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Water quality — Determination of total cyanide and free cyanide using flow analysis (FIA and CFA) —

Part 1:
Method using flow injection analysis (FIA)

Qualité de l'eau — Dosage des cyanures totaux et des cyanures libres par analyse en flux (FIA et CFA) —

Partie 1: Méthode par analyse avec injection de flux (FIA)

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 14403-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

ISO 14403 consists of the following parts, under the general title *Water quality — Determination of total cyanide and free cyanide using flow analysis (FIA and CFA)*:

— *Part 1: Method using flow injection analysis (FIA)*

— *Part 2: Method using continuous flow analysis (CFA)*

Introduction

Methods using flow analysis automate wet chemical procedures and are particularly suitable for the processing of many analytes in water in large series of samples at a high frequency of analysis.

Analysis can be performed by flow injection analysis (FIA) or continuous flow analysis (CFA). Both methods share the feature of an automatic introduction of the sample into a flow system (manifold) in which analytes in the sample react with reagent solutions on their way through the manifold. Sample preparation may be integrated in the manifold. The reaction product is measured in a flow detector (e.g. flow photometer).

See the foreword for a list of parts of this International Standard.

It should be investigated whether and to what extent particular problems require the specification of additional marginal conditions.

Water quality — Determination of total cyanide and free cyanide using flow analysis (FIA and CFA) —

Part 1:
Method using flow injection analysis (FIA)

WARNING — Persons using this part of ISO 14403 should be familiar with normal laboratory practice. This part of ISO 14403 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this part of ISO 14403 be carried out by suitably trained staff.

1 Scope

This part of ISO 14403 specifies methods for the determination of cyanide in various types of water (such as ground, drinking, surface, leachate, and waste water) with cyanide concentrations from 2 µg/l to 500 µg/l expressed as cyanide ions in the undiluted sample. The range of application can be changed by varying the operation conditions, e.g. by diluting the original sample or using a different injection volume.

In this part of ISO 14403, a suitable mass concentration range from 20 µg/l to 200 µg/l is described.

Seawater can be analysed with possible changes in sensitivity and adaptation of the reagent and calibration solutions to the salinity of the samples.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical and laboratory use — Specification and test methods*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
free cyanide
easily liberatable cyanide
sum of cyanide ions and the cyanide bound in weak metal cyanide complexes that liberate HCN at pH 3,8

3.2
total cyanide
free cyanide (3.1), and in addition stronger metal–cyanide complex compounds, with the exception of cyanide bound in gold, platinum, cobalt, ruthenium, and rhodium complexes from which recovery can be partial

4 Interferences

4.1 Interferences by oxidizing agents

Oxidizing agents such as chlorine decompose most of the cyanides. If the presence of oxidizing agents cannot be excluded, treat the sample immediately after sampling. Test a drop of the sample with potassium iodide-starch test paper (KI starch paper); a blue colour indicates the need for treatment. Add sodium thiosulfate, a few crystals at a time, until a drop of sample produces no colour on the indicator paper.

Carry out a holding time study at the sampling point in order to determine whether the sample is stable for the time period for preservation and whether the preservation is effective. If this preservation is ineffective, online measurement instrumentation may be required.

4.2 Interferences by sulfide, sulfite, nitrite, and carbonyl compounds

Interferences by sulfide start at 20 mg/l. If a drop of the sample on lead acetate test paper indicates the presence of sulfide, treat an additional 25 ml of the stabilized sample (pH >12) to that required for the cyanide determination with powdered lead carbonate.

Lead sulfide precipitates if the sample contains sulfide.

Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper.

Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of lead and a long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.

Aldehydes and ketones can, under certain conditions, absorb cyanide by nucleophilic addition. To avoid this interference ethylenediamine can be added to the sample.

Interference by nitrite occurs above concentrations of 2 mg/l and can be avoided by addition of sulfamic acid (6.8) to the buffer (pH 3,8) for the gas diffusion method (6.20.1).

Sulfite interferes above concentrations of 1 mg/l.

4.3 Other interferences

Particulate matter in the sample can lead to clogging of the transport tubes and interferes with the photometric measurement. Particles of diameter >0,1 mm should be removed by filtration.

Thiocyanate can slightly interfere and lead to positive bias (9.3.2). Significant interferences can arise from cyanide impurities in thiocyanate (6.16).

5 Principle

5.1 Determination of total cyanide

Complex-bound cyanide is decomposed by UV light at pH 3,8. A UV-B lamp (emission maximum >310 nm to 400 nm) and a digestion coil of perfluoro (ethylene/propylene) (FEP) or polytetrafluorethylene (PTFE) is used to filter off UV light with a wavelength <290 nm thus preventing the conversion of thiocyanate into cyanide. A hydrolytic treatment in a thermoreactor (85 °C) assists the decomposition.

The hydrogen cyanide present at pH 3,8 is separated by diffusion at 30 °C to 40 °C across a hydrophobic membrane. Hydrogen cyanide is absorbed in a sodium hydroxide solution.

The absorbed cyanide is then determined by the reaction of cyanide with chloramine-T to cyanogen chloride. This reacts with pyridine-4-carboxylic acid and 1,3-dimethylbarbituric acid to give a red dye.

5.2 Determination of free cyanide

During the procedure specified in 5.1, the UV-B lamp is switched off when determining the free cyanide content. A thermal decomposition with a citrate and succinate buffer is performed.

To liberate cyanide from the nickel complex, 50 µl tetraethylenepentamine solution (6.11) per 30 ml sample shall be added prior to the analysis (see Reference [8]).

For detection, see 5.1.

6 Reagents

WARNING — KCN, $K_2Zn(CN)_4$, their solutions, and wastes are toxic. Waste containing these substances shall be removed appropriately.

Use only reagents of recognized analytical grade.

Smaller portions of the following solutions can be applied provided the ratios of the prescribed volumes and mass concentrations are maintained.

6.1 Water, grade 1, as defined in ISO 3696.

6.2 Hydrochloric acid, c(HCl) = 1 mol/l.

6.3 Sodium hydroxide solution I, carrier solution, c(NaOH) = 0,4 mol/l (C2 in Figure A.1).

6.4 Sodium hydroxide solution II, c(NaOH) = 1,0 mol/l.

6.5 Sodium hydroxide solution III, c(NaOH) = 0,01 mol/l.

6.6 Citric acid monohydrate, $C_6H_8O_7 \cdot H_2O$.

6.7 Succinic acid, $C_4H_6O_4$.

6.8 Sulfamic acid, H_3SO_3N.

6.9 Disodium ethylenediamine tetraacetic acid, Na_2EDTA, $C_{10}H_{14}N_2O_8Na_2$.

6.10 Tetraethylenepentamine, $C_8H_{23}N_5$.

6.11 Tetraethylenepentamine solution (for free cyanide only).

Dissolve 0,75 g of tetraethylenepentamine (6.10) in 250 ml of water.

This solution is stable for 1 month if stored at room temperature.

6.12 Potassium cyanide, KCN.

6.13 Chloramine-T trihydrate, $C_7H_7ClNNaO_2S \cdot 3H_2O$.

6.14 1,3-Dimethylbarbituric acid, $C_6H_8N_2O_3$.

6.15 Pyridine-4-carboxylic acid, $C_6H_5NO_2$.

6.16 Potassium thiocyanate, KSCN.

6.17 Potassium hexacyanoferrate(III), $K_3Fe(CN)_6$.

6.18 Cyanide standards.

6.18.1 Potassium cyanide solution, KCN, ρ_{CN} = 1 000 mg/l (see Annex B).

Dissolve 2 500 mg ± 1 mg of potassium cyanide, KCN (6.12), in sodium hydroxide solution III (6.5) in a 1 000 ml volumetric flask, and make up to volume with sodium hydroxide solution III (6.5).

This solution is stable for 6 months at 2 °C to 8 °C.

Alternatively, a potassium tetracyanozincate solution (6.18.2) may be used.

6.18.2 Potassium tetracyanozincate solution, $K_2Zn(CN)_4$, ρ_{CN} = 1 000 mg/l ± 2 mg/l, commercially available.

This solution is stable for 6 months at 2 °C to 8 °C.

6.18.3 Cyanide solution I, ρ_{CN} = 10 mg/l.

Pipette 1 ml of the potassium tetracyanozincate solution I (6.18.2) or 1 ml of the potassium cyanide solution (6.18.1) into a 100 ml volumetric flask, and make up to volume with sodium hydroxide solution III (6.5).

This solution is stable for 1 week if stored at 2 °C to 8 °C.

6.19 Calibration solutions.

Prepare at least five calibration solutions with cyanide concentrations, regularly distributed over the working range, by appropriate dilution of the cyanide solution I (6.18.3). If, for example, six calibration solutions should be prepared, proceed as follows.

Pipette 10 ml of the cyanide solution I (6.18.3) into a 100 ml volumetric flask, and make up to volume with sodium hydroxide solution III (6.5). This solution contains 1 mg/l cyanide.

Pipette, into 50 ml volumetric flasks, 1 ml, 3 ml, 5 ml, 6 ml, 8 ml, or 10 ml, respectively, of the previously mentioned 1 mg/l cyanide solution and make up to volume with sodium hydroxide solution III (6.5).

These solutions contain 20 µg/l, 60 µg/l, 100 µg/l, 120 µg/l, 160 µg/l, and 200 µg/l of cyanide, respectively [except for corrections in the concentration found on titration of the potassium cyanide solution (6.18.1), (see Annex B].

These solutions are stable for 2 d if stored in a refrigerator at 2 °C to 8 °C.

6.20 Reagents for the determination of cyanide.

6.20.1 Buffer, pH 3,8, for gas diffusion method.

Dissolve, in about 350 ml water (6.1), 10,5 g of sodium hydroxide, 12,0 g of Na_2EDTA (6.9), 15,2 g of succinic acid (6.7), 27,0 g of citric acid monohydrate (6.6), and 12,5 g of sulfamic acid (6.8). Dilute to 500 ml with water.

This solution is stable for 1 week if stored in a refrigerator (1 °C to 5 °C).

NOTE The decomposition is performed with a citrate and succinate buffer, because this buffer has a higher capacity at pH 3,8 than a pure citrate buffer. Citrate and EDTA are added, because of their ability to support the decomposition of hexacyanoferrate. EDTA also avoids the precipitation of insoluble cyanides in the thermoreactor. Sulfamic acid is added to remove nitrite (see 4.2).

6.20.2 Buffer solution for the final photometric determination (R1 in Figure A.1).

Dissolve 7,0 g of sodium hydroxide (NaOH) in 250 ml of water. Add 35,4 g of succinic acid (6.7) and dilute to 500 ml with water.

The solution has a pH of approximately 4,3. When mixed with sodium hydroxide solution I (6.3; C2 in Figure A.1) a pH of 5,2 shall be achieved.

This solution is stable for 1 week if stored in a refrigerator at 1 °C to 5 °C.

6.20.3 Chloramine-T trihydrate solution (R2 in Figure A.1).

Dissolve 0,14 g of chloramine-T (6.13) in 100 ml of water.

This solution is stable for 1 week if stored in a refrigerator at 1 °C to 5 °C.

For best results, prepare the solution daily.

6.20.4 Colour reagent (R3 in Figure A.1).

Carefully dissolve, in a 1 000 ml volumetric flask, 7,0 g of sodium hydroxide, NaOH, in about 500 ml of water (6.1). Add 16,8 g ± 0,1 g of 1,3-dimethylbarbituric acid (6.14), and 13,6 g ± 0,1 g of pyridine-4-carboxylic acid (6.15), and dilute to approximately 975 ml with water (6.1).

If necessary, adjust the solution to pH 5,2 with hydrochloric acid (6.2) or sodium hydroxide solution II (6.4).

Make up to 1 000 ml with water (6.1). Mix this solution intensively (e.g. by using a magnetic stirrer) for 1 h at 30 °C and then filter over a pleated filter (e.g. hardened ashless paper).

This solution is stable for 1 month if stored in a refrigerator at 2 °C to 5 °C.

6.21 Thiocyanate solution, calculated cyanide concentration: ρ_{CN} = 100 mg/l.

Dissolve, in a 1 000 ml volumetric flask, 373 mg ± 1 mg of potassium thiocyanate (6.16) in sodium hydroxide solution III (6.5), and make up to volume with sodium hydroxide solution III (6.5).

This solution is stable for 2 months if stored in an amber bottle and refrigerated at 1 °C to 5 °C.

6.22 Potassium hexacyanoferrate(III) solution, calculated cyanide concentration ρ_{CN} = 10 mg/l.

6.22.1 Concentration, ρ_{CN}: 1 000 mg/l.

Dissolve, in a 100 ml volumetric flask, 211 mg ± 1 mg of potassium hexacyanoferrate(III) (6.17) in sodium hydroxide solution III (6.5), and make up to volume with sodium hydroxide solution III (6.5).

6.22.2 Concentration, ρ_{CN}: 10 mg/l.

Make up to volume, in a 100 ml volumetric flask, 1 ml of 1 000 mg/l CN solution (6.22.1) with sodium hydroxide solution III (6.5).

This solution is stable for 2 months if stored in a refrigerator at 1 °C to 5 °C.

7 Apparatus

Usual laboratory apparatus and in particular the following.

7.1 Flow injection analysis system for gas diffusion method.

7.1.1 General. A suitable example of the system contains the components specified in 7.1.2 to 7.1.11 (see Figure A.1). Alternative systems are also applicable if the requirements of Clause 9 are achieved.

7.1.2 Autosampler, or other device allowing a reproducible introduction of the sample.