BRITISH STANDARD

BS 6068-2.18: 1986

Water quality —

Part 2: Physical, chemical and biochemical methods —

Section 2.18 Methods for determination of easily liberatable cyanide

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Contents

Foreword

This Section of this British Standard, which has been prepared under the direction of the Environment and Pollution Standards Committee, is based on ISO 6703-2:1984 "*Water quality — Determination of cyanide — Part 2: Determination of easily liberatable cyanide*" but is not equivalent in technical content.

ISO 6703-2 was prepared by subcommittee 2, Physical, chemical and biochemical methods, of Technical Committee 147, Water quality, of the International Organization for Standardization (ISO) as a result of discussion in which the UK participated. For ease of publication, the text of ISO 6703-2 has been used as a basis for this Section of this British Standard and a number of amendments have been incorporated. The principal changes now incorporated are that the text has been amplified, to improve clarity and avoid misunderstandings in the following clauses: **1**, **8**, **12.2**, **13**, **16**, **20**, **21**, **24**, and **29**. In addition clause **8** now allows the use of smaller test portions in addition to dilution of absorption solutions with the sodium hydroxide solution.

This British Standard is being published in a series of Parts subdivided into Sections that will generally correspond to particular International Standards. Sections are being, or will be, published in Parts 1 to 6, which, together with Part 0, are listed below.

— *Part 0: Introduction;*

— *Part 1: Glossary;*

— *Part 2: Physical, chemical and biochemical methods;*

— *Part 3: Radiological methods*;

— *Part 4: Microbiological methods;*

— *Part 5: Biological methods;*

— *Part 6: Sampling.*

Terminology and conventions. As a result of using the ISO text some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

The comma has been used as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

In British Standards it is current practice to use the symbol "L" for litre (and its submultiples) rather than "l" and to use the spelling "sulphur" etc., instead of "sulfur", etc.

Additional information. If a high intensity beam of light is passed through a colloidal solution and the solution viewed at a right angle to the incident light, a scattering of light is observed. This is known as the Tyndall effect.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 12, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Attention is drawn to the toxicity of cyanide and to the need to take extreme care when handling cyanides and their solutions.

Carry out all operations in a fume cupboard. Avoid contact with the skin and eyes. When pipetting, always use a safety pipette (pipette by bulb). Detoxify samples and solutions containing cyanides or heavy metals in accordance with local official regulations.

Other chemical specified in this Section of this British Standard are also hazardous, for example pyridine.

0 Introduction

Cyanides may be present in water as hydrocyanic acid (prussic acid), as cyanide ions and as complex cyanides. They may be determined as total cyanide or as easily liberatable cyanide. If cyanide compounds are chlorinated, cyanogen chloride (CICN) is produced, and this compound has to be determined separately.

There are 4 Sections in BS 6068 for the determination of cyanides in water as follows:

BS 6068-2.17:1986, *Methods for determination of total cyanide.*

BS 6068-2.18:1986, *Methods for determination of easily liberatable cyanide.*

BS 6068-2.19:1986, *Method for determination of cyanogen chloride.*

BS 6068-2.20:1986, *Method for determination of cyanide by diffusion at pH 6.*

The methods described in Sections **2.17**, **2.18** and **2.19** are suitable for controlling the quality of water and for the examination of municipal sewage and industrial effluents. They are appropriate to the technology available for the destruction of cyanides in treatment plants, and are based on the separation of liberated hydrogen cyanide (or in the case of BS 6068-2.19, of cyanogen chloride) by stripping with a carrier gas.

The method specified in BS 6068-2.20, using diffusion separation, is suitable for the determination of smaller amounts of cyanide, depending on the concentrations of copper and nickel.

This Section of this British Standard comprises 4 subsections. Subsection 1 deals with the liberation and absorption of hydrogen cyanide. The other 3 subsections deal with alternative methods for the quantitative determination of cyanide ions, as follows:

— photometric method with pyridine/barbituric acid (subsection 2);

— titrimetric method using the Tyndall effect (subsection 3);

— titrimetric method using an indicator (subsection 4).

The specification of three alternative methods is necessary because each of the methods has its advantages and disadvantages. None can be quoted as applicable in all cases.

The applicability of each method is described in clauses **8**, **16** and **24**.

NOTE Due to the different chemical behaviour of cyanide-containing or cyanide-producing substances, it is not possible to specify only one method for the quantitative determination of cyanide ions.

1 Scope and field of application

This Section of this British Standard specifies three methods for the determination of easily liberatable cyanide (see clause **2**) in water.

The methods are applicable to water containing less than 50 mg of easily liberatable cyanide (as cyanide ions) per litre, and less than 100 mg of total cyanide (as cyanide ions) per litre, but higher concentrations may be determined by suitable dilution of the sample.

The methods and corresponding ranges of easily liberatable cyanide contents for which they are suitable are as follows:

— Photometric method with pyridine/barbituric acid: applicable when the absorption solution contains 0,002 to 0,025 mg of cyanide, corresponding to 0,02 to 0,25 mg/l in a 100 ml aliquot portion of the undiluted sample;

— Titrimetric method using the Tyndall effect: applicable when the absorption solution contains > 0,005 mg of cyanide, corresponding to > 0,05 mg/l in a 100 ml aliquot portion of the undiluted sample;

— Titrimetric method using an indicator: applicable when the absorption solution contains > 0,05 mg of cyanide, corresponding to > 0,5 mg/l in a 100 ml aliquote portion of the undiluted sample.

A large number of ions and compounds interfere with the determination. These are listed in Table 1, together with the concentrations below which they do not interfere. If present singly or in combination, up to limiting concentrations, they do not interfere with the separation of hydrogen cyanide. The list is not exhaustive.

Table 1 — Interferences

Interference	Limiting concentration, mg/l
Sulfide ions	1 000
Polysulfide ions	500
Sulfide and polysulfide ions	1 000
Sulfide ions	500
Thiosulfate ions	1 000
Thiocyanate ions	1 000
Carbonate ions	1 000
Cyanate ions	1 000
Nitrate ions	500
Nitrite ions	500
Ammonium ions	2 000
Iron(II) and iron(III) ions	5 000
Copper(II) ions	100
Nickel(II) ions	50
Silver ions	50
Mercury ions	50
Chromate ions	300
Propionic acid	1 000
Phenol	1 000
Anthracene	100
Naphthalene	100
Anisaldehyde	10
Piperonal	10
Pyrrole	100
Pyridine	10
Chlorine (elemental)	250
Hydrogen peroxide	10
Perborate ions	10

If any of the limiting concentrations of the influences are likely to be exceeded, dilute the sample with distilled water before stabilization (see clause **6**).

Prussiates (pentacyano complexes with iron), which cannot be destroyed by chlorination under normal conditions of waste water treatment, partly decompose (up to 50 %), releasing hydrocyanic acid under the conditions specified. If it is desired to exclude prussiates, the procedure specified in clause **6** and **7.1** has to be used. This procedure is only applicable, however, if the concentration of copper ions in the sample is less than 1 mg/l. The presence of aldehydes, e.g. formaldehyde, may give lower cyanide values because of the formation of cyanohydrin.

2 Definition

For the purpose of this Section of this British Standard the following definition applies.

easily liberatable cyanide

cyanide from substances with cyanide groups and a measurable hydrocyanic acid vapour pressure at pH 4 and room temperature

such substances include all cyanides which will undergo chlorination, especially hydrocyanic acid, alkali- and alkali earth metal cyanides, and complex cyanides of zinc, cadmium, silver, copper and nickel. Complex cyanides of iron and cobalt, nitriles, cyanates, thiocyanates and cyanogen chloride are not included

Subsection 1. Liberation and absorption of hydrogen cyanide

3 Principle

Liberation of hydrogen cyanide from the sample by treatment at pH 4 with metallic zinc and EDTA. Entrainment of the hydrogen cyanide in a current of air into an absorption vessel containing sodium hydroxide solution.

4 Reagents

All reagents shall be of recognized analytical grade and the water used shall be distilled or deionized water.

4.1 *Hydrochloric acid*, solution, ϱ 1,12 g/ml.

4.2 *Hydrochloric acid*, solution, c(HCl) = 1 mol/l.

4.3 *Sodium hydroxide,* solution, c(NaOH) = 1 mol/l.

4.4 *Sodium hydroxide,* solution, c(NaOH) = 5 mol/l.

4.5 *Tin(II) chloride,* solution.

Dissolve 50 g of tin(II) chloride dihydrate ($SnCl_2.2H_2O$) in 40 ml of the hydrochloric acid solution (**4.2**) and dilute with water to 100 ml.

Prepare a fresh solution each week.

4.6 *Phenolphthalein,* solution, containing chloroform.

Dissolve 0,03 g of phenolphthalein in 90 ml of ethanol and add 10 ml of chloroform.

4.7 *Zinc- and cadmium sulfate,* solution.[1)]

Dissolve 100 g of zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) and 100 g of cadmium sulfate octahydrate ($3CdSO_4.8H_2O$) in water and dilute with water to 1 000 ml.

4.8 *Buffer solution,* of pH 4,0.

Dissolve 80 g of potassium hydrogen phthalate ($C_8H_5KO_4$) in 920 ml of warm water.

4.9 *EDTA,* solution.

Dissolve 100 g of ethylenedinitrilotetraacetic acid, *dis*odium salt dihydrate ($C_{10}H_{14}N_2Na_2O_8.2H_2O$) in 940 ml of warm water.

4.10 *Zinc dust*

5 Apparatus

Usual laboratory equipment, and

5.1 *Apparatus for the separation of hydrogen cyanide by stripping*

The apparatus shown in Figure 1, or its equivalent, is recommended and comprises the following components.

5.1.1 *Three-necked distillation flask,* of capacity 500 ml, with standard conical joints (centre neck 29/32, side necks 14,5/23).

5.1.2 *Reflux condenser (Liebig condenser)*

5.1.3 *Absorption vessels,* protected against return of liquid.

5.1.4 *Funnel*

5.1.5 *Flowmeter*

5.1.6 *Wash bottle,* of capacity 250 ml, for purification of the air.

5.2 *pH meter,* with a glass electrode which will fit into the side necks of the distillation flask.

5.3 *One-mark volumetric flasks,* of capacities 25, 50, 250 and 1 000 ml.

6 Sampling and samples

6.1 If the sample contains undissolved cyanides, it is necessary to ensure homogeneous distribution of the undissolved substances in the sample and its dilutions. Immediately after sampling, add 5 ml of the sodium hydroxide solution (**4.4**), 10 ml of the phenolphthalein solution (**4.6**) and 5 ml of the tin(II) chloride solution (**4.5**) to each litre of sample or diluted sample. Adjust the pH to about 8 by adding the hydrochloric acid solution (**4.2**), or the sodium hydroxide solution (**4.3**), drop by drop, until the water turns slightly red. Adjust the pH value of highly coloured samples in the same way after checking with the pH-meter (**5.2**) or with an indicator paper. Finally, add 10 ml of the zinc- and cadmium sulfate solution (**4.8**) to each litre of sample.

Analyse the sample as soon as possible. If it is necessary to store it, keep it cool and in the dark.

After addition of the zinc- and cadmium sulfate solution, a precipitate which may contain hexacyanoferrate, is formed. Accordingly, the sample should be rendered homogeneous immediately prior to taking aliquot portions. If replicate determinations are to be carried out, the aliquot portions shall be taken as quickly as possible in order to minimize any losses of gaseous hydrogen cyanide due to disturbance of the equilibrium between the gaseous hydrogen cyanide and the hydrocyanic acid in the liquid phase of the pretreated sample. If the required volume of sample is already known before sampling, it is advisable to take only this volume and to carry out the determination on the whole sample.

6.2 If prussiates are to be excluded from the determination, adjust the amount of tin(II) chloride solution (**4.5**) added so as to correspond to the content of oxidizing agents. The excess of tin(II) chloride solution shall be limited to 0,1 ml for each sample.

[1)] Zinc salt is added to provide stable zinc hexacyanoferrates, cadmium salt is added as sulfide acceptor and because of its bactericidal effect.

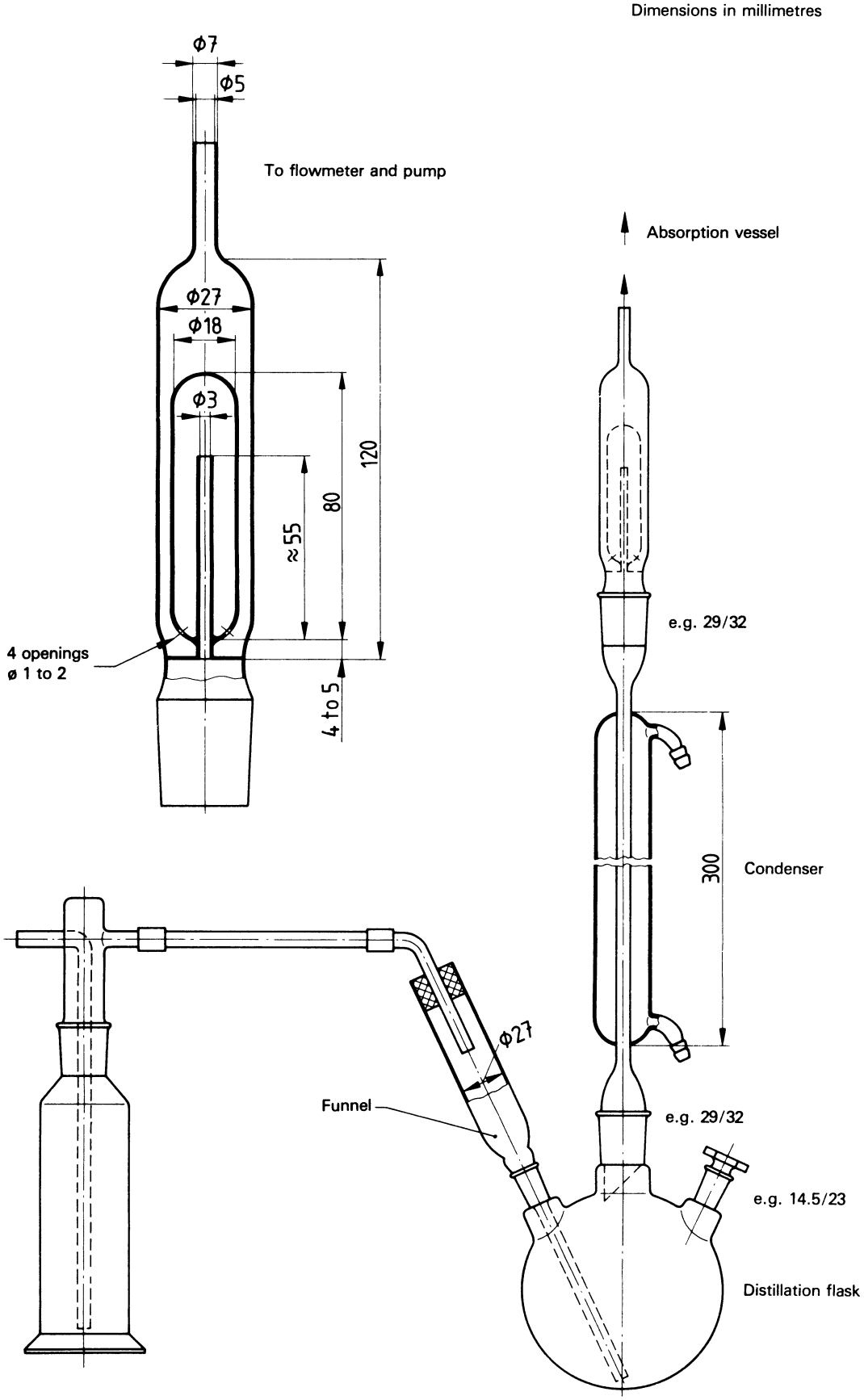

Figure 1 — Apparatus for separation of hydrogen cyanide by stripping

7 Procedure

7.1 Liberation and absorption of hydrogen cyanide

Pour 10 ml of the sodium hydroxide solution (**4.3**) into the absorption vessel (**5.1.3**), connect the vessel to the condenser, connect the suction tube and adjust the air flow to between 30 to 60 l/h. Pour into the disatillation flask, in the following order, 10 ml of the zinc- and cadmium sulfate solution (**4.7**), 10 ml of the EDTA solution (**4.9**), 50 ml of the buffer solution (**4.8**) and 100 ml of the sample (see clause **6**). Adjust the pH, checking by means of a glass electrode, by adding, drop by drop, the hydrochloric acid solution (**4.2**) or the sodium hydroxide solution (**4.3**), until the pH is 3,9 ± 0,1. Remove the glass electrode, add 0,3 g of the zinc dust (**4.10**)[2)] through the side neck and stopper the flask. Connect the wash bottle containing approximately 100 ml of the sodium hydroxide solution (**4.3**), to the funnel and adjust the air flow rate to 60 l/h. After 4 h, discontinue the stripping. If low cyanide concentrations (less than 0,1 mg/l) are expected, the volume of the sample may be increased to 200 ml, but the concentration of total cyanide shall not exceed 50 mg/l. In this case, increase the volumes of the zinc- and cadmium sulfate solution (**4.7**) to 20 ml and of the buffer solution (**4.8**) to 100 ml, and the amount of zinc dust (**4.10**) to 0,6 g.

7.2 Blank test

Carry out a blank test in parallel with the determination, proceeding as specified in **7.1** and section 2, 3 or 4 as appropriate, but replacing the sample by cyanide-free water treated in the same way as the sample (see clause **6**).

7.3 Quantitative determination of cyanide ions

Proceed as specified in subsection 2 (photometric method with pyridine/barbituric acid), subsection 3 (titrimetric method with end-point determination using the Tyndall effect) or subsection 4 (titrimetric method using an indicator).

[2)] If prussiates are to be excluded omit the zinc dust.

Subsection 2. Determination of cyanide ions — Photometric method with pyridine/barbituric acid

8 Applicability

This method may be applied to absorption solutions which contain 0,002 to 0,025 mg of cyanide. This corresponds to sample concentrations in the range 0,02 to 0,25mg/l when using the full test portion volume of 100 ml specified in **7.1**. Absorption solutions with higher cyanide contents may be diluted with the sodium hydroxide solution (**10.2**); alternatively use smaller test portions in **7.1**.

The method is not applicable if oxides of nitrogen or sulfur dioxide reach the absorption vessel during separation of the cyanides. Other interferences include substances that influence the action of the chloramine-T solution.

In addition, coloured or turbid absorption solutions and absorption solutions containing compounds forming dyes cannot be analysed by this method.

In view of these possible interferences, it is recommended that the results are checked by titration with silver nitrate solution (see subsections 3 and 4).

9 Principle

Reaction of the cyanide ions with the active chlorine of chloramine-T, leading to the formation of cyanogen chloride which reacts with pyridine to form glutacondialdehyde, which, in turn, condenses with barbituric acid to form a red-violet dye.

10 Reagents

All reagents shall be of recognized analytical grade and the water used shall be distilled or deionized water.

10.1 *Buffer solution,* of pH 5,4.

Dissolve 6 g of sodium hydroxide in approximately 50 ml of water. Add 11,8 g of succinic acid ($C_4H_6O_4$), and dilute with water to 100 ml.

10.2 *Sodium hydroxide,* solution, c(NaOH) = 0,4 mol/l.

10.3 *Potassium cyanide* (KCN).

10.4 *Chloramine-T,* solution.

Dissolve 0,5 g of chloramine-T trihydrate ($C_7H_7ClNNaO_2S.3H_2O$) in water in a 50 ml one-mark volumetric flask and dilute to the mark.

Prepare a fresh solution each week.

10.5 *Pyridine/barbituric acid,* solution.

Place 3 g of barbituric acid ($C_4H_4N_2O_3$) in a 50 ml one-mark volumetric flask, wash down the walls of the flask with just enough water to moisten the barbituric acid, add 15 ml of pyridine (C_5H_5N) and swirl to mix. Add 3 ml of the hydrochloric acid solution (**4.1**) and dilute to the mark with water.

Store overnight in a refrigerator and, if necessary, filter to eliminate any undissolved barbituric acid.

The solution is stable for 1 day if stored in the dark and for 1 week if stored in a refrigerator.

10.6 *Potassium cyanide,* standard solution corresponding to 10 mg of CN^- per litre.

Dissolve 25 mg of potassium cyanide (**10.3**) in the sodium hydroxide solution (**10.2**) and dilute with the same sodium hydroxide solution to 1 000 ml in a one-mark volumetric flask.

Standardize this solution by titration with the silver nitrate solution (**18.1**), immediately before use or once each day if numerous determinations are carried out.

11 Apparatus

Usual laboratory equipment, and

11.1 *Photometer,* with cells of optical path length 10 mm.

12 Procedure

12.1 Transfer the contents of the absorption vessel to a 25 ml one-mark volumetric flask. Rinse the absorption vessel three times with approximately 3 ml portions of water, transfer the rinsings to the flask, dilute to the mark with water and mix.

Transfer, by means of a pipette, 10 ml of this solution into a second 25 ml one-mark volumetric flask, and add, whilst mixing, 2 ml of the buffer solution (**10.1**), 4 ml of the hydrochloric acid solution (**4.2**) and 1 ml of the chloramine-T solution (**10.4**). Stopper the flask and leave for 5 ± 1 min.

Add 3 ml of the pyridine/barbituric acid solution (**10.5**), dilute with water to the mark and mix.

Measure the absorbance at 578 nm in a cell of optical path length 10 mm against a reference liquid[3)]. Carry out the measurement 20 ± 5 min after addition of the pyridine/barbituric acid solution.

Measure the absorbance of the blank test solution (**7.2**) similarly.

[3)] Prepare this reference liquid using 10 ml of the sodium hydroxide solution (**10.2**) instead of the absorption solution.

12.2 Preparation of calibration graph

12.2.1 *Preparation of standard solutions*

Transfer, by means of a pipette 2, 5, 20 and 25 ml respectively of the standard potassium cyanide solution (**10.6**) into a series of four 250 ml one-mark volumetric flasks. Dilute to the mark with the sodium hydroxide solution (**10.2**) and mix. The cyanide contents of the solutions thus prepared will be 0,0008, 0,002, 0,008 and 0,010 mg respectively. These are the values to be used when plotting the graph (**12.2.3**).

Proceed as specified in **12.1**, second and third paragraphs.

12.2.2 *Photometric measurements*

Proceed as specified in **12.1**, fourth paragraph.

12.2.3 *Plotting the graph*

Plot a graph of absorbance against the cyanide contents, in milligrams, of the solutions. The relationship between absorbance and content is linear. Check the graph from time to time, especially if new batches of chemicals are used.

13 Expression of results

The easily liberatable cyanide concentration, expressed in milligrams per litre, is given by the formula

$$\frac{(m_a - m_b)\, f_3 1\,000}{f_1 f_2 V_s}$$

where

m_a is the cyanide content, in milligrams, of the test solution read from the calibration curve;

m_b is the cyanide content, in milligrams, of the blank test solution;

V_s is the volume, in millilitres, of the test portion;

f_1 is the volume, in millilitres of the aliquot portion of absorption solution taken for analysis;

$f_2 = 0{,}97$, as the volume of the sample is increased by the addition of preservatives immediately after sampling. This factor is lowered by 0,01 for each 10 ml, if, during neutralization, more than 10 ml of reagent were used for each litre of sample;

f_3 is the volume, in millilitres, to which the absorption solution is diluted before analysis (see clauses **8** and **12.1**).

Report results in milligrams per litre, taking into account the precision shown in Table 2.

14 Precision

The precision data shown in Table 2 were obtained in interlaboratory trials; the samples were taken from the ground water of a landfill area.

15 Test report

The test report shall include the following information:

a) the reference of the method used (i.e. BS 6068-2.18, photometric method);

b) the results and the method of expression used;

c) any unusual features noticed during the determination;

d) details of any operating procedures not specified in subsections 1 and 2 of this Section of this British Standard, or regarded as optional, together with any incidents likely to have affected the results.

Table 2 — Precision data (photometric method)

Sample	Number of laboratories	Cyanide content mg/l	Comparative variation coefficient %
Potassium cyanide solution	16	4,6	6
Stabilized sample	16	0,13	31
Stabilized sample with addition of potassium cyanide	16	0,32	22

Subsection 3. Determination of cyanide ions — Titrimetric method using the Tyndall effect

16 Applicability

This method may be applied to absorption solutions which contain more than 0,005 mg of cyanide. This corresponds to sample concentrations > 0,05 mg/l when using the full test portion volume of 100 ml specified in **7.1**.

The method is not applicable if the absorption solution is turbid, although slightly turbid solutions may still be titrated. In many cases, highly turbid solutions can be "cleaned up" by shaking with 1 to 2 ml of carbon tetrachloride. Phase separation may be accelerated by using a centrifuge.

17 Principle and reactions

Formation of complex silver cyanide ions in accordance with the equation:

$$2CN + Ag^+ \rightarrow [Ag(CN)_2]^-$$

which, in the presence of an excess of silver ions, results in the precipitation of silver cyanide:

$$[Ag(CN)_2]^- + Ag^+ \rightarrow 2AgCN$$

The addition of potassium iodide improves detection of the end-point (as the solubility product of silver iodide is lower than that of silver cyanide):

$$I + Ag^+ \rightarrow AgI$$

The formation of colloidal silver iodide is indicated by the Tyndall effect.

18 Reagents

All reagents shall be of recognized analytical grade and the water used shall be distilled or deionized water.

18.1 *Silver nitrate,* solution, $c(AgNO_3)$ = 0,01 mol/l.

18.2 *Silver nitrate,* solution, $c(AgNO_3)$ = 0,001 mol/l.

Store this solution, and the burette in which it is used, in the dark. Check the titre of the solution at frequent intervals or prepare a fresh solution prior to each use from the silver nitrate solution (**18.1**).

18.3 *Potassium iodide,* solution.

Dissolve 20 g of potassium iodide in water and dilute with water to 100 ml.

19 Apparatus (see Figure 2)

Usual laboratory equipment, and

19.1 *Automatic (dark glass) burette,* of capacity 10 ml, capable of measuring volumes to an accuracy of better than 0,005 ml, or, if an automatic burette is not available, a microburette.

19.2 *Magnetic stirrer* with a black plattorm and black stirring bar.

19.3 *High intensity light source,* for example a microscope lamp with an adjustable focussing lens and a diaphragm, or a slide projector with a diaphragm or a double-beam lamp with fibre-optics system. The diameter of the aperture shall be 4 to 6 mm.

19.4 *Titration vessels,* made of glass, unmarked, of internal diameter about 25 mm and capacity 20 ml.

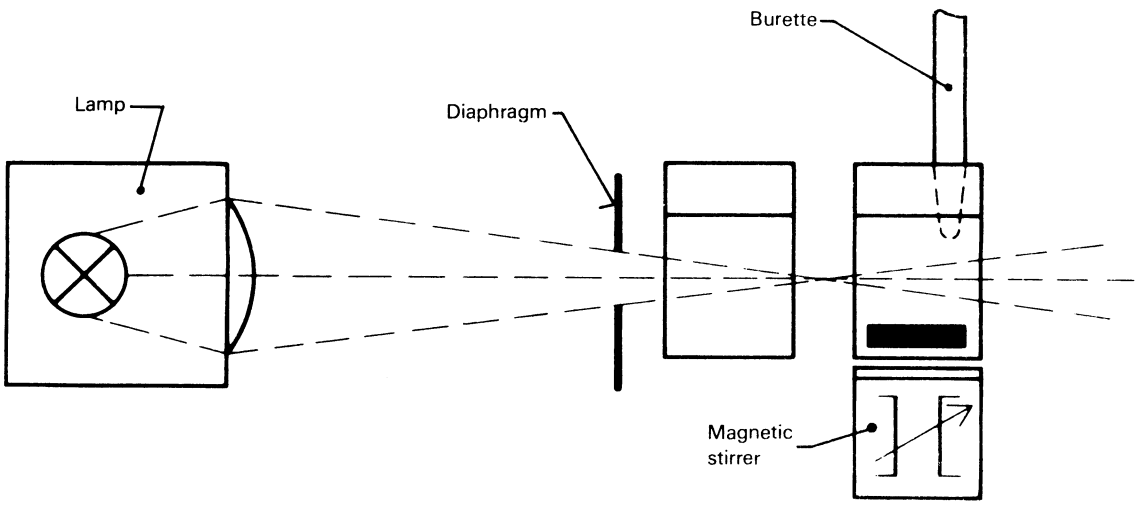

Figure 2 — Apparatus for determination of cyanide ions using Tyndall effect

20 Procedure

Transfer the contents of the absorption vessel into a 25 ml one-mark volumetric flask. Rinse the vessel three times with approximately 3 ml portions of water, transfer the rinsings to the flask, dilute to the mark with water and mix (volume $f4$).

The titration should preferably be performed in a darkened room.

Place the volumetric flask in the light beam (see Figure 2). If the solution is turbid, see clause **16**. If a Tyndall effect is not clearly visible, transfer, by means of a pipette, two 10 ml aliquot portions of the solution to two titration vessels (**19.4**) and add 1 drop of the potassium iodide solution (**18.3**) to each.

Place one titration vessel on the magnetic stirrer and add the stirring bar. Place the other vessel between the first one and the light source (see Figure 2). If a double-beam lamp is used, place the vessels side by side. Immerse the tip of the burette containing the silver nitrate solution (**18.2**) in the solution, switch on the magnetic stirrer and start the titration. Titrate slowly because the formation of silver iodide is slow.

The end-point is reached when the turbidity caused by the Tyndall effect is clearly visible. This can be easily recognized by comparison with the reference sample to which the silver nitrate solution has not been added. Record the volume of the silver nitrate solution used. If this volume is more than 5 ml transfer by means of a pipette, two smaller aliquot portions (for example 1 ml) of the solution in the volumetric flask to titration vessels and add sufficient sodium hydroxide solution (**10.2**) to bring the total volume up to 10 ml. Repeat the titration.

Exchange the titration vessels and transfer the stirring bar. Titrate the second solution to the same degree of turbidity as the first one. Record the volume of silver nitrate solution used for both titrations and calculate the mean titration (V_A).

Proceed similarly using the blank test solution. The total volume of silver nitrate solution used in the two titrations in this blank test is usually 0,02 ml but it shall not exceed 0,04 ml in each case. Calculate the mean value (V_B)

21 Expression of results

The easily liberatable cyanide concentration, expressed in milligrams per litre, is given by the formula

$$\frac{(V_A - V_B) f_1 f_4 1\,000}{f_2 f_3 V_s}$$

where

V_B is the mean volume, in millilitres, of silver nitrate solution (**18.2**) required for the two titrations in the blank test;

V_A is the mean volume, in millilitres, of silver nitrate solution (**18.2**) required for the two absorption solution titrations;

V_s is the volume, in millilitres, of the sample (see clause **7.1**);

$f_1 = 0{,}052$, i.e. the mass, in milligrams, of CN^- equivalent to 1 ml of 0,001 mol/l silver nitrate solution;

f_2 is the volume, in millilitres, of aliquot portion of absorption solution taken for titration;

$f_3 = 0{,}97$, as the volume of the sample is increased by the addition of preservatives immediately after sampling. This factor is lowered by 0,01 for each 10 ml, if, during neutralization, more than 10 ml of reagent were used for each litre of sample.

f_4 is the volume, in millilitres, to which the absorption solution is diluted before analysis (see clause **20**).

Report results in milligrams per litre, taking into account the precision shown in Table 3.

22 Precision

The precision data shown in Table 3 were obtained in interlaboratory trials; the samples were taken from the ground water of a landfill area.

23 Test report

The test report shall include the following information:

a) the reference of the method used (i.e. BS 6068-2.18 titrimetric method using the Tyndall effect);

b) the results and the method of expression used;

c) any unusual features noticed during the determination;

d) details of any operating procedures not specified in subsections 1 and 3 of this Section of this British Standard, or regarded as optional, together with any incidents likely to have affected the results.

Table 3 — Precision data (titrimetric method)

Sample	Number of laboratories	Cyanide content mg/l	Comparative variation coefficient %
Potassium cyanide solution	16	4,6	5
Stabilized sample	16	0,15	33
Stabilized sample with addition of potassium cyanide	16	0,31	19

Subsection 4. Determination of cyanide ions — Titrimetric method using an indicator

24 Applicability

This method may be applied to absorption solutions containing more than 0,05 mg of cyanide ions. This corresponds to sample concentrations > 0,5 mg/l when using the full test portion volume of 100 ml specified in **7.1**.

The method is not applicable if the absorption solution is coloured or highly turbid[4)].

25 Principle

Titration of the contents of the absorption vessel with silver nitrate solution, the silver ions, when in excess, forming a red silver complex with 5-(4-dimethylaminobenzylidene)rhodanine.

26 Reagents

All reagents shall be of recognized analytical grade and the water used shall be distilled or deionized water.

The reagents specified in clause **18**, together with

26.1 *Indicator solution*

Dissolve 0,02 g of 5-(4-dimethylaminobenzylidene)rhodanine in acetone and dilute with acetone to 100 ml.

This solution is stable for about 1 week if kept in the dark.

27 Apparatus

Usual laboratory equipment, and

27.1 *Magnetic stirrer,* with bar.

27.2 *Burette,* of capacity 10 ml.

27.3 *Titration vessels,* made of glass, of capacity 50 ml.

28 Procedure

Transfer the contents of the absorption vessel into a 50 ml beaker. Rinse the absorption vessel three times with approximately 5 ml portions of water, and add rinsings to the beaker. Add 0,1 ml of the indicator solution (**26.1**), immerse the tip of the burette containing the silver nitrate solution (**18.2**) in the solution, switch on the magnetic stirrer and titrate until the colour changes from yellow to red.

The colour is stable only for a short time.

If more than 10 ml of the silver nitrate solution (**18.2**) are necessary, carry out the titration using the silver nitrate solution (**18.1**).

Proceed similarly using the blank test solution.[5)]

The volume of the silver nitrate solution (**18.2**) used in this blank test is usually 0,08 ml, but it shall not exceed 0,2 ml.

29 Expression of results

The easily liberatable cyanide concentration, expressed in milligrams per litre, is given by the formula

$$\frac{(V_1 - V_0) \times f_1 \times 1\,000}{f_2 V_s}$$

where

V_0 is the volume, in millilitres, of silver nitrate solution (**18.2**) required for the blank test;

V_1 is the volume, in millilitres, of silver nitrate solution (**18.2**) required for the titration;

V_s is the volume, in millilitres, of the sample;

f_1 is the mass of cyanide equivalent to 1 ml of silver nitrate solution.

For solution **18.2**, f_1 = 0,052 mg of CN^-.

For solution **18.1**, f_1 = 0,52 mg of CN^-.

f_2 = 0,97, as the volume of the sample is increased by the addition of preservatives immediately after sampling. This factor is lowered by 0,01 for each 10 ml, if, during neutralization, more than 10 ml of reagent were used for each litre of sample.

Report the result to the nearest 0,1 mg/l.

30 Test report

The test report shall include the following information:

a) the reference of the method used (i.e. BS 6068-2.18 titrimetric method using an indicator);

b) the results and the method of expression used;

c) any unusual features noticed during the determination;

d) details of any operating procedures not specified in subsections 1 and 4 of this Section of this British Standard, or regarded as optional, together with any incidents likely to have affected the results.

[4)] The method may be carried out potentiometrically in which case it can be used for coloured or highly turbid solutions.

[5)] Prepare this blank test solution using 10 ml of the sodium hydroxide solution (**4.3**) and 20 ml of water.

Bibliography

MERTENS, H., *Z.f. Wasser und Abwasser-Forschung,* **9**, (1976), pp. 183–195.
MERTENS, H., *Vom Wasser,* **52**, (1979), pp. 61–74.

Publications referred to

BS 6068, *Water quality*.
BS 6068-2.17, *Determination of total cyanide.*
BS 6068-2.18, *Determination of easily liberatable cyanide.*
BS 6068-2.19, *Determination of cyanogen chloride.*
BS 6068-2.20, *Determination of cyanide by diffusion at pH 6.*

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