International Standard 6703/4

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Water quality — Determination of cyanide — Part 4 : Determination of cyanide by diffusion at pH 6

Qualité de l'eau — Dosage des cyanures — Partie 4 : Dosage des cyanures par diffusion à pH 6

First edition — 1985-05-15

UDC 543.3 : 546.267 **Ref. No. ISO 6703/4-1985 (E)**

Descriptors : water, quality, chemical analysis, determination of content, cyanides, diffusion, water pollution.

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6703/4 was prepared by Technical Committee ISO/TC 147, *Water quality*.

Contents

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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 in accordance with local official regulations.

Other chemicals specified in this part of ISO 6703 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.

This International Standard comprises four parts as follows :

Part 1 : Determination of total cyanide

Part 2 : Determination of easily liberatable cyanide

Part 3 : Determination of cyanogen chloride

Part 4 : Determination of cyanide by diffusion at pH 6

The methods described in parts 1, 2 and 3 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 ISO 6703/3, of cyanogen chloride) by stripping with a carrier gas.

The method specified in part 4 is suitable for the determination of smaller amounts of cyanide. In the presence of large amounts of copper and nickel, this method will not give quantitative results.

1 Scope and field of application

This part of ISO 6703 specifies a method for the detemination of free cyanide (see clause 2) in photographic effluents and wastewaters.

The method is applicable to water containing from 10 to 150 µg of free cyanide per litre, but higher concentrations may be determined by suitable dilution of the sample. The response is linear over the range indicated.

For possible interferences, see clause 9.

NOTES

1 The given test procedure is sophisticated and calls for care in sample storage and manipulation of the samples and equipment. The method requires practice and manual dexterity.

2 It is not the purpose of this part of ISO 6703 to specify the measurement of the amount of potentially available cyanide, but rather the amount being already present and determinable by this method (see clause 2).

2 Definition

For the purpose of this part of ISO 6703, the following definition applies.

cyanide : Under the conditions of this method, liberatable cyanide which diffuses as hydrogen cyanide (HCN) at room temperature from a solution at pH 6, including simple compounds of cyanide and its easily dissociated complexes. It does not include complexes that resist dissociation, such as iron cyanide and gold cyanide, although these chemical species can, under appropriate conditions such as heat and radiant energy, form cyanide.

3 Principle

Transfer of a test portion to a microdiffusion cell and treatment with cadmium ions to precipitate cyanoferrates. Buffering of the solution to pH 6, and diffusion of the hydrogen cyanide produced into a sodium hydroxide absorber solution. Treatment of this test solution with chloramine-T, and reaction of the cyanogen chloride (CICN) formed with barbituric acid in pyridine to form a coloured complex. Measurement of the absorbance of this complex at 580 nm, which is directly related to the amount of cyanide in the test portion.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Sodium hydroxide, 0,1 mol/l solution.

Add 4,0 g of sodium hydroxide to 800 ml water in a 1 000 ml one-mark volumetric flask. Stir until dissolved, cool the solution to room temperature, and make up to the mark with water.

4.2 Sodium hydroxide, 0,05 mol/l solution.

Dilute one part by volume of sodium hydroxide solution (4.1) with one part by volume of water.

4.3 Potassium dihydrogenphosphate (KH_2PO_4), 190 g/l solution.

Add, to 150 ml sodium hydroxide solution (ϱ = 100 g/l), 190 g potassium dihydrogenphosphate in a 2 l beaker. Add water to 800 ml to aid dissolution. Adjust the solution to pH 5,9 to 6,1 using the same sodium hydroxide solution. Transfer the solution to a 1 000 ml volumetric flask and make up to the mark with water.

4.4 Cadmium chloride ($CdCl_2$), 10 g/l solution.

Dissolve 10,0 g of anhydrous cadmium chloride in about 200 ml of water in a 1 000 ml one-mark volumetric flask and make up to the mark with water.

4.5 Chloramine-T
($C_7H_7ClNNa_2O_2S{\cdot}3H_2O$),[1] 10 g/l solution.

Dissolve 1,0 g of chloramine-T in 50 ml water in a 100 ml one-mark volumetric flask, and make up to the mark with water.

This reagent should be prepared daily.

4.6 Pyridine-barbituric acid, solution.

Add 3,0 g barbituric acid trihydrate ($C_4H_4N_2O_3{\cdot}3H_2O$) to a 50 ml one-mark volumetric flask. Wash down the sides of the flask with just enough water to moisten the barbituric acid. Add 15 ml pyridine (C_5H_5N) and swirl to mix. Add 3 ml hydrochloric acid, ϱ = 1,12 g/ml, and make up 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 at room temperature, and for 1 week if stored under refrigeration.

NOTE — The optimum wavelength for absorbance measurements may vary due to impurities in various batches of barbituric acid (see 7.3.3).

4.7 Cyanide, standard solution corresponding to about 2 mg of CN^- per litre.

4.7.1 Silver nitrate ($AgNO_3$), standard solution, 0,02 mol/l.

Dissolve 3,397 g silver nitrate in water in a 1 000 ml one-mark volumetric flask and make up to the mark with water.

Store in an amber glass bottle.

4.7.2 Cyanide, stock solution, $\varrho(CN^-) \approx 1{,}0$ g/l.

Dissolve 2,5 g potassium cyanide in 500 ml sodium hydroxide solution (4.2) in a 1 000 ml one-mark volumetric flask, and make up to the mark with sodium hydroxide solution (4.2).

Standardization of the cyanide stock solution is carried out by potentiometric titration with silver nitrate to form silver cyanide as follows. Standardize the solution periodically or before use, as appropriate.

Transfer 20,0 ml of the stock solution to a glass beaker on a magnetic stirring apparatus. Immerse the electrodes [5.6 and 5.7, appropriately connected to the pH meter (5.8)] in the solution, turn on the stirrer, and add silver nitrate solution (4.7.1) in small increments from a burette.

Record the potential indicated by the pH meter after each increment, then plot these potentials against the volume of silver nitrate added, producing a sharp bend near the equivalence point. The end-point of the titration is at the intersection of the vertical and horizontal parts of the titration curve, and 1 ml of silver nitrate solution is equivalent to 1,04 mg of cyanide.

Alternative methods for standardization may be used.

4.7.3 Cyanide, standard solution.

In a 1 000 ml volumetric flask, place a volume of 100 ml of cyanide stock solution (4.7.2). Make up to the mark with sodium hydroxide solution (4.2). Dilute in the same way a volume of 20 ml of the solution thus obtained to 1 000 ml.

After the second dilution, the final concentration is about 2 mg/l. The exact value is derived from the value found in the standardization of the stock solution.

Prepare both solutions daily or as required.

1 ml of this standard solution contains about 2 µg of CN^-.

4.8 Phosphoric acid-dihydrogenphosphate, buffer solution.

Add 8,0 ml phosphoric acid, ϱ = 1,70 g/ml, to 100 ml of potassium dihydrogenphosphate solution (4.3).

4.9 Petroleum jelly.

1) *N*-chloro-4-toluenesulfonamide, sodium salt trihydrate.

5 Apparatus

Usual laboratory equipment, and

5.1 Diffusion cell, of glass or porcelain, for example see the figure. The cell shall be fitted with a glass cover-plate with one surface ground, capable of achieving an airtight seal.

5.2 Micropipettes or **calibrated syringes**, to deliver 0,10, 0,50; or 1,00 ml.

5.3 Spectrometer, fitted with tungsten lamp, suitable for measurements between 570 and 594 nm, and equipped with optical cells of thickness 10 mm with watertight stoppers.

NOTE — Optical cells of different thicknesses may be used.

5.4 Adjustable pipette or **syringe**, to deliver 1,30 ml.

5.5 Calomel reference electrode, with saturated KNO_3 electrolyte, or equivalent.

5.6 Silver electrode.

5.7 pH meter, with millivolt scale.

6 Sampling and samples

Immediately after sampling, laboratory samples shall be adjusted with sodium hydroxide solution (4.1) to above pH 10 for preservation. Samples should be analysed as quickly as possible after sampling, and in any case within 24 h. Tests have shown that diffused cyanide samples in strong sodium hydroxide solution are stable for 4 days. Samples shall be kept in the dark because light can decompose complex cyanide and give high values.

7 Procedure

NOTE — The volumes of reagents given in the procedure are for use with the microdiffusion and optical cell sizes given. Different volumes will be required for different cell sizes.

7.1 Test portion

Pipette 3,00 ml of the laboratory sample (clause 6) into the outer ring of a clean, dry microdiffusion cell (5.1). With samples of free cyanide content exceeding 150 µg/l, add either a smaller volume of laboratory sample or 3,00 ml of a pre-diluted solution (using water) of the laboratory sample into the outer ring of the microdiffusion cell.

Using an adjustable pipette (5.4), introduce 1,30 ml (other volumes may be used) of sodium hydroxide solution (4.1) into the centre chamber of the cell. At this time, smear the ground glass side of a glass cell cover plate with a sufficiently heavy layer of petroleum jelly (4.9) or stopcock grease to achieve an airtight seal.

Using a micropipette (5.2), transfer 0,5 ml cadmium chloride solution (4.4) into the test portion in the outer ring of the microdiffusion cell. Carefully tilt and rotate the cell for 15 s to ensure mixing. This shall be done so as to mix the solution thoroughly without spilling or splashing liquid from one compartment to the other.

Immediately inject 1,0 ml of potassium dihydrogenphosphate solution (4.3) into the test portion. Quickly seal the cell with the greased glass plate. Tilt and rotate the cell for 15 s to ensure proper mixing. (Avoid spilling and splashing from one compartment to the other.)

Keep the covered cell in the dark for a period of at least 4 h.

7.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, using the same quantities of all the reagents as in the determination, but substituting water for the test portion.

7.3 Calibration

7.3.1 Preparation of the set of calibration solutions

Pipette 0,50; 2,50; 5,00; and 7,50 ml of cyanide standard solution (4.7) into four 100 ml one-mark volumetric flasks, and dilute to the mark with sodium hydroxide (4.2). The dilutions yield calibration solutions containing approximately 10; 50; 100; and 150 µg/l cyanide, respectively.

7.3.2 Colour development

Treat each calibration solution in accordance with 7.1.

At the end of the diffusion period, transfer 1,00 ml of each solution from the centre chamber of the microdiffusion cell into clean, dry optical cells (5.3), fitted with watertight stoppers.

Add 0,10 ml of buffer solution (4.8) to each optical cell. Seal the cells and invert four to five times to mix.

Add 0,50 ml chloramine-T solution (4.5) to each optical cell. Seal the cells and invert four to five times to mix. Complete mixing at this point is critical.

After 5 min add 1,00 ml pyridine-barbituric acid solution (4.6) to each optical cell. Note the time, seal the cells and invert eight to 10 times to mix.

NOTE — As an alternative, colour development may be carried out in small one-mark volumetric flasks of, for example, capacity 5,00 or 10,00 ml using water or buffer solution (4.8) to make the solution up to the mark before thorough mixing.

7.3.3 Spectrometric measurements

After 15 min, read the absorbance of each solution against water as calibration compensation solution at the optimum wavelength determined as follows.

Due to impurities present in various batches of barbituric acid, the optimum wavelength for absorbance measurements has been found to vary from 578 to 586 nm. For each new bottle of barbituric acid used, a wavelength scan shall be run to determine the optimum wavelength (near 580 nm) using the 100 µg/l cyanide calibration solution. Proceed according to 7.3.2 and about 5 min after adding the pyridine-barbituric acid solution, follow either 7.3.3.1 or 7.3.3.2.

7.3.3.1 If the laboratory is equipped with a recording spectrometer, then a scan shall be performed according to the manufacturer's instructions.

7.3.3.2 If the laboratory is not equipped with a recording spectrometer, then the scan shall be made manually (within a 5 min period). Set the wavelength knob at 570 nm and zero the instrument. Slowly increase the wavelength to 594 nm, observing at which wavelength the maximum absorbance is obtained.

7.3.4 Plotting the calibration graph

Plot a calibration graph of concentration of cyanide versus absorbance using the blank test value for the zero member. A new calibration graph based upon a set of freshly prepared calibration solutions shall be established with every new batch of barbituric acid (see 7.3.3).

7.4 Determination

7.4.1 Colour development

At the end of the diffusion period, transfer 1,00 ml of the solution from the centre chamber of the microdiffusion cell (7.1) into a clean, dry optical cell (5.3) fitted with a watertight stopper.

Add 0,10 ml of buffer solution (4.8) to the optical cell. Seal the cell and invert four to five times to mix.

Add 0,50 ml chloramine-T solution (4.5) to the optical cell. Seal the cell and invert four to five times to mix. Complete mixing at this point is critical.

Add 1,00 ml pyridine-barbituric acid solution (4.6) to the optical cell. Note the time, seal the cell and invert eight to 10 times to mix.

7.4.2 Spectrometric measurements

After 15 min, read the absorbance of the solution against water as compensation solution at the optimum wavelength determined as indicated in 7.3.3.

NOTE — The total volume of liquid in the optical cell is 2,6 ml, which is normally sufficient to fill it. If not, the buffer volume may be increased by a standard amount. This will require a different calibration graph.

Alternatively, if volumetric flasks (see the note to 7.3.2) were used for colour development for the calibration graph, use volumetric flasks of the same capacity to those used previously and make the solution up to the mark with water or buffer solution (4.8).

8 Expression of results

8.1 Calculation

The mass concentration, ϱ, expressed in micrograms per litre, of cyanide, of the sample may be read directly from the calibration graph (see 7.3), if an undiluted 3 ml test portion of the laboratory sample (clause 6) has been introduced into the microdiffusion cell, or alternatively is given by the equation

$$\varrho = \frac{(A - A_0)\, f\, V_{max}}{V}$$

where

A is the absorbance of the sample;

A_0 is the absorbance of the blank;

f is the calibration factor, expressed in micrograms per litre (the reciprocal of the slope of the calibration graph);

V_{max} is the maximal volume, in millilitres, of the test portion (3 ml);

V is either the actual volume, in millilitres, of the test portion (i.e. when less than 3 ml), or where 3 ml of a pre-diluted test portion has been used it is equal to 3 ml divided by the ratio of the final and initial volumes of the solutions when the dilution took place.

(V and V_{max} are only necessary if either a smaller test portion than 3 ml or a pre-diluted test portion were introduced into the microdiffusion cell.)

8.2 Bias

Results of determinations on solutions containing known amounts of diffusable cyanide in type II reagent water and selected water media, are given in the table.

Table — Determination of known amounts of cyanide

Sample	Amount of cyanide added	Amount of cyanide found	Bias	Statistically significant (95 % confidence level)
	µg/l	µg/l	%	
Reagent water	32	31	−1,9	no
	80	76	−5,0	yes
	144	138	−4,2	yes
Water of choice	32	31	−4,0	no
	80	74	−7,5	yes
	144	130	−9,7	yes

9 Interferences

9.1 Sulfite

Sulfite at levels above 0,25 mg/l results in low cyanide values.

9.2 Formaldehyde

Formaldehyde present in typical effluents complexes with cyanide to form cyanohydrin. Increasing amounts of formaldehyde result in decreasing amounts of free cyanide determined due to the formation of cyanohydrin.

NOTE — Cyanohydrin, thiocyanate and cyanogen bromide do not interfere with the analysis.

10 Test report

The test report shall contain the following information :

a) a reference to this part of ISO 6703;

b) the date and place of testing;

c) a precise identification of the sample;

d) any deviation from the procedure specified or any other circumstances that may have affected the results.