
$[Mo(CN)_8]^{3-}$					
$[W(CN)_8]^{4-}$	$[Re(CN)_6]^{5-}$			$[Pt(CN)_6]^{4-}$	
$[W(CN)_8]^{3-}$	$[Re(CN)_8]^{3-}$	$[Os(CN)_6]^{2-}$	$[Ir(CN)_6]^{3-}$	$[Pd(CN)_6]^{2-}$	$[Au(CN)_4]^{-}$
	$[Re(CN)_8]^{2-}$				

Some of these complexes will break down, at least partially, when using the most severe procedures in the preceding methods. However, much depends on other co-ordinating ligands (i.e. whether other non-cyanide ligands are present, and if so, their nature) and the metal valence.

F3 Preliminary procedure if highly stable cyanides are suspected

Firstly, determine whether the sample contains any of the above metals in any substantial amount. A portion of the digest solution from the methods above may be used. As cyanides can interfere strongly with most chemical methods of analysis, spectroscopic methods may need to be used. Suitable methods are:

X-ray fluorescence
DC arc emission spectroscopy
ICP spectrophotometry

If none of the metals listed in Table F1 are present in the sample to be investigated, it is very unlikely that any stable cyanide complex will be present, and the easily liberated cyanide value represents all the cyanide present, i.e “total” cyanide.

F4 Procedures for determining cyanide if these metals are present

Two techniques are available if the metals shown in Table F1 are present:

Infra-red absorptiometry
Liquid chromatography

Both are highly species and sample dependent, giving separate signals for each individual complex present in the sample, which need measuring individually and summing to determine the total cyanide. General outlines of the procedures follow, with references to the literature for further information. Analysts with need for such analyses are advised to evaluate these procedures prior to use.

F4.1 Infra-red absorptiometry

The cyanide bond absorbs in the infra-red region at 2040-2170 cm^{-1} and even up to 2210 cm^{-1}, the actual absorption maximum being determined by the metal to which the cyano group is complexed. Other substances also absorb in this region.

Evaluation tests have shown that unless the cyanide concentration is relatively high (about 1000 mg/l) direct measurement on water samples using special cells is insensitive and evaporation to dryness followed by the potassium bromide disc technique is necessary. Such evaporation should be carried out using samples already depleted of their easily liberated cyanide which might otherwise be lost during the evaporation stage. If the total dissolved salts content is high, further concentration may be necessary

In order to identify and quantify the cyanide peak, prepare a solution containing the various metals found to be present, in approximately the same concentration found in the sample. Use this metal solution to prepare a series of cyanide standards of increasing strength from zero complexation, up to complete complexation, of all the complexing metals present. The number in brackets in Table F1 indicate the common valence states of the metals when forming cyano complexes; the number to the right of the brackets in Table F1 is the maximum number of cyano groups that can be co-ordinated per atom of metal.

Treat these standards in exactly the same way as samples, and compare to identify and quantify the sample peaks.

F4.2 Liquid chromatography

Normal ion chromatography (with anion exchange resins) and reversed-phase HPLC have been used to analyse a variety of aqueous eluents. Detectors, involving ultra-violet absorption, pulsed amperometry, conductivity and flame atomic absorption have all been used to locate and quantify various cyano complexes as they elute. Ultra-violet absorption detectors are liable to interference from other ions. Conductivity and pulsed amperometric detectors merely indicate a complex has eluted, which should then be identified and confirmed by comparison with single complex metal standards. Use a mixture of the cyano complexes of the metals identified in the preliminary examination as controls. Also use varying amounts of cyanide as, when there are several complexes for one metal valence state, the complex formed is often dependent on the amount of cyanide present.

F5 Stable organic cyanides

Stable organic cyanides hydrolyse to organic acid and ammonia when refluxed with alkalis or acids, and may not cause problems. Organic isocyanides may be recognisable by their smell, and are reduced to amines.

F6 Calculation of total cyanide

As some complex cyanides in solution are in reversible equilibrium with free cyanide ion, there is a possibility of errors occurring in the results, if, from these methods in Part F, the results are simply added to the cyanide concentration obtained by the earlier methods. If the methods are used in conjunction, the procedures in Part F should only be used on samples from which the easily liberated cyanide has been removed by an appropriate method. The procedures in Part F can be used to determine simple cyanide, if in the appropriate concentration range.

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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