Cyanide in Waters etc 1988

Methods for the Examination of Waters and Associated Materials

Her Majesty's Stationery Office

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Methods for the Examination of Waters and Associated Materials

This booklet contains three methods for the determination of Cyanide in water. It starts with a general introduction which explains the forms of cyanide determinable by the various methods. Other general information is also given including a titrimetric procedure for standardizing single solutions of cyanide ion. Two further sections (E and F) give information on coping with stable complex cyanides and compounds and on analysing sludges and soils.

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Contents

About this Series		4
Warning to Users		5
A	**General Information**	6
A1	Introduction to the methods	6
A1.1	Cyanogen Chloride	6
A1.2	Hazards	6
A2	Sample collection and preservation	7
A3	Standard Solutions of Cyanide	7
A4	Checking the stock standard cyanide solution	7
A4.1	Principle	7
A4.2	Reagents	7
A4.3	Apparatus	8
A4.4	Procedure	8
A4.5	Calculation	8
B.	**Determination of Total Cyanide by Reflux Distillation with either Potentiometry using a Cyanide Selective Electrode or Colorimetry**	9
B1	Performance Characteristics of the Method	9
B2	Principle	11
B3	Interferences	11
B4	Hazards	12
B5	Reagents	12
B6	Apparatus	14
B7	Procedure	15
B7.1- 8	Reflux Distillation Procedure	15
B7.9 20	Electrode Procedure	15
B7.21- 29	Colorimetric Procedure	17
C.	**Continuous Flow Determination of Cyanide (Tentative Method)**	19
C1	Performance Characteristics of the Method	19
C2	Principle	20
C3	Interferences	20
C4	Hazards	20
C5	Reagents	21
C6	Apparatus	22
C7	Procedure	23
C7.1- 12	Simple Cyanide and Total Cyanide in the Absence of Thiocyanate	23
C7.13- 20	Total Cyanide in the Presence of Thiocyanate (Initial Pretreatment prior to steps C7.1- 12).	24
C8	Preparation of Calibration Curve	25
D.	**Determination of Cyanide by Microdiffusion (Tentative Method)**	26
D1	Performance Characteristics of the Method	26
D2	Principle	27
D3	Interferences	27
D4	Hazards	28
D5	Reagents	28
D6	Apparatus	29
D7	Procedure	29
D8	Sources of Error	30
Figures 1–4		32
E.	**Advice on the Determination of Total Cyanide in the Presence of Strongly Interfering Metals and Similar Substances**	36
E1	Introduction	36
E2	Metals forming Stable Complex Cyanides	36
E3	Preliminary Procedure if Highly Stable Cyanides are Suspected	36
E4	Procedures for Determining Cyanide if these Metals are Present	37
E5	Stable Organic Cyanides	37
E6	Calculation of Total Cyanide	38
F.	**Notes on the Determination of Cyanide in Sludges and Soils**	39
F1	Introduction	39
F2	Substances Determined	39
F3	Reagents	39
F4	Apparatus	39
F5	Procedure	39
F6	Concentration Range of the Method	40
G.	**Checking the Accuracy of Analytical Results**	41
G1	Routine Analytical Quality Control	41
G2	Estimation of the Analytical Accuracy of these Methods	41
References		44
Address for Correspondence		46
Membership responsible for these methods		47

About This Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirements for that particular method, tentative methods and notes being issued when necessary.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users- the senior technical staff--to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has 9 Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage Works Control Methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee.

The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text to discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R Pittwell
Secretary and Chairman

11 August 1988

Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field Operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

Lone working, whether in the laboratory or field, should be discouraged.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', issued by the Royal Society of Chemistry, London: 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5. The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Aequired Infection', Public Health Laboratory Service Monograph 6, HMSO, London.

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

A General Information

A1 Introduction to the Methods

Three full methods are given in this booklet for the determination of cyanide—in various forms—in water. Method B is a reflux distillation method for the recovery of 'total' cyanide—meaning free cyanide and cyanide in most of its complexed forms, although strongly complexed cyanides (notably the cobalt complex) are incompletely recovered by this or similar methods. Final determination of liberated hydrogen cyanide, after absorption in alkaline solution, can be by either colorimetry or ion selective electrode potentiometry.

Method C provides an air segmented continuous flow automated procedure for the determination of simple cyanides by passage of hydrogen cyanide from acidified solution through a gas permeable membrane into the reagent stream. With the addition of UV irradiation, total cyanide (subject to restrictions similar to those of Method B) can be determined. Preliminary reflux distillation is prescribed for samples containing thiocyanate which would otherwise interfere.

Method D determines easily liberatable cyanide ion by microdiffusion from a sample portion adjusted to pH 6. This method is similar to an International Standard (6) and is suitable for the determination of low levels of cyanide in relatively weakly complexed forms which can be dissociated at the standard pH value of 6.

Part E gives advice on the determination of very strongly complexed forms of cyanide, by means of liquid chromatography or infra-red aborptiometry. However, such stable complexes are infrequently of interest and so no full method is given.

Part F gives procedures for the determination of cyanide in soils and sludges. These presently have no performance data available for them and are given for advice only.

A1.1 Cyanogen Chloride

No method is given in this booklet for the determination of cyanogen chloride. This compound is formed when cyanide compounds are chlorinated—a process often used for the destruction of cyanide-containing wastes. Cyanogen chloride is a gas, slightly soluble in water but highly toxic even at low concentrations. If a method for its determination is required, refer to the British Standard (16), which is similar to the final part of the colorimetric sections of methods C and D.

A1.2 Hazards

A1.2.1 Cyanides

With only a very few exceptions cyanides are rapidly acting poisons both by mouth and inhalation, which can also be absorbed through the skin. Under no circumstances should they be pipetted by mouth, fumes should not be inhaled and any skin contact should be washed off immediately. First aid should be started immediately if poisoning is suspected, while medical help is being summoned. In severe cases, two amyl nitrite capsules may be administered by inhalation. Consideration should be given to having available on site persons qualified to administer an antidote by intravenous injection. See reference 22.

A1.2.2 Barbituric Acid and its salts

While Barbituric acid (pyrimidine trione or malonylurea) itself is not at present covered by the 'Misuse of Drugs Acts' and related Statutory Instruments, users are advised to keep abreast of these regulations as they are changed periodically. Bonafide laboratory use of regulated substances is permitted provided precautions to stop misuse are taken.

A2 Sample Collection and Preservation

These instructions are common to all three methods.

A2.1 **All samples must be made 0.05 ± 0.02 M in sodium hydroxide as soon as possible after sampling.** For the majority of samples, this may most readily be achieved by collecting them in polyethylene bottles already containing the necessary amount of sodium hydroxide, either as a solid or as a concentrated solution. For a 100 ml sample bottle, this will require about 0.2 g of solid sodium hydroxide for most waters.

A2.2 **The sodium hydroxide used for this purpose must be shown not to contribute cyanide to the samples.** The methods of analysis all involve sodium hydroxide as reagent and wherever possible the same batch of analytical reagent-grade material should be used both for preservation and for reagents.

A2.3 Samples already strongly alkaline need not be so preserved. However, the analyst should ensure that any extremes of alkalinity in samples do not cause deviations from the desired pH value during analysis.

A2.4 **The preserved samples must be stored in the dark in order to avoid light-induced decomposition of cyanides.** The sample should be analysed as quickly as possible after collection, certainly within 5 days.

A3 Standard Solutions of Cyanide

All standard solutions of cyanide shall be prepared in dilute sodium hydroxide solution.

A3.1 0.1 M Sodium hydroxide solution

Dissolve 4.0 ± 0.2 g of sodium hydroxide in about 800 ml of water and make up to 1 litre with water in a measuring cylinder. Store in a polyethylene bottle. This solution is stable indefinitely.

A3.2 Stock standard cyanide solution 100 mg CN/L.

Dissolve 0.250 ± 0.005 g of potassium cyanide in 500 ± 5 ml of 0.1 M sodium hydroxide solution (reagent A3.1). Make up to 1 litre with water in a calibrated flask. Store the solution in a stoppered glass bottle labelled TOXIC. This solution is stable for at least one week. However, its concentration may be checked by titration with standard silver nitrate solution (Section A4).

A3.3 Working standard cyanide solution, 1 mg CN/L.

Add 1.00 ± 0.01 ml of the stock standard cyanide solution (A3.2) to a 100 ml calibrated flask and add 50 ± 0.5 ml of 0.1 M sodium hydroxide solution (A3.1). Make up to volume with water. Prepare this solution freshly for each batch of determinations.

A4 Checking the stock standard cyanide solution

A4.1 Principle

Titration with silver nitrate solution to an excess of silver ions which is indicated by the formation of a red complex with 5- (4-dimethylamino benzylidene) rhodanine.

A4.2 Reagents

A4.2.1 Indicator solution.

Dissolve 0.020 ± 0.002 g of 5- (4-dimethylamino benzylidene) rhodanine in about 80 ml of acetone and make up to 100 ± 2 ml with acetone. Store the solution in an amber bottle. It is stable for about one week.

A4.2.2 Silver nitrate solution, 0.01 M.

Dissolve 1.699 ± 0.001 g of silver nitrate (dried at 105°C) in water and dilute to 1 litre with water in a calibrated flask. If stored in the dark, this solution is stable indefinitely.

A4.3 Apparatus

A4.3.1 Magnetic stirrer, with bar.

A4.3.2 Burette, grade A, 10 mL capacity.

A4.3.3 Conical flask, 50 mL capacity.

A4.4 Procedure

A4.4.1 Pipette 25 mL of the stock standard cyanide solution (A3.2) into a 50 mL conical flask (A4.3.3).

A4.4.2 Add 0.10 ± 0.02 ml of the indicator solution (A4.2.1).

A4.4.3 Fill the burette (A4.3.2) with the silver nitrate solution.

A4.4.4 Put a stirring bar into the conical flask and place it on the stirrer. Insert the tip of the burette beneath the liquid level in the flask and turn on the stirrer.

A4.4.5 Titrate until the colour changes from yellow to red. The colour is stable for only a short time. Record the volume, V, of silver nitrate solution used.

A4.5 Calculation

The concentration in mg CN/L of the stock standard solution is given by:

$$\frac{V \times 260.17}{25} \quad \text{mg CN/L}$$

where V is the volume of 0.01 M silver nitrate solution required for the titration of 25 mL of the stock standard cyanide solution.

B. Determination of Total Cyanide by Reflux Distillation followed by either Potentiometry using a Cyanide Selective Electrode or Colorimetry

B1 Performance Characteristics of the Method

B1.1	Substance Determined	Simple and Complex Cyanides.
B1.2	Type of Sample	Raw and Portable Waters, Wastewaters and Sludges.
B1.3	Basis of Method	Cyanide and complex cyanide, are converted by acidification to hydrogen cyanide, which is liberated from the sample solution by distillation and purging with nitrogen. The hydrogen cyanide is collected by passing it through an alkaline 'trap'. Cyanide ion concentration is determinted in the alkaline 'trap' either potentiometrically using a cyanide-selective electrode or colorimetrically.
B1.4	Range of Application[a][b]	1. Electrode Method: 0.05 to 10 mg CN/L for aqueous samples, (range may be extended by dilution). 2. Colorimetric Method: 0.01 to 1 mg CN/L for aqueous samples which may be extended by dilution.
B1.5	Calibration Curve[a][b]	1. Electrode Method: a standard addition technique is used to determine the concentration of cyanide ion in the trap; the electrode producing a log-linear response typically within the range 0.05 to 20 mg CN/L. 2. Colorimetric Method: a linear calibration curve is prepared using a series of standards containing from 0.1 to 10 μg CN.

B1.6 Within-batch Standard Deviation

1. Electrode Method: (a)

Sample Type	Concentration (mg CN/L)	Standard Deviation (mg CN/L)	Degrees of Freedom
Standard solution[1]	0.1	0.0045	4
Standard solution[2]	5.0	0.067	5
Effluent[3]	7.75	0.007	4
Sludge[4]	555*	11.2*	5

(1) = potassium cyanide
(2) = potassium ferrocyanide ($K_4Fe(CN)_63H_2O$)
(3), (4) = mixed metal effluent and sludge from metal finishing industry
* = results expressed as mg/kg on a dry weight basis.

2. Colorimetric Method (b):
(Information on degrees of freedom is lacking)

Sample Type	Concentration (mg CN/L)	Standard Deviation (mg CN/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

B1.7 Limit of Detection[a][b]

1. Electrode Method: based on limit of Nernstian response and practical aspects of the addition technique the limit of detection is 0.05 mg CN/L in the trap solution, corresponding to 0.01 mg CN/L in the sample when using a 500 ml sample volume and a 100 ml final volume for the trap solution.

2. Colorimetric Method: detection limit, based on 100 mL of sample is 0.01 mg CN/L. Lower limits can be achieved using larger sample aliquots.

B1.8 Sensitivity[a]

1. Electrode Method: 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). In practice the change in e.m.f. 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.

2. Colorimetric Method: a standard solution containing 1 μg CN in 25 mL of solution gives an absorbance change of approximately 0.125 absorbance units using 1 cm path-length cell.

B1.9	Bias[a]	Typically better than ± 5% for simple cyanides and most metallocyanide complexes; large negative bias for cobalticyanide complexes, see Table B1.
B1.10	Interferences [a],[b]	The effects of the principal potentially interfering substances, eg sulphide, thiocyanate and thiosulphate are minimized and, in many cases, eliminated in this method, see Tables B2 and B3.
B1.11	Time required for Analysis	A batch of six samples takes approximately 3½ hours operator time and 5 hours total time.

(a) Data obtained by Bostock Hill and Rigby Limited: Consulting Scientists and Analysts, Birmingham.

(b) Data obtained by Wastewater Technology Centre, Environmental Protection Service, Burlington, Ontario, L7R 4A6, Canada.

Table B1 Recovery of Cyanide from Standard Solutions: Electrode Method[a]

Solution	Cyanide concentration mg CN/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 $K_4Fe(CN)_63H_2O$)	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 x 2 (ie 90 minutes). Further increase of reflux time gives no significant further improvement in recovery.

B2 Principle

Simple and most complex cyanides are decomposed by reflux distillation, with a mixture of hydrochloric acid and hydroxylamine, and purging with nitrogen to liberate hydrogen cyanide[1,2]. The hydrogen cyanide liberated is trapped in an absorbing solution of sodium hydroxide and cadmium chloride.

After filtration, cyanide ion is determined in the absorbing solution either using a cyanide selective electrode together with a standard addition procedure[3,4] or by a colorimetric procedure[1].

B3 Interferences

The effects of some potentially interfering substances have been tested as shown in Tables 2 and 3. Additionally, the presence of urea at 10 mg N/L in blank solution has been shown not to produce any significant effect on the blank measurement.

Table B2 Interference Effects: Electrode Method[a]

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

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

Table B3 Interference Effects: Colorimetric Method[b]

Interfering Substances		Cyanide Added (mg CN/L)	Cyanide Measured (mg CN/L)*
Thiocyanate (mg CNS/L)	Iron (mg Fe/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

* Information on maximum effect to be expected assuming no interference is lacking.

B4 Hazards

B4.1 Cyanide presents a serious risk of poisoning if swallowed or by skin contact. Hydrogen cyanide is a highly toxic gas. See also A1.2.

B4.2 Sodium hydroxide in pellet form is extremely corrosive.

B4.3 Cadmium chloride is toxic by inhalation, in contact with skin and if swallowed.

B4.5 Concentrated hydrochloric acid is extremely corrosive.

B4.6 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.

B4.7 Barbituric acid is an irritant. Skin contact with the solid and reagents incorporating it must be avoided. See also A1.2.

B5 Reagents

All reagents should be of analytical grade and distilled or deionized water should be used throughout. Reagents are stable for at least two months except where otherwise stated.

B5.1 Reflux-distillation reagents

B5.1.1 Sodium hydroxide solution 1M

Dissolve 40.0 ± 0.1 g of sodium hydroxide in water, cool and transfer to a 1 litre calibrated flask and make up to the mark with water. Store the solution in a polyethylene container. This solution is stable indefinitely if properly stored.

B5.1.2 Hydrochloric acid–hydroxylamine hydrochloride mixed reagent

Dissolve 100.0 ± 0.1 g of hydroxylamine hydrochloride in approximately 400 mL of water first before adding the acid. Transfer this solution to a 1 litre calibrated flask. To the solution add slowly and carefully 500 ± 5 mL of hydrochloric acid (d_{20} 1.18), mix, allow to cool and dilute with water to the mark. Store in a polyethylene bottle. This solution is stable for at least one week.

B5.1.3 Cadmium chloride (powdered)

B5.1.4 Hydrochloric acid (25% v/v)

Dilute 250 ± 5 mL of hydrochloric acid (d_{20} 1.18) to 1000 ±10 mL with water. This solution is stable indefinitely.

B5.2 Colorimetric method reagents

B5.2.1 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.

B5.2.2 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. Do NOT dry them at 110°C as this makes subsequent redissolution difficult.

B5.2.3 Isonicotinate–barbiturate mixed reagent

Dissolve 1.00 ± 0.05 g of sodium isonicotinate (B5.2.1) and 1.00 ± 0.05 g of sodium barbiturate (B5.2.2) in 80 ± 10 mL of water at 65 ± 5°C with stirring. Allow the solution to cool and then filter through a No. 42 or equivalent filter paper into a 100 mL calibrated flask. Make up to volume with water. The solution should be clear, pale yellow and have a pH value of 6.5 ± 0.3. If not, repeat the preparation. The solution is stable for at least one week.

NOTE: This reagent can be prepared from commercially available sodium isonicotinate and sodium barbiturate, subject to the correct characteristics being attained.

B5.2.4 Acetic acid solution, (20% v/v)

Mix 1 volume of glacial acetic acid with 4 volumes of water. This solution is stable indefinitely.

B5.2.5 p-nitrophenol indicator (0.1% w/v in ethanol). This solution is stable for at least one month.

B5.2.6 Chloramine-T solution

Dissolve 1.0 ± 0.01 g chloramine-T, (sodium p-toluene-sulphonchloramide), in 100 mL of water. Prepare weekly and store in a refrigerator.

B5.3 Electrode method standard solutions (see B7.10)

B5.3.1 Working standard cyanide solution, 10 mg CN/L

Add 10.0 ± 0.1 mL of the stock standard cyanide solution (A3.2) to a 100 mL calibrated flask and add 45 ± 0.5 ml of 0.1 M sodium hydroxide solution (A3.1). Make up to volume with water. Prepare this solution freshly for each batch of determinations.

B5.3.2 Working standard cyanide solution, 1 mg CN/L

Proceed as in Section A3.3.

B5.3.3 Working standard cyanide solution, 0.1 mg CN/L

Add 10.0 ± 0.1 mL of the working standard cyanide solution, 1 mg CN/L (B5.3.2, A3.3) to a 100 mL calibrated flask and add 45 ± 0.5 mL of 0.1M sodium hydroxide solution (A3.1). Make up to volume with water. Prepare this solution freshly for each batch of determinations.

B5.3.4 Standard cyanide solution, 1000 mg CN/L
(For standard addition in the electrate procedure, step B7.18)

Dissolve 0.250 ± 0.005 g of potassium cyanide in 50 ± 1 mL of 0.1 M sodium hydroxide solution (A3.1). Make up to 100 mL with water in a calibrated flask. Store the solution in a clearly labelled stoppered glass bottle also labelled TOXIC. This solution is stable for at least one week. Its concentration may be checked by titration with standard silver nitrate solution (Section A4) after making a ten-fold dilution of the standard to bring it into the checking method's working range.

B5.3.5 Standard cyanide solution, 100 mg CN/L
(For standard addition in the electrode procedure, step B7.18)

Proceed as in Section A3.2. However, it may be convenient to prepare only 100 mL of this solution for standard addition purposes.

B6 Apparatus

B6.1 Reflux Distillation

B6.1.1 A reflux distillation apparatus is required, as shown in Fig 1, incorporating:

- 1000 mL distillation flask with 2-neck parallel adaptor
- a double surface (Davies) condenser (200 mm effective length)
- an absorption trap consisting of a trap head with a fine/medium porosity sintered outlet and a test tube (29 x 200 mm)
- an adjustable heating element
- a needle valve for adjustment of the nitrogen purge
- a 500 mL suction flask
- glass and transparent PVC tubing (nominally 8 mm ID)

B6.1.2 A nitrogen gas cylinder or supply with a regulator is required capable of providing a flow rate of up to 15 L/min at a pressure of up to 1.5 kg/cm^2.

B6.1.3 Two Dreschel gas washing bottles (nominal capacity 500 mL) and bottle heads with medium porosity sintered outlets are required for pre- and post-scrubbing of the nitrogen purge. Fill the bottles to about three-quarters capacity with soda lime granules (4- 10 mesh).

B6.1.4 Whatman 40 filter papers, or equivalent, washed in 25% v/v hydrochloric acid solution and rinsed with two portions of water, are required for filtration of the absorption tube contents.

B6.2 Electrode Method

B6.2.1 A millivolt meter incorporating an expanded scale or digital meter with impedance of not less than 10^{12} ohms capable of resolving potential changes to at least 0.1 mV is required.

B6.2.2 An ion-selective electrode is required. The e.m.f. response (on standard solutions) per decade change in cyanide concentration should not be less than 54 mV, or as recommended by electrode manufacturer, over the range of CN concentrations 0.05 to 20 mg/L.

B6.2.3 A double-junction sleeve type reference electrode is required. Use the manufacturer's recommended filling solution.

B6.3 Colorimetric Method

B6.3.1 A spectrophotometer capable of operating at 600 nm and equipped with 1 cm pathlength cells is required.

Step	Procedure	Notes
	Reflux distillation procedure	
B7.1	Add to a 1000 mL distillation flask (note a) a sample aliquot expected to contain no more than 1 mg of cyanide or, if the colorimetric method is to be used, no more than 0.1 mg. The aliquot volume must not exceed 500 mL. Add water to smaller aliquots to bring the total volume to about 500 mL. Use a grade A measuring cylinder for the sample aliquot.	(a) The entire distillation system must be rinsed thoroughly between samples using 25% v/v hydrochloric acid.
B7.2	Add 50.0 ± 0.5 mL of sodium hydroxide (1 M) and 0.25 ± 0.05 g of cadmium chloride to the absorption tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber (ie above the level of the frit).	
B7.3	Connect the distillation flask, condenser, absorber and trap. (Figure 1).	
B7.4	Start a slow stream of nitrogen 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 (B5.1.2) through the gas inlet tube. Rinse the tube with water and reconnect the pre-scrubber tube. Allow the gasflow 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. Turn off heat and continue the gasflow for at least 15 minutes. After cooling the boiling flask disconnect and close off the gas flow.	(b) Caution: the bubbling rate will not remain constant after the regents have been added and while heat is being applied to the flask. It will 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 calibrated flask and bring up to volume with distilled water washings from the absorption tube (Note c).	(c) Any sodium hydroxide solution trapped inside the sintered disc of the gas absorption tube must be transferred to the sodium hydroxide solution inside the bottle by washing with water.
B7.8	Filter the solution from step B7.7 through acid-washed Whatman 40 paper (B6.1.4)	
	Electrode Procedure	
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 (B5.3).	

Step	Procedure	Notes
B7.11	Transfer 50.0 ± 0.5 mL of the lowest (note d) concentration working standard (B5.3.3) into a clean 100 mL plastic beaker pre-rinsed with a small portion of standard being tested.	(d) Always progress from the lowest to the highest concentration of standard because otherwise equilibrium is reached only slowly.
B7.12	Place a magnetic follower in the beaker and put on to the platform of the magnetic stirrer (Note e). Switch on the stirrer and adjust the stirring rate so the liquid is thoroughly mixed but no vortex or air bubbles are formed. Maintain the same stirring rate for both samples and standards.	(e) It is desirable that some form of thermal insulation is provided between sample beaker and magnetic stirrer.
B7.13	After a steady reading is reached (at least 5 minutes and not more than 10 minutes) record the potential (millivolt) reading.	
B7.14	Lift electrodes out of the solution and wash with water. Remove stirrer and follower. Repeat steps B7.11- B7.14 with the other two working standard solution (B5.3.2 and B5.3.1) in ascending order of concentration (see Notes f and g).	(f) Sample beakers should be washed thoroughly with water immediately after use. (g) When measuring low cyanide concentrations first rinse beakers and electrodes with a small volume of sample.
B7.15	Plot a graph on semi-log paper of emf in millivolts (linear scale) against cyanide concentration of the calibration standards (logarithmetic scale). Measure the slope of the line obtained millivolts/decade of concentration) (Note h).	(h) The slope may vary somewhat from the theoretical value of 59.16 mV/decade because of manufacturing variation and reference electrode liquid junction potentials.
B7.16	Carry out sample analysis by repeating the procedures described under B7.11- B7.13, using 50.00 ± 0.02 mL of the absorption solution obtained at step B7.8 in place of the calibration standards (Note i).	(i) Greater precision for the volume of the absorption solution is necessary because of the impending standard addition.
B7.17	When a steady reading is reached (at least 5 minutes and not more than 10 minutes) record the potential reading (A mV).	
B7.18	Choose one of the three standard solutions of potassium cyanide, 1000 mg CN/L (B5.3.4), 100 mg CN/L (B5.3.5) or 10 mg CN/L (B5.3.1) such that its mg CN/L concentration is between 100 and 1000 times the expected mg CN amount in the sample aliquot (B7.1)	
B7.19	Transfer 1.00 ± 0.01 mL of the chosen cyanide standard solution into the sample. Allow sufficient time for equilibration (at least 5 minutes and not more than 10 minutes) and record the new potential reading (B mV).	
B7.20	Calculate the cyanide concentration in the original sample from: $\frac{C_o \times D}{E}$ mg CN/L where $C_o = \frac{0.02}{1.02 \text{ antilog } (A-B)/S} C_s$ and	

C_o = Cyanide concentration in sample used for potentiometric measurement, mg/L.
D = Final volume of absorbing solution (B7.7), mL.
E = Volume of sample distilled (B7.1), mL.
A - B = Absolute value of potential change, mV.
C_s = Cyanide concentration of the standard solution added at step B7.19, mg/L.
S = Electrode slope, mV/decade, measured at step B7.15

Colorimetric Procedure

B7.21 Use the dilute and intermediate standard solutions of potassium cyanide (B5.3.2 and B5.3.3) to prepare a series of standards containing from 0.1 to 10 μg CN in 25 mL calibrated flasks. Add 10 mL of 1 M sodium hydroxide solution (B5.1.1) and adjust the volume in each flask to approximately 15 mL with water. Mix well.

B7.22 Add two drops of p-nitrophenol indicator (B5.2.5) and neutralize the solution to a colourless end point using the acetic acid solution (B5.2.4).

B7.23 Add 0.200 ± 0.002 mL of the chloramine T reagent (B5.2.6), mix and allow to stand for at least 2 minutes.

B7.24 Add 5.00 ± 0.05 ml of the sodium barbiturate-sodium isonicotinate mixed reagent (B5.2.3) and mix. Make up to volume with water and mix well. Leave to stand for at least 30 minutes at 20–25°C (Note j).

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

B7.25 Prepare a blank solution by carrying out steps B7.21 to B7.24 but omitting any addition of potassium cyanide solution in step B7.21.

B7.26 Measure the absorbance of the solution at 600 nm (Note k) in 1 cm pathlength cells using the blank solution (B7.25) as reference.

(k) The exact wavelength of maximum absorption should be determined and used.

B7.27 Plot a graph of the absorbance against amount of cyanide (μg CN).

B7.28 Carry out sample analysis by repeating the procedures described in steps B7.22–B7.25, adding 10.0 ± 0.1 mL of the filtered absorbing solution obtained at step B7.8 in place of the calibration standards. (Note l).

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

B7.29 Calculate the cyanide concentration in the original sample from:

$$\frac{A \times B}{C \times D} \text{ mg CN/L}$$

where:

Step	Procedure	Notes
	A = μg CN read from calibration curve (B7.28). B = final volume of absorbing solution (B7.7), mL. C = volume of original sample used in the distillation (B7.1), mL. D = volume of absorbing solution used in the colorimetric determination (B7.28), mL.	

C Continuous Flow Determination of Cyanide (Tentative Method)

C1 Performance Characteristics of the Method

C1.1	Substance determined:	Most cyanide ions
C1.2	Type of Sample:	Raw, potable and waste water
C1.3	Basis of Method:	Continuous flow colorimetry, using reactions described in Section C2. UV radiation is used to release cyanide ion from complex cyanides.
C1.4	Range of application:	Ca: Up to 5 mg CN/L Cb: Up to 0.16 mg CN/L
C1.5	Calibration curves:	Linear
C1.6	Within-batch Standard Deviation (a):	

Sample Type	Concentration Range		Standard Deviation	Degrees of Freedom
	mg CN/L		mg CN/L	
Standard Solution	0.05	Cb	0.0011	9
Standard Solution	0.10	Cb	0.0015	9
Standard Solution	0.15	Cb	0.002	9
Standard Solution	1.00	Ca	0.012	9
Standard Solution	2.50	Ca	0.006	9
Standard Solution	5.00	Ca	0.007	9

C1.7	Limit of Detection:	Range Ca 0.4 mg CN/L Range Cb 0.003 mg CN/L
C1.8	Bias (a)	Cyanide is incompletely recovered from certain complexes. Interferences may arise. See Section C3
C1.9	Interferences (a)	Principal interferences arise from sulphide and thiocyanate. See Section C3
C1.10	Time Required for Analysis (a):	The automated system described is capable of operating at up to 30 determinations per hour in range Ca and at up to 10 samples per hour in range Cb.

Note: (a) Data obtained by Yorkshire Water Authority, Sheffield Laboratory

C2 Principle

The sample is acidified with a mixture of phosphoric, hydrochloric and hypophosphorous acids (the last-mentioned acts as an oxygen scavenger and helps prevent oxidation of cyanide during UV irradiation). The hydrogen cyanide thus formed is separated from the reaction mixture by passage through a gas permeable silicone rubber membrane into dilute sodium hydroxide solution and then converted to cyanogen chloride by reaction with chloramine-T. The cyanogen chloride is reacted with pyridine and barbituric acid to form a reddish-violet coloured complex which is measured colorimetrically at 520 nm.

All these reactions are carried out automatically using continuous flow techniques. (5)

When total cyanide is required for determination, the acidified sample is irradiated with ultraviolet light to convert complex cyanides into simple hydrogen cyanide prior to dialysis. Table C1 shows the recovery of cyanide from certain complexes when using irradiation. The very stable nickel and cobalt complexes yielded low amounts of cyanide.

Thiocyanate, if present in the sample will be quantitively converted to cyanide by UV irradiation at the intensity which is required for satisfactory recovery of cyanide from iron complexes. Therefore, a prior reflux distillation of the thiocyanate-containing sample with EDTA is 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 C2 shows the recovery of cyanide from certain compounds by this reflux distillation procedure.

Table C1 Recovery of cyanide from complexes (a)

Solution	Cyanide concentration mg CN/L	Cyanide recovery %
Potassium ferricyanide	0.10	99
Potassium ferrocyanide	0.10	97
Sodium nitroprusside	0.10	91

a. Data from Yorkshire Water Authority, Sheffield Laboratory.

Table C2 Recovery of cyanide using the reflux distillation procedure (a)

Solution	Cyanide concentration mg CN/L	Cyanide recovery %
Cyanide Standard	0.1	98
Cyanide Standard	0.2	103
Thiocyanate (10 mg CNS/L)	—	1
Ferricyanide	0.1	95
Ferrocyanide	0.1	96
Cyanide Standard + Thiocyanate (20 mg CNS/L)	0.2	106
Ferrocyanide + Thiocyanate (20 mg CNS/L)	0.2	119

(a) Data from Yorkshire Water Authority, Sheffield Laboratory.

C3 Interferences

The principal interference arises from sulphide. A concentration of 1 mg/L sulphide depresses results by 13% and 20 mg/L causes 100% depression.

Thiocyanate interferes in the determination of total cyanide using UV irradiation, however the procedure given in steps C7.13 to C7.20 will remove this source of intereference.

C4 Hazards

C4.1 The precautions given in reference 2 should be observed.

C4.2 **Cyanide presents a serious risk of poisoning if swallowed or by skin contact. Hydrogen cyanide is a highly toxic gas. See also A1.2.**

C4.3 Pyridine is highly flammable and harmful by inhalation, in contact with skin and by ingestion.

C4.4 Barbituric acid is an irritant. Skin contact with the solid and reagents incorporating it must be avoided. See also A1.2.

C4.5 The UV radiation unit presents a potential hazard to the operator's eyes when lit. It may also produce ozone gas. See C6.3.

C5 Reagents

C5.1 Phosphoric acid/hydrochloric acid solution.

Carefully add 500 ± 5 ml of phosphoric acid (d_{20} 1.70) to 200 ± 20 ml of water, stirring all the time. Then add to the mixture 200 ± 20 ml hydrochloric acid (d_{20} 1.18). Mix well and dilute to 1 litre with water in a measuring cylinder. This solution is stable indefinitely.

C5.2 Hypophosphorous acid solution, 5% m/v.

Dilute 100 ± 1 ml of hypophosphorous acid (H_3PO_2, d_{20} 1.21) to 1 litre with water in a measuring cylinder. This solution is stable indefinitely.

C5.3 Mixed acid reagent 1.

Mix together 200 ± 2 ml of phosphoric/hydrochloric acid solution and 200 ± 2 ml of hypophosphorous acid solution. Add 0.5 ± 0.1 ml of Triton X-100 detergent (or equivalent wetting agent). This solution is stable indefinitely.

C5.4 Mixed acid reagent 2

Mix together 200 ± 2 ml of phosphoric/hydrochloric acid solution and 200 ± 2 ml of water. Add 0.5 ± 0.1 ml of Triton X-100 detergent (or equivalent wetting agent). This solution is stable indefinitely.

C5.5 1.25 M sodium hydroxide solution

Dissolve 50 ± 1 g of sodium hydroxide pellets in about 800 ml of water. Dilute to 1 litre with water in a calibrated flask. Store in a plastic bottle. This solution is stable for at least 4 weeks.

C5.6 0.01 M sodium hydroxide solution

Dilute 8.0 ± 0.1 ml of 1.25 M sodium hydroxide solution (C5.5) to 1 litre with water in a measuring cylinder. Add 0.5 ± 0.1 ml of Triton X-100 detergent solution. Store in a plastic bottle. This solution is stable for at least 4 weeks.

C5.7 Chloramine-T solution

Dissolve 0.4 ± 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. Dissolve and dilute to 1 litre with water in a calibrated flask. This solution is stable for up to one week.

The pH value of this solution must be 5.2 ± 0.1. Adjust to this value with sodium hydroxide solution (C5.5) or phosphoric acid as appropriate.

C5.8 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 (d_{20} 1.18). Then add 1.50 ± 0.01 g of barbituric acid and 50 ± 5 ml of water to dissolve. Warm the mixture gently if necessary to achieve dissolution. Then

dilute to 100 ml with water in a measuring cylinder. Store in an amber glass bottle labelled TOXIC for up to 3 days.

C5.9 Saturated disodium EDTA solution

C5.10 Sodium acetate buffer solution, pH value 4.5

Dissolve 243 ± 1 g of sodium acetate trihydrate and 465 ± 5 ml of acetic acid (d_{20} 1.05) in about 900 ml of water and dilute to 1 litre with water in a measuring cylinder. This solution is stable for at least 6 months. It is available commercially.

C5.11 1 M hydrochloric acid solution

Dilute 89 ± 1 ml of hydrochloric acid (d_{20} 1.18) to 1 litre with water in a measuring cylinder. This solution is stable indefinitely.

C5.12 Indicator solution for pH 4.5

Suitable solutions are available commercially.

C6 Apparatus

C6.1 Apparatus for this continuous flow method consists basically of the following:

Sample presentation unit (sampler).

Multichannel peristaltic pump.

Analytical cartridge (manifold) including pump tubes, mixing coils and gas permeable dialyser unit.

Colorimeter, incorporating a flow cell.

Recorder.

Consult the essay review (reference 5) on continuous flow analysis for further information.

C6.2 The design of the manifold depends on the concentration range of the method. Figure 2 shows the design for range Ca, with notes on the modifications required to provide for range Cb. Also shown is the need for a changed mixed acid reagent when determining total cyanide.

NOTE THAT ALL WASTE RECEPTACLES CONNECTED TO THE MANIFOLD MUST CONTAIN ABOUT 10 PELLETS OF SODIUM HYDROXIDE BEFORE STARTING THE ANALYSIS. This is a precaution against possible release of hydrogen cyanide from acidic waste solutions. The waste receptacles should be emptied at the end of each operating period.

C6.3 The manifold incorporates a UV radiation unit. This comprises a quartz glass 48 turn coil, with a coil diameter of about 30 mm and 200 mm in length, surrounding a 10- 5 W ultraviolet lamp. Such a unit may be available commercially, or else it may be assembled to order by specialist firms. Care must be taken in its design to avoid exposure of the operator's eyes to UV irradiation and to vent any ozone gas which may be produced by the lamp.

The UV lamp is switched on for total cyanide determination. It remains unlit for the determination of simple cyanide.

C6.4 The reflux distillation apparatus depicted in Figure 3 is required for the analysis of thiocyanate-containing samples.

Step	Procedure	Notes
	Simple Cyanide and Total Cyanide in the Absence of Thiocyanate	
	Starting Operation	
C7.1	Connect the system as shown in Figure 2 (notes a and b).	(a) Follow the manufacturer's general operating instructions. (b) See reference (5).
C7.2	With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents (note c) start the pump and switch on detection and measurement units (note d). Switch on the UV radiation unit only if total cyanide determinations are required.	(c) Ensure that there is sufficient of each reagent to avoid 'topping up' during one batch of analyses. (d) Allow the system to equilibrate for at least 20 minutes 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 C7.3.
C7.3	Set the colorimeter control to suit the concentration range of the samples if the instrument has the facility to attenuate the absorbance range (note e).	(e) See notes to Section C1 and the data in Section C1.6 for illustration of appropriate absorbance ranges.
	Initial Sensitivity Setting	
C7.4	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 f) with the zero control, and then transfer the sample probe into a C_m standard solution (note g).	(f) An elevated setting of the baseline allows for any negative drift that may occur. (g) C_m is the greatest concentration that the calibration is intended to cover.
C7.5	When there is a positive stable response at the measurement unit due to the colour produced from the standard solution (note h) adjust this response to read between 90 and 95% of full scale (notes i and j).	(h) The sample probe need remain only in the C_m standard solution for sufficient time to give a steady reading. (i) A setting 5 to 10% below full scale allows for any increase in sensitivity that may occur. (j) This may be directly possible on some measurement units but others may require range expansion facilities.
C7.6	Return the sample probe to rest in the wash position (note k).	(k) First remove any traces of standard solution from the outside of the sample probe.
	Analysis of Samples	
C7.7	Load the sample turntable in the following order (notes l and m).	(l) The turntable can be loaded during the initial stablization period (steps C7.2 to C7.4) (m) The order given is a suggestion. Other loading patterns may be used (5).

Position No on turntable	Solution	
1- 5	Calibration standards in ascending order, see Section C8.	
6- 9	Blank (note n).	(n) Water.

Step	Procedure	Notes

Position No on turntable	Solution
10 17	Samples.
18	Calibration standard (note p).
19 22	Blanks (note n).
23 30	Samples.
31	Calibration standard (note p).
32 35	Blanks (note n).
36 40	Calibration standards in ascending order.

(p) The standard which occupies position No 4 is used to check the calibration.

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

(q) 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.

C7.8 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.

C7.9 When all the system responses due to the processed solutions have appeared on the measurement unit and a final baseline has been obtained, this unit can be switched off.

Calculation of Results

C7.10 Plot a calibration curve of measurement unit responses (y axis) against concentration (x axis) of standard solutions (note r).

(r) Providing 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. If not, refer to reference (5)(Part I.) for a suggested procedure to obtain calibration curves.

C7.11 Using the calibration curve(s) convert the measurement unit responses due to the samples into concentrations in the samples (note s).

(s) The measurement unit responses of the samples must first be corrected for any baseline and sensitivity changes. The results are expressed as mg CN/L.

Shut-down Procedure

C7.12 Immerse the reagent lines in water and continue pumping for a further 20 mins. Then 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

C7.13 Measure 200 ± 2 mL of sample into a 500 mL round-bottomed flask, add one glass bead and 3 ± 1 drops of pH 4.5 indicator solution.

C7.14 Attach the flask to the apparatus assembled as shown in Figure 3.

Step	Procedure	Notes
C7.15	Measure 20 ± 1 mL of 1.25 M sodium hydroxide solution into a 150 mL beaker and place the beaker under the delivery adaptor, with the tip of the adaptor under the liquid surface.	
C7.16	Add 10.0 ± 0.5 mL of acetate buffer solution (C5.10) and 10.0 ± 0.5 mL of saturated EDTA solution to the sample in the distillation flask through the dropping funnel.	
C7.17	Add 1 M hydrochloric acid solution dropwise to the distillation flask through the dropping funnel until the colour change characteristic of the indicator has just occurred (note t).	(t) The colour change will depend on the nature of the commercial indicator used.
C7.18	Heat the distillation flask and distil until about 100 mL of distillate has been collected in the receiving beaker (note u).	(u) This step takes about 30 minutes from the beginning of distillation.
C7.19	Quantitatively transfer the distillate to a 200 mL calibrated flask and make up to volume with water.	
C7.20	Determine cyanide in the distillate by the procedure described in steps C7.1 to C7.12. The UV radiation unit is not switched on for this determination.	

C8 Preparation of Calibration Curve

As indicated in step C7.6, 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 must be selected having regard for the expected sample cyanide concentration and of the manifold configuration in use. Working standard cyanide solutions prepared as detailed in Part D7.1 may be used for calibration in range Cb.

For calibration in range Ca, 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 (A3.2). Add to each flask 25.0 ± 0.5 mL of 0.1 M sodium hydroxide solution (A3.1) and make up 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 C7.10.

D Determination of Cyanide by Microdiffusion (Tentative Method)

D1 Performance characteristics of the Method

D1.1	Substance Determined	Easily liberated cyanide ion.
D1.2	Type of Sample	Raw, potable and waste waters.
D1.3	Basis of Method	Diffusion of hydrogen cyanide released at pH6 into dilute sodium hydroxide, and subsequent spectrophotometric determination.
D1.4	Range of Application	Up to 160 μg CN/L. The range can be extended upwards by taking a smaller sample volume.
D1.5	Calibration Curve	Linear to at least 160 μg CN/L.
D1.6	Total Standard Deviation (a):	

Sample Type	Concentration μg CN/L	Standard Deviation μg CN/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

D1.7	Limit of Detection (a)	3 μg CN/L (11 degrees of freedom).
D1.8	Sensitivity (a)	120 μg CN/L gives an absorbance value of about 0.38 units.
D1.9	Bias (b)	

Sample Type	Concentration μg CN/L	Bias μg CN/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

D1.10	Interferences	See section D3.
D1.11	Time required for Analysis	About 5 hours total analytical time, 1 hour operator time, for a batch of 8 determinations.

(a) Data from Thames Water Authority, New River Head Laboratories.
(b) Data from ISO 6703/4 (reference 6).

D2 Principle

The method relies upon diffusion of hydrogen cyanide—liberated from simple cyanide compounds by adjustment of the solution to pH6—into a dilute sodium hydroxide receiving solution. The diffusion process is carried out in Conway-type glass diffusion cells and occupies 4 hours, although 95% recovery of cyanide is completed within 3 hours (7).

Cyanide complexes that resist dissociation at pH6 are not included in this determination. Chief among such complexes are the hexacyanoferrates; another method in this booklet is provided for the inclusion of such complexes in the total cyanide concentration.

'Easily liberated cyanide' is therefore defined as the cyanide which diffuses as hydrogen cyanide from a solution at pH6, at room temperature.

The addition of cadmium chloride to the sample before addition of pH6 buffer solution serves as a precaution against interference from large concentrations of hexacyanoferrates by precipitating them as cadmium salts (see section D3).

The spectrophotometric determination involves the reaction of cyanogen chloride—formed by reaction of cyanide with N-chlorosuccinimide with barbituric acid in a pyridine-containing solution to form a purple-coloured complex whose absorbance is measured at 580 nm.

D3 Interference

Limited interference testing has been carried out, using a method similar in all essentials to this method. Table D1 shows these results; note that no estimate of the significance of the effects is available.

Table D1 Interference Effects (a)

Other Substance (expressed in terms of substance in brackets)	Concentration of other substance	Effect in μg CN/L of other substance at a cyanide concentration of	
	mg/L	0 μg/L	100 μg/L
Sulphite (SO_3)	250	*	− 2
(as Na_2SO_3)	330	*	− 10
	500	*	− 50
	1000	*	− 70
Cyanohydrin ($CH_2(OH)CN$)	117	<2	*
	234	4	*
	467	8	*
	700	11	*
	1116	18	*
Formaldehyde (HCHO)	200	*	− 6
	500	*	− 16
	1000	*	− 27
	2000	*	− 35
Hexacyanoferrates			
$K_3Fe(CN)_6$	50	1	*
$K_3Fe(CN)_6$	200	10	*
$K_4Fe(CN)_6.3H_2O$	50	2	*
$K_4Fe(CN)_6.3H_2O$	200	9	*
Thiocyanate (NaCNS)	350	1	*

* Not evaluated.
(a) Data from reference 7.

D4 Hazards

D4.1 Potassium cyanide and concentrated solutions of it present a serious risk of poisoning if swallowed, or by skin contact. Contact with acids will liberate highly toxic hydrogen cyanide gas. See also A1.2.

D4.2 Pyridine is highly flammable, and harmful by inhalation, in contact with skin, and if swallowed.

D4.3 N-chlorosuccinimide reacts explosively with aliphatic alcohols.

D4.4 Cadmium chloride is toxic by inhalation, in contact with skin and if swallowed, presenting the danger of cumulative, irreversible effects.

D4.5 Barbituric acid is an irritant; skin contact with the solid and reagents incorporating it must be avoided. See also A1.2.

D5 Reagents

Analytical-Grade reagents must be used wherever possible. Distilled or deionized water must be used throughout.

D5.1 2 M Sodium hydroxide solution

Carefully dissolve 80 ± 1 g of sodium hydroxide pellets in about 900 mL of water and dilute to 1 litre with water in a measuring cylinder. Store in a stoppered polyethylene bottle. This solution is stable indefinitely.

D5.2 0.1 M Sodium hydroxide solution

Dilute 50 ± 1 mL of 2 M sodium hydroxide solution (D5.1) to 1 litre with water in a measuring cylinder. Store in a stoppered polyethylene bottle. This solution is stable indefinitely.

D5.3 19% m/v potassium dihydrogen orthophosphate solution

Dissolve 14.5 ± 0.1 g of sodium hydroxide pellets in about 400 mL of water contained in a 2 litre beaker. Dissolve 190 ± 1 g of potassium dihydrogen orthophosphate in this mixture; add more water up to a volume of 950 mL to aid dissolution.

Adjust the pH value of this solution to pH5.9–6.1 using dropwise addition of 2 M sodium hydroxide solution, monitoring the pH change with a calibrated pH electrode system.

When the correct pH value is obtained, transfer the solution to a 1 litre calibrated flask and make up to volume with water. Store in a polyethylene container. This solution is stable indefinitely.

D5.4 Buffer Solution

Mix together 8.0 ± 0.1 ml of Phosphoric acid (d_{20}1.70) and 100 ± 1 ml of 19% m/v potassium dihydrogenorthophosphate solution (reagent D5.3). Store in a polyethylene bottle. This solution is stable indefinitely.

D5.5 1% m/v cadmium chloride solution

Dissolve 10.0 ± 0.1 g of anhydrous cadmium chloride in about 200 mL of water and dilute to 1 litre with water in a measuring cylinder. Store in a glass bottle labelled TOXIC. This solution is stable indefinitely.

D5.6 N-Chlorosuccinimide/succinimide reagent

Dissolve 10.0 ± 0.1 g of succinimide in about 900 ml of water. Add 1.00 ± 0.01 g of N-Chlorosuccinimide and dissolve. Make up to 1 litre with water in a measuring cylinder. Store in an amber glass bottle. This reagent is stable for 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 hydrochloric acid (d_{20} 1.18). Then add 1.50 ± 0.01 g of barbituric acid and 50 ± 5 mL of water to dissolve. Warm the mixture gently if necessary to achieve dissolution. Then dilute to 100 mL with water in a measuring cylinder. Store in an amber glass bottle labelled TOXIC. This solution is stable for up to 3 days.

D6 Apparatus

D6.1 Conway-type glass diffusion cells are required. Figure 4 shows their design.

An alternative based on petri dishes may be used.

D6.2 A fume cupboard is desirable for handling pyridine.

D6.3 A spectrophotometer operating at 580 mm and equipped with 10 mm cells is required.

D7 Procedure

Step	Procedure	Notes
	Calibration (To be carried out when this method is first put into use and thereafter with each new batch of solid barbituric acid)	
D7.1	Into a series of 50 mL calibrated flasks add, from a burette, 1, 2, 4, 6 and 8 mL of working standard cyanide solution (A3.3). Add to each flask 25.0 ± 0.5 mL of 0.1 M sodium hydroxide solution (D5.2) and make up to volume with water. These flasks now contain 20, 40, 80, 120 and 160 μg CN/L respectively.	
D7.2	Pipette 10 mL of a standard solution into the outer ring of a diffusion cell.	
D7.3	Pipette 5 mL of 0.1 M sodium hydroxide solution (D5.2) into the centre ring of the diffusion cell.	
D7.4	Pippette 2 mL of 1% m/v cadmium chloride solution (D5.5) into the outer ring and mix carefully (note a).	(a) Gentle tilting of the cell will achieve mixing. Take care to avoid splashing into the centre ring.
D7.5	Pipette 4 mL of 19% m/v potassium dihydrogen orthophosphate solution (D5.3) into the outer ring. Immediately cover the cell (note b) and then mix the outer ring contents (note a). Place the diffusion cell carefully in a dark cupboard at room temperature. Repeat steps D7.2 to D7.4 for the other standard solutions (D7.1) in turn.	(b) Ensure the seal is air-tight. This is most easily achieved by smearing a small quantity of petroleum jelly on the joint surface.
D7.6	After at least 4.0 hours (note c), remove the diffusion cells. Uncover each in turn and transfer, by pipette, 4 mL of the sodium hydroxide solution from the centre ring to a separate 10 mL calibrated flask.	(c) Tests have shown that the diffusion can be left in progress for at least 16 hours with no ill effect.
D7.7	Add 0.400 ± 0.004 mL of buffer solution (D5.4) to the calibrated flask and mix.	

Step	Procedure	Notes
D7.8	Add 0.400 ± 0.004 mL of N-Chlorosuccinimide/ succinimide reagent (D5.6) to the calibrated flask and mix. Allow to stand for at least 2 minutes.	
D7.9	Add 0.400 ± 0.004 mL of barbituric acid/ pyridine reagent (D5.7) to the calibrated flask and mix.	
D7.10	Make up to volume with water and mix well. After 10 ± 5 minutes (note d), measure the absorbance of the solution at 580 nm (note e) in 10 mm cells, using water in the reference cell. Let the absorbance measured be A_S units.	(d) The absorbance increases to a maximum value which is effectively attained within this time interval. Beyond 15 minutes, the absorbance decreases at a rate of about 5% in 35 minutes. (e) The exact wavelength of maximum absorbance should be checked, and rechecked for each new batch of solid barbituric acid. Use the wavelength in all subsequent measurements.
D7.11	Subtract the absorbance of the blank solution (step D7.12) from the absorbance of each of the standard solutions and plot a graph of absorbance against cyanide concentration (μg CN/L). This should be linear through the origin.	
	Blank determination	
D7.12	Pipette 5 mL of 0.1 M sodium hydroxide solution (D5.2) and 5 mL of water into the outer ring of a diffusion cell and mix. Then proceed with steps D7.2 to D7.10. Let the absorbance (step D7.10) be A_B units (note f).	(f) In order to avoid the measurement of the diffusion blank on every occasion, the analyst may compare this blank value with a blank value obtained from steps D7.6 to D7.10, ie taking the sodium hydroxide receiving solution with no prior diffusion. If the 2 values do not differ significantly in the analyst's judgement, it will suffice thereafter to obtain a blank value without diffusion, until new batches of the solid components of reagents D5.3 and D5.5 are brought into use, when the entire blank must be checked afresh.
	Analysis of Samples	
D7.13	Pipette 10 mL of the sample (note g) into the outer ring of a diffusion cell and proceed with steps D7.2 to D7.10. Let the absorbance measured be A_R units.	(g) Samples preserved by the addition of sodium hydroxide as specified in part A 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 must first be partially neutralized. See also Section D9.2.
	Calculation of Results	
D7.14	Calculate the absorbance due to cyanide in the sample, A_R; from:— $A_R = A_S - A_B$ Determine the concentration of cyanide in the sample from the $A_S - A_B$ calibration curve (D7.11). Report the result in μg CN/L.	

D8 Sources of Error

D8.1 The pH value of the sample during diffusion is not critical from the point of view of efficiency; tests have shown (6) that 100% recovery is obtained in the pH range

6.5 to 3.5. However, any significant lowering of pH below 6.0 may increase the diffusion of potentially interfering acids.

D8.2 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 no effect upon the method.

D8.3 The pH value of the diffusate should be in the range of 6.2 to 5.8 for maximum absorbance, although a range of 6.4 to 5.3 is tolerable.

D8.4 There is no significant effect of temperature in the range 5–31°C on the efficiency of the diffusion process.

Figure 1 Reflux distillation apparatus

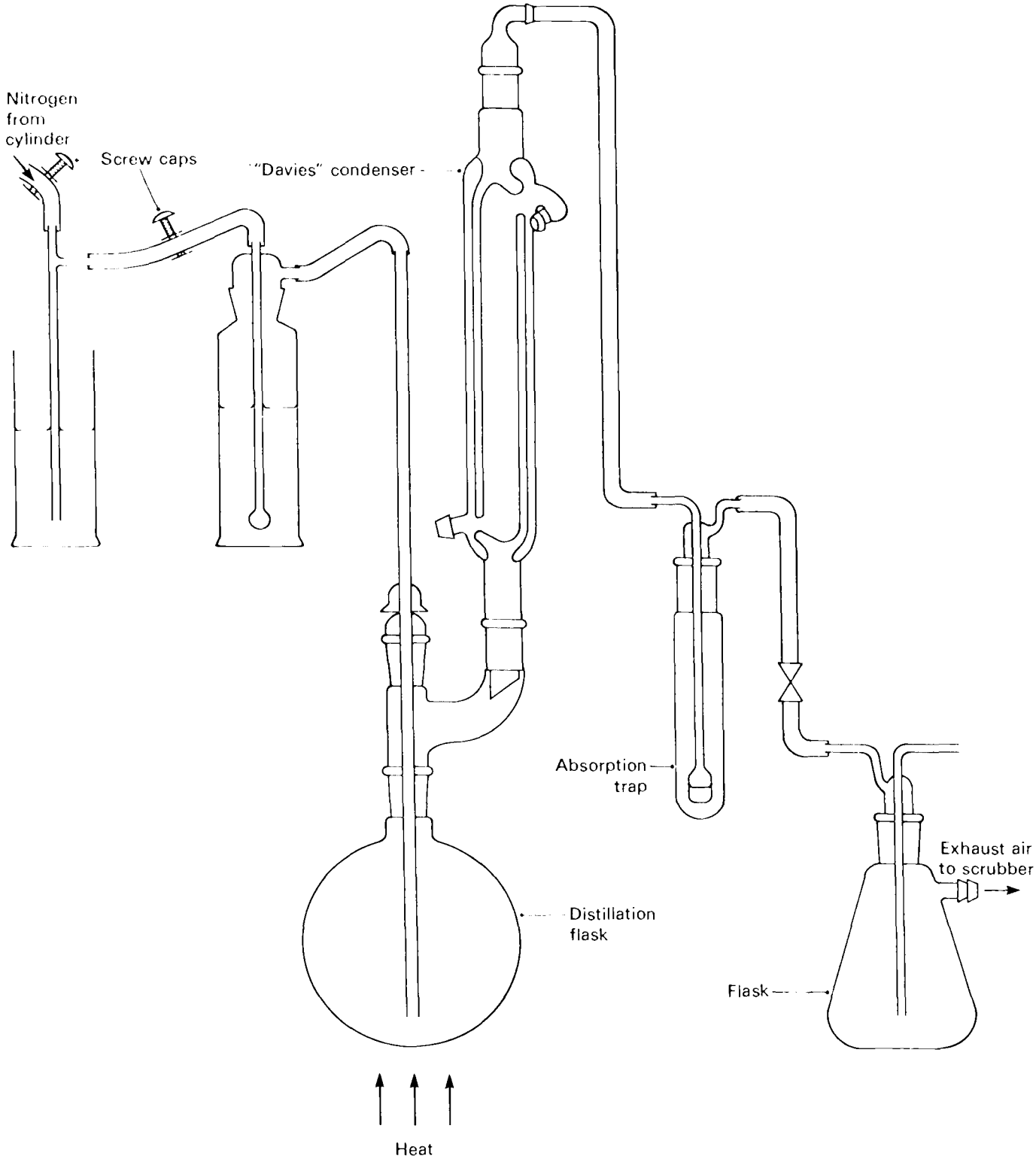
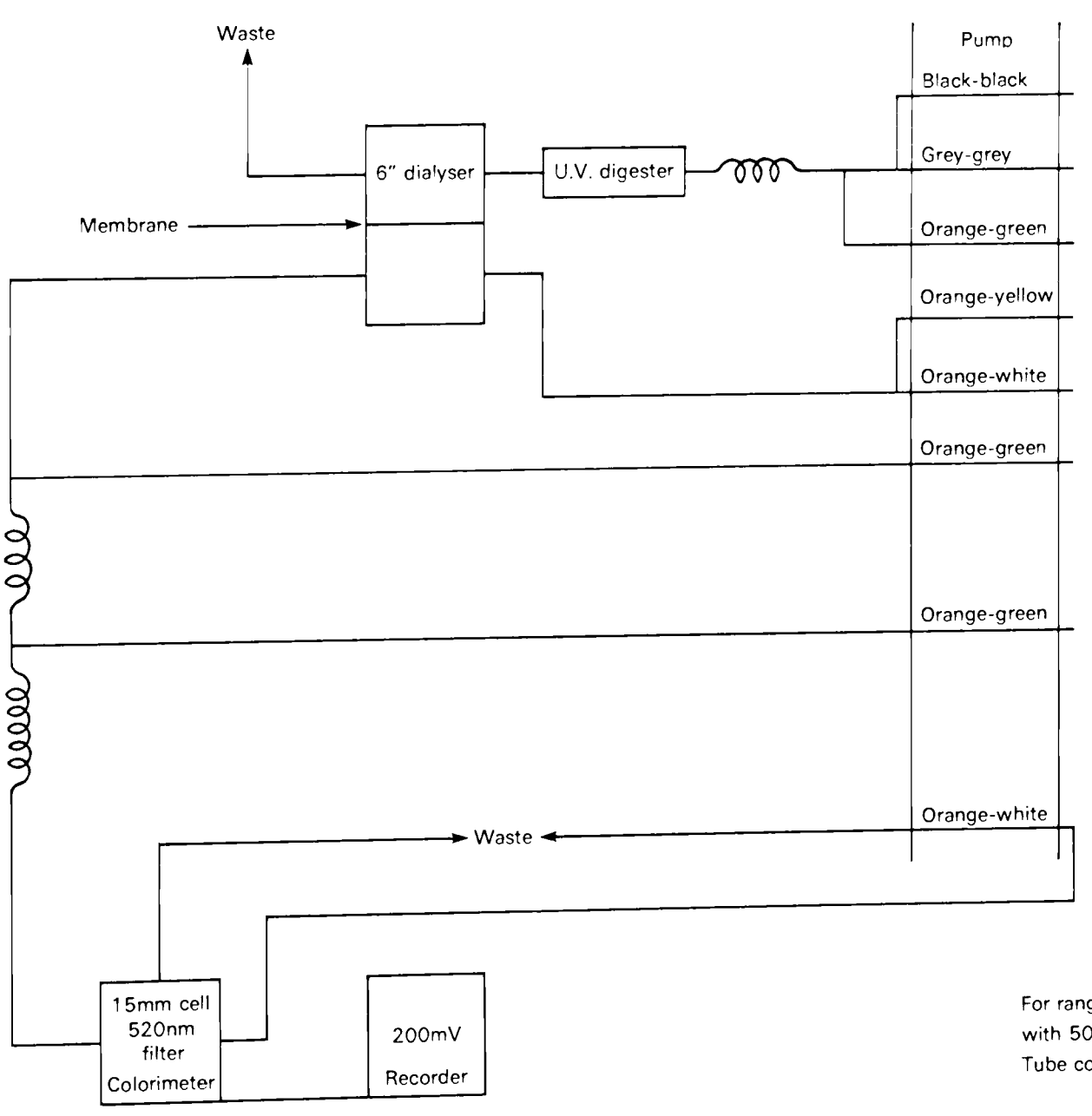


Figure 2 Manifold design for cyanide on the range up to 5mg/L (Range [a])



Pump	Flow rate (mL/min)	Reagent
Black-black	0.32	Air
Grey-grey	1.00	Sample
Orange-green	0.10	Mixed acid
Orange-yellow	0.16	Air
Orange-white	0.23	0.01N NaOH
Orange-green	0.10	Chloramine
Orange-green	0.10	Pyridine-barbituric
Orange-white	0.23	Pull-through

For range [b] (up to 0.16mg/L): as above with 50mm cell and 0.3mL/min pull-through. Tube colour codes only given for convenience

Figure 3 Reflux distillation apparatus

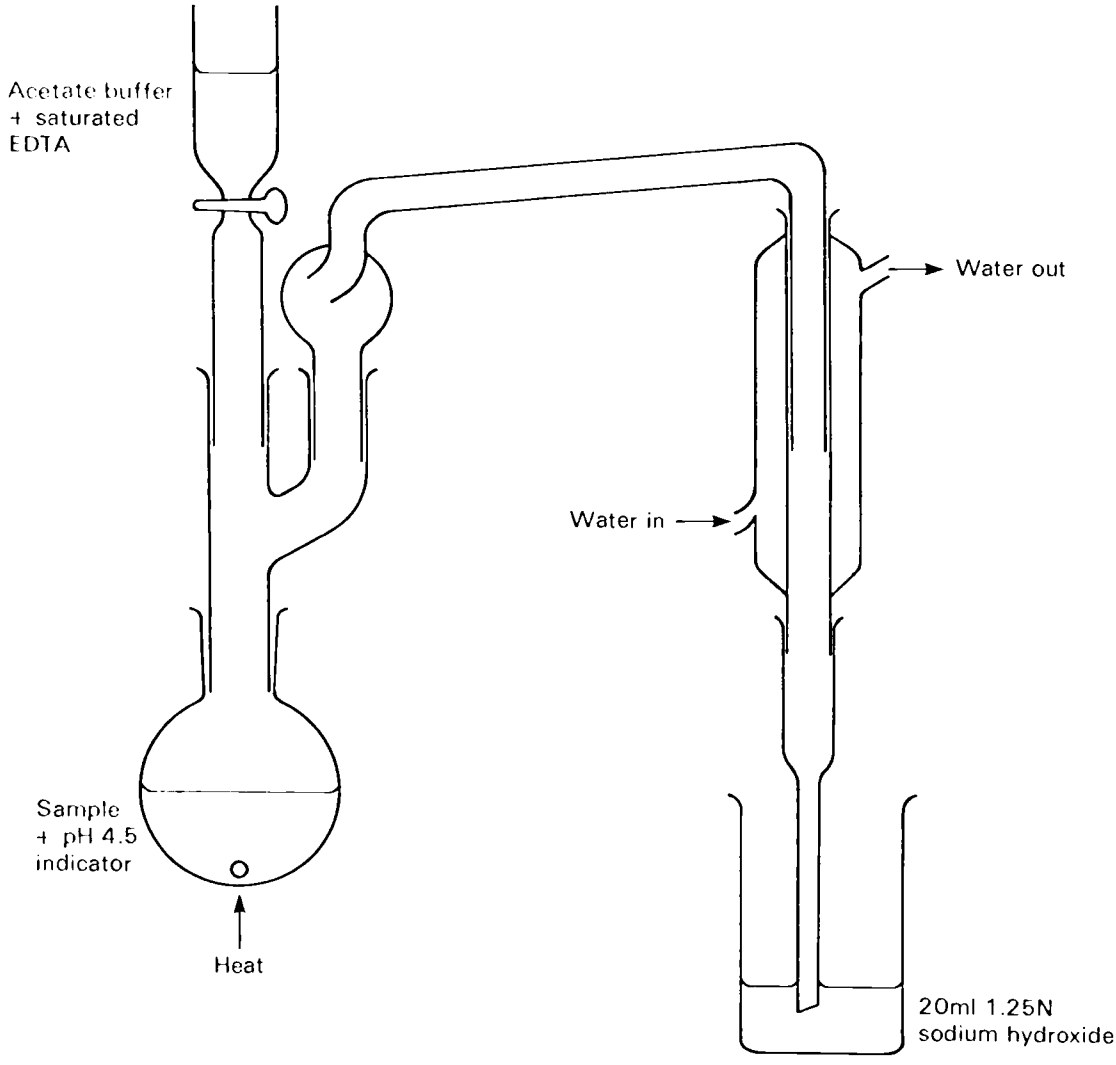
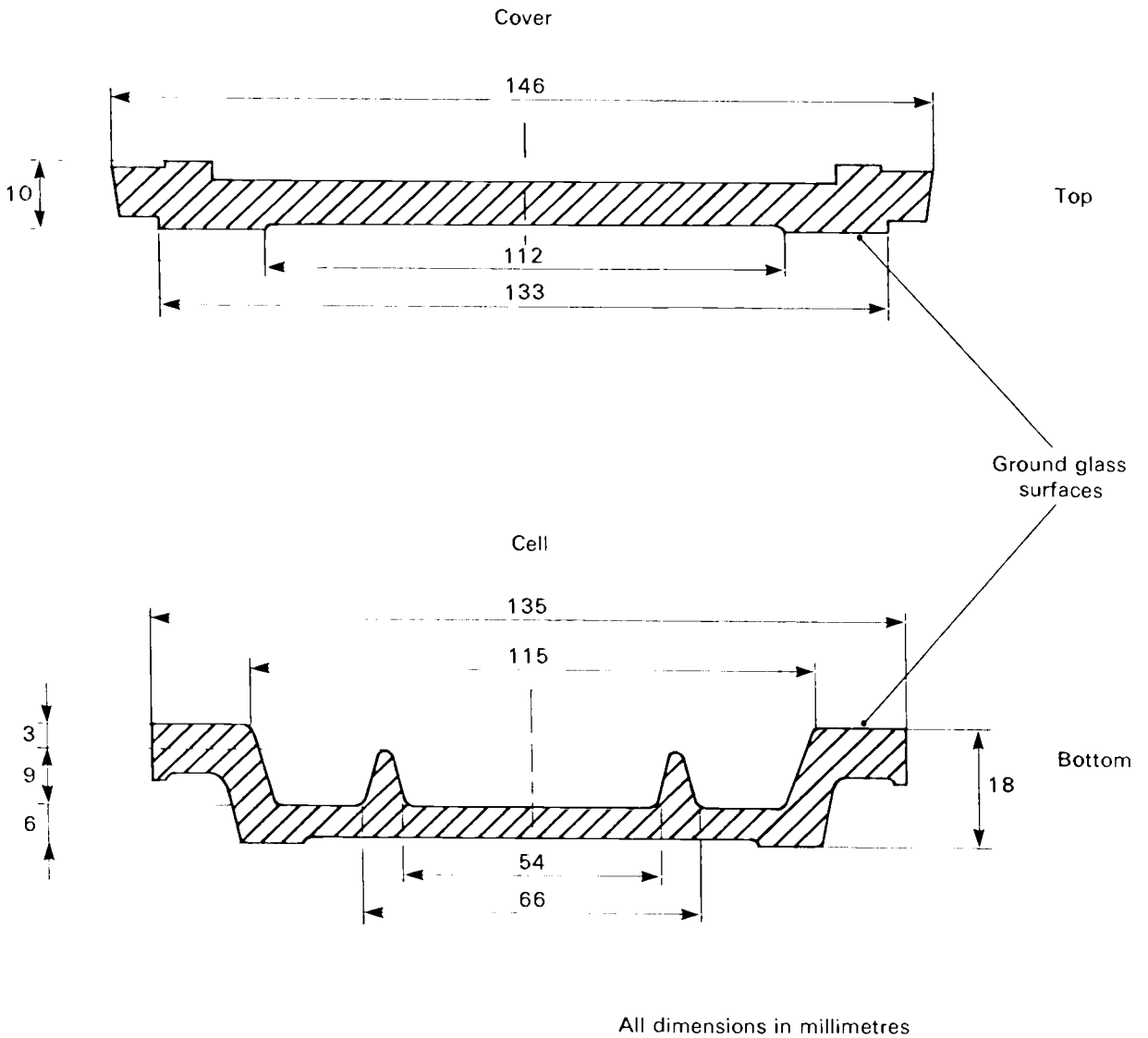


Figure 4 Diffusion cell



All dimensions in millimetres

E Advice on the Determination of Total Cyanide in the Presence of Strongly Interfering Metals and Similar Substances

E1 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 free cyanide, or the complex itself is toxic, knowledge of the amount of such ultrastable complexed cyanide may be unimportant or misleading. An example of such a cyanide is cyanocobalamin—vitamin B12, which is not only essential for human and animal health, but produced in some sewage treatment processes and in some rivers.

E2 Metals forming Stable Complex Cyanides

Stable cyanides are reported for the following metals:

Table E1 Metals forming Stable Complex Cyanides

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

The metals underlined form some of the strongest complexes. The numbers in brackets are the valance states of these metals forming complex cyanides. The numbers to the right are the maximum number of cyanide groups which can be co-ordinated in that valence state. Other groups than cyanide may also be co-ordinated to the metal.

Some of these complexes will break down at least partially when using the most severe procedures in the preceding methods. However, much depends on the other co-ordinating ligands and the metal valence given in brackets above.

E3 Preliminary procedure if highly stable cyanides are suspected

First 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 should be used. Suitable methods are:

X-ray fluorescence	**(see Ref 14)**
DC arc emission spectroscopy	**(see Ref 15)**
ICP spectrophotometry	**(see Ref 17)**

If none of the metals listed in Table E1 are present, it is very unlikely that any stable cyanide is present, and the total liberable cyanide value represents all the cyanide present.

E4 Procedures for determining cyanide if these metals are present

E4.1 Two techniques are available:

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 analysis are advised to evaluate these procedures prior to use.

E4.2 Infra-Red Absorptiometry

The cyanide CN bond absorbs in the infra-red in the region 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 (by Southern WA, Capstone Lane Laboratory) have shown that unless the cyanide concentration is relatively high (about 1000 mg CN/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 done using samples already stripped of readily determinable cyanide which might be lost during evaporation. If the total dissolved salts content is high, further prior concentration will be necessary. HPLC is suggested, the infra-red absorption serving to confirm that the separated material is indeed a complex cyanide.

In order to identify and quantify the cyanide peak, prepare a solution containing the various metals found to be present, in approximately the concentration found in the sample. Use this master metal solution to prepare a series of cyanide standards of increasing strength from nil up to complete complexation of all the complexing metal present. The numbers in brackets in Table E1 indicate the common valence states of the metals when forming cyano complexes, the unbracketted numbers to the right in that table are the maximum number of cyano groups that can be co-ordinated per atom of metal.

Treat these standards in exactly the same way as the sample and compare to identify and quantify the sample peaks. If the complexes have been prior separated, only the metals concerned need be used. A useful general text which includes information on cyanides as well as techniques and other references is reference 10.

E4.3 Liquid Chromatography

Both normal Ion Chromatography (with anion exchange resins) and reverse phase HPLC have been used with a variety of aqueous eluents. Ultra-violet absorption, pulsed amperometry, conductivity and flame atomic absorption detectors have all been used to locate and quantify the peaks of the various cyano-complexes as they elute. This method may also be combined with the preceding one using infra-red absorptiometry. Ultra-violet absorption detectors are liable to interference from other ions. Conductivity and pulsed amperometric detectors merely indicate that something has eluted which must then be identified by comparison with single complex standards or other means. 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. For general information on Liquid Chromatography see References 11 and 12. A recent paper (13) gives specific details on separation of complex cyanides using reversed-phase ion-pair partition chromatography with UV detection. For additional information on the analysis of complex mixtures of cyanide, thiocyanate, and related metal complexes see References 18 to 21.

E5 Stable Organic Cyanides

These hydrolyse to organic acid and ammonia when refluxed with alkalis or acids, and are unlikely to cause problems. Isocyanides (RNC) are recognisable by their smell and are reducible to amines.

E6 Calculation of total cyanide

As some complex cyanides are in readily reversible equilibrium with free cyanide ion, there is a danger of error if results from these methods in Part E are simply added to the cyanide concentration obtained by the earlier methods. If the methods are used in conjunction, the procedures in Part E should only be used on samples from which the free or liberatable cyanide has been removed by the appropriate method. Note that both procedures in Part E can be used to determine simple cyanide too, if in the appropriate concentration range.

F Notes on the Determination of Cyanide in Sludges and Soils

F1 Introduction

Cyanide in sludge or soil may be determined under 3 classifications:

Total cyanide
Alkali extractable cyanide
Water soluble cyanide

The alkali extractable cyanide classification is widely used in the analysis of soils.

The procedure given below is an extension of Method B. Performance data which are lacking may be dependent on soil etc, type. Users are advised to evaluate for themselves.

F2 Substances Determined

Total cyanide
Alkali extractable cyanide
Water soluble cyanide

F3 Reagents

Those specified in Section B5, plus the following:

F3.1 Sodium hydroxide solution, 1 M.

Dissolve 40.0 ± 0.5 g of sodium hydroxide in about 900 mL of water with care and stirring. Cool the solution to room temperature and make up to 1 litre with water in a calibrated flask. Store the solution in a polyethylene container. It is stable indefinitely.

F4 Apparatus

All as described in Section B6.

F5 Procedures

F5.1 **Determine the percentage dry solids of the sample** by initial weighing of a suitable portion and drying at 110°C to constant weight. Let the percentage dry solids be P%.

F5.2 **Total cyanide**

F5.2.1 Accurately weigh about 10 g of the sludge or soil sample as received, at the same time as the determination of percentage dry solids (F5.1). Let the weight taken be W g.

F5.2.2 Quantitatively transfer the weighed sample portion to a 1 litre distillation flask, using up to 500 mL of water.

F5.2.3 Add more water if necessary to give a total volume in the flask of 500 mL, then follow the Analytical Procedure given in Section B7, starting at step B7.2 and using either the colorimetric or electrode procedure for cyanide measurement.

F5.2.4 In the electrode procedure, calculate the cyanide concentration in the sample from:

$$\frac{C_0}{W} \times D \times \frac{100}{P} \text{ mg/Kg dry weight}$$

where C_0 and D are as defined in step B7.20 and P and W are as above.

F5.2.5 In the colorimetric procedure, calculate the cyanide concentration on the sample from:

$$\frac{A \times B}{D \times W} \times \frac{100}{P} \text{ mg/Kg dry weight}$$

where A, B and D are as defined in step B7.29 and P and W are as above.

F5.3 **Alkali extractable cyanide**

F5.3.1 Accurately weigh a 300 mL capacity glass or plastic bottle. Then add 50 ± 0.5 g of the sludge or soil sample as received, accurately reweigh and calculate the weight of sample taken. Let this be Wg. Carry out the determination of percentage dry solids (F5.1) at the same time.

F5.3.2 Add 250 ± 2 mL of sodium hydroxide solution (F3.1). Secure the bottle cap and place on a mechanical shaker.

F5.3.3 Shake gently but continuously for 60 ± 5 minutes. Remove the bottle from the shaker and allow to stand until the sample has settled.

F5.3.4 Decant or pipette an aliquot of at least 80 mL of the supernatant liquid and filter through a GF/C paper under suction. Discard the first 10 mL of filtrate.

F5.3.5 Transfer 50.0 ± 0.5 mL of the filtrate from step F5.3.4 to a 1 litre distillation flask and add 450 ± 20 mL of water. Then follow the Analytical Procedure given in Section B7, starting at step B7.2 and using either the colorimetric or electrode procedure for cyanide measurement. In either procedure, let the concentration of cyanide determined in the filtrate be E mg CN/L.

F5.3.6 Calculate the alkali extractable cyanide in the original sample from:

$$\frac{250 \times E}{W} \times \frac{100}{P} \text{ mg/Kg dry weight}$$

where E, P and W are as above.

F5.4 **Water soluble cyanide**

Proceed as in Section F5.3, but using 250 ± 2 mL of water instead of sodium hydroxide solution at step F5.3.2.

F6 Concentration ranges of the method

The weight of sample specified in the procedures is for guidance only. The analyst must vary the sample size in the light of the actual percentage dry solids of each sample and of its expected cyanide content, bearing in mind the range of application of the cyanide determination method B.

G Checking the Accuracy of Analytical Results

G1 Routine Analytical Quality Control

Once the methods have been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check sources of inaccuracy should be made regularly. Many types of test are possible and they should be used as appropriate. As a minimum, however, it is suggested that a standard solution of cyanide of suitable concentration be analysed at the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated. It is suggested that corrective action should be taken if one value falls outside of the action limit (at ± 3s) or 2 values exceed the warning limit (at ± 2s). As more data is acquired, the standard deviation, s, should be updated and the control chart limits recalculated. (8, 9, 23, 24)

G2 Estimation of the Analytical Accuracy of these Methods

G2.1 Introduction

Not all the methods given in this booklet have been thoroughly investigated in more than 5 laboratories. Before firmly recommending a method for general use, it is desirable to know the accuracy achievable. It would, therefore, be of great value if any laboratory using or considering the use of any of these methods would estimate the accuracy of its own analytical results and report the findings to the Secretary of the Department of the Environment's Standing Committee of Analysts.

The precision achieved and the effects of any interfering substances that may be present in samples are of particular interest. Information on these aspects would be useful, but the value of such information would be greatly enhanced if it were obtained to a common plan so that such information can be compared and valid conclusions drawn. Accordingly, suggestions for a suitable experimental design and analysis of results are given in the following sections and it is suggested that laboratories follow this design whenever possible. The design has been chosen to be as simple as possible; more complex designs are possible and would give more information.

G2.2 Basis of Suggested Tests

The limit of detection is governed by the within-batch variability of blank determinations. The precision of analytical results may depend on the concentration of determinand in the sample analysed and on the type of sample, eg worse precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion of each of the following solutions on each of n days, where n is at least 5 and preferably up to 10.

Solution No	Description
1	Blank
2	Another blank
3	Standard solution low concentration
4	Standard solution high concentration
5	Typical sample
6	Same sample spiked with a known amount of cyanide c mg CN/L

It is essential that these solutions be treated exactly as if they were samples and the appropriate specified procedure be rigidly followed. These solutions should be analysed in random order in each batch of analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method and should be treated exactly as routine samples. The same batch of water should be used on each day to prepare all 4 solutions. For solutions 5 and 6 a total of 5 litres of typical sample are required.

Prepare solution 6 each day when required by spiking solution 5. The results of the analyses of solutions 5 and 6 will provide a check of the effect of sample type on precision. Any deviation of the recovery of spiked cyanide from 100% may give an indication of the presence of interfering substances. Drift in results from solution 5 (and hence 6) may indicate sample instability on storage.

Note that the Blank water should be as appropriate for the method being evaluated.

G2.3 Evaluation of Results

The raw experimental results may be sent direct to the Department of the Environment for evaluation together with the results obtained from the standards used to establish the calibration curve in each batch of analyses. However, for those laboratories wishing to make the calculations themselves, the details are given below.

G2.3.1 Convert all results to concentrations as described in the method. Deduct the first of the 2 blank values (solution 1) from each of the other solution values.

G2.3.2 Calculate the mean concentration of the n results for each solution.

G2.3.3 Calculate the standard deviation, s, of the n results for each solution from:

$$s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n-1}}$$

where x_i = the result from the ith batch
$\bar{x}$ = the mean value of x_i.

G2.3.4 Calculate the within-batch standard deviations, s_w, of the blank from:

$$s_w = \sqrt{\frac{(\bar{x}_{1i} - \bar{x}_{2i})^2}{2n}}$$

where x_{1i} = the 1st blank result (solution 1) from the ith batch.
x_{2i} = the 2nd blank result (solution 2) from the ith batch.

G2.3.5 Calculate the mean percentage recovery, R, of the spiked sulphate in solution 6 from:

$$R = \frac{(\bar{x}_6 - \bar{x}_5)}{c} \times 100$$

where $\bar{x}_5$ = the mean value of the results of solution 5.
$\bar{x}_6$ = the mean value of the results for solution 6.
c = spike increment.

G2.3.6 Summarise the results as in the following table:

Solution	No of results n	Mean Sulphate Concentration	Standard Deviation	Mean Recovery %
2 Blank				—
3 Standard, low				—
4 Standard, high				—
5 Sample.....				—
6 Solution 5 + spike				—

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step 3.4 is entered for the blank solution 2 and the standard deviations from step 3.3 are entered for solutions 3 to 6.

G2.4 Evaluation of Interference Effects

If interference effects are suspected, analyse a series of standard samples with and without known amounts of interference plus also real samples, spiked real samples and spiked real samples with interferent added. If interference removal is contemplated, this should be evaluated in the same way.

For more detailed information on the types of test available and the interpretation of their results, standard texts—such as those published by the Water Research Centre (8) and by the DOE Standing Committee of Analysts (9) appropriate British Standards (23) and ref 24 should be consulted.

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Address for Correspondence

However thoroughly a method may be tested there is always the possibility of a user encountering a hitherto unreported problem.

Correspondence about these methods should be addressed to:—

The Secretary
The Standing Committee of Analysts
Department of the Environment
Romney House
43 Marsham Street
LONDON
SW1P 3PY

Membership responsible for these methods.

This booklet has been 10 years in preparation due to the difficulty of accurately determining complex cyanides which have varying degrees of stability. Hence there has been a great turnover in membership at all levels. Only those Main Committee and Working Group members who were actually concerned with this method are listed. Several correspondents have provided very valuable information though never actually attending meetings. This is acknowledged, as is a valuable liaison with the British Standards Institution, the Deutsches Institut für Normung, and the Canada Centre for Inland Waters (Burlington).

A Adam 1
G W Ashley 3
Dr P Bailey 3
H T Barnhoorn 1
D Bennett 2
F B Basketter 1
Dr G A Best 1
P A Chave 1
Dr B T Croll 1
Dr J V Dadswell 1
K G Darrell 3
J A Davis 2
E Donaldson 1
Mrs E Dryburgh 1
M C Finnear 1
I Fox 2.4
M Gardner 1
J R Garlick 1
D Gelsthorpe 2.3
G I Goodfellow 1.2.3
P Green 2.3
B L Hampson 3
T R Hayes 3
W Hepple 3
A S Holmes 3
M R Hurcombe 1
H James 3
Dr J G Jones 1
R Law 1
J S Leahy 1
R Mackison 4
D McIntyre 3
D Mealor 4
Dr D Midgley 2
P Morries 1.2.3
Dr R Mounce 2.4
C C Musselwhite 2.3
D Myles (deceased) 1.2.3
Dr H A Painter 1
K W Petts 2.3
L R Pittwell 1.2.3
L D Purdie 1
L A Richards 1
Prof J P Riley 1
A Robinson 3
P Robinson 3
C C Scott 2.3
Dr R Smithers 3
M Stockley 2.3
Dr D Taylor 1
Dr W M Thomas 3
Dr K C Thompson 1
Dr A M Ure 1
R J Vincent 1.2.3
P J Walker 1
Dr R J Watling 4
D Westwood 2.3
Dr A Williams 1
Dr R Woods 1
D Woods 2.3

Main Committee 1
Working Group 2
Panel 3
Correspondent 4

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