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Water quality — Determination of total cyanide — Method using segmented flow injection, in-line ultraviolet digestion analysis by gas diffusion and amperometric detection

Qualité de l'eau — Dosage du cyanure total — Méthode utilisant l'injection en flux segmenté, l'analyse par digestion UV continue par diffusion de gaz et la détection ampérométrique

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Methods using flow analysis automated wet chemical procedures are particularly suitable for the determination of many analytes in water in large sample series at a high analysis frequency.

Analyses can be performed by segmented flow injection analysis (SFIA) using the feature of an automatic dosage of the sample into a flow system (manifold) where the analyte in the sample is digested with ultraviolet radiation at 312 nm and the reagent solutions on its way through the manifold. The reaction product is measured by a flow detector (for example amperometer).

Speciation of cyanide species can be inferred by comparing free cyanide in accordance with ISO 17690:2015, available weak and dissociable cyanide in accordance with ISO 20950-1, and total cyanide using this method.

Water quality — Determination of total cyanide — Method using segmented flow injection, in-line ultraviolet digestion analysis by gas diffusion and amperometric detection

IMPORTANT NOTE — – The performance of this method has been established for a range of sample matrices, which are reported in ANNEX C. These matrices represent environmental, mining influenced and metallurgical process samples. This method is therefore recommended for mining impacted samples. Caution is recommended for the application of alternative ISO methods to mining influenced and metallurgical process samples if those matrices are not explicitly mentioned in the scope; as potential biases and interferences typical for them have not been sufficiently investigated and may not be properly mitigated.

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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 neutralization and proper disposal of waste solutions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

1 Scope

This document specifies operationally defined methods for the determination of total cyanide in various types of water such as drinking water, ground water, surface water, wastewaters, metallurgical processing tailings reclaim solution, heap leach barren solution, mill slurry tailings filtrate and leaching solutions, with cyanide concentrations from 5 µg/l to 2 000 mg/l expressed as cyanide ions in the undiluted sample. The range of application can be extended by reducing the sensitivity (Figure A.1.).

NOTE ISO 2080:2008, 3.105, defines free cyanide. The concentration of total cyanide as defined in ISO 2080:2008, 3.191 includes free cyanide, cyanide complexed with metals in solution as cyanide anion, but not necessarily all of the metal cyanide complexes present as determined by a specified analytical method.

In this method, six suitable mass concentration ranges from 5 µg/l to 50 µg/l, from 50 µg/l to 500 µg/l, from 0,5 mg/l to 5 mg/l, from 5 mg/l to 50 mg/l, from 50 mg/l to 500 mg/l and from 500 mg/l to 2 000 mg/l are described.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 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.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
total cyanide
sum of HCN, cyanide ions and cyanide bound in the metal-cyano complexes that are dissociated, using digestion in the presence of ultraviolet (UV) radiation at 312 nm and sulfuric acid into HCN/CN^- in accordance with this document

4 Principle

In the analytical procedure employed for determination of total cyanide the sample is treated with ultraviolet (UV) radiation at 312 nm and sulfuric acid resulting in the release of bound cyanide ion from some metal-cyano complexes. Cyanide is not totally released from the more stable gold and cobalt cyanide complexes.

The sample is introduced into a carrier solution of the segmented flow analysis (SFA) system via a valve and confluence downstream with a sulfuric acid solution containing sulfide removal reagent and digested in the presence of UV radiation at 312 nm to measure total cyanide. The released hydrogen cyanide (HCN) gas diffuses through a hydrophobic gas diffusion membrane into an alkaline acceptor stream where the CN^- is captured and sent to an amperometric flow cell detector with a silver-working electrode. In the presence of cyanide, silver electrode surface is oxidized at the applied potential (E_{app} = 0,0 V vs. the reference electrode). The anodic current measured is proportional to the concentration of cyanide in the standard or sample injected.

Calibrations and sample data are processed with the instrument's data acquisition software.

The user should be aware that the described method is operationally defined, the analytical protocol of the standard has to be followed strictly to assure comparable results and the actual method conditions used can affect the result obtained.

5 Interferences

5.1 Interferences by oxidizing agents

Oxidizing agents react with cyanide causing low results. The presence of oxidizing agents shall be tested and treated, if present, just prior to pH adjustment for cyanide measurement.

5.2 Interferences by sulfide

Sulfide will diffuse through the gas diffusion membrane and can be detected in the amperometric flow cell, causing the measurement to be biased high. Oxidized products of sulfide can also rapidly convert CN^- to SCN^- at a high pH. A two-stage process is specified for sulfide removal. The initial lead carbonate (6.9.4) addition treatment stage and filtration shall be carried out as soon as possible. The sulfide removal and acidification reagent (6.8.14) is specified in this method. Its use will ensure removal of sulfide interference up to 50 mg/l of sulfide. This shall be applied and analysis completed within 24 h of taking the sample (see Clause 8).

NOTE In the absence of sulfide in the samples 0,1 mol/l HCl (6.2) as acidification as practiced in the original USEPA method 1677 can also be used.

6 Reagents

WARNING — Cyanide solutions and wastes are toxic. Waste containing these substances shall be removed appropriately. Perform work in a fume hood. Avoid contacting cyanides with acids and aeration. Harmful if swallowed and if inhaled, very toxic to aquatic life with long lasting effects. Handle carefully using personal protective equipment and dispose properly. Oxidation of cyanide wastes is commonly used for cyanide waste detoxification. Calcium hypochlorite is suitable at pH 10, using proper ventilation to capture any cyanogen chloride generated.

Use only reagents of recognized analytical grade.

6.1 **Water**, grade 1, as specified in ISO 3696.

6.2 **Sodium hydroxide solution I**, acceptor solution, $c(\mathrm{NaOH}) = 0{,}1$ mol/l.

6.3 **Sodium hydroxide solution II**, $c(\mathrm{NaOH}) = 1{,}0$ mol/l.

6.4 **Sodium hydroxide solution III**, $c(\mathrm{NaOH}) = 0{,}01$ mol/l.

6.5 **Potassium cyanide**, KCN.

6.5.1 **Potassium cyanide solution**, KCN, $\rho(\mathrm{CN}) = 1\ 000$ mg/l, (see Annex B).

Dissolve (2 503 ± 1) mg of potassium cyanide, KCN, (6.5), in sodium hydroxide solution III (6.4) in a 1 000 ml graduated flask and make up to volume with sodium hydroxide solution III (6.4). Sodium cyanide (1 884 mg) may be substituted for potassium cyanide for stock solution preparation.

This solution is stable for six months at (5 ± 3) °C, if stored in the dark or brown bottles.

Alternatively, a potassium tetracyanozincate (2 380 mg/l) solution (6.6.1) may be used.

6.5.2 **Cyanide solution I**, $\rho(\mathrm{CN}) = 10$ mg/l.

Pipette 1,00 ml of the potassium cyanide solution (6.5.1) in a 100 ml graduated flask and bring to volume with sodium hydroxide solution III (6.4).

This solution is stable for one week at (5 ± 3) °C, if stored in the dark or brown bottles.

NOTE 1 Some laboratories substituted sodium cyanide for potassium cyanide for stock solution preparation during the interlaboratory test for ISO 20950-1.

6.6 **Potassium tetracyanozincate**, $K_2Zn(CN)_4$.

6.6.1 **Potassium tetracyanozincate solution**, $K_2Zn(CN)_4$, $\rho(\mathrm{CN}) = (1\ 000 \pm 2)$ mg/l, commercially available.

This solution is stable for six months at (5 ± 3) °C, if stored in the dark.

6.6.2 **Potassium tetracyanozincate solution I**, $\rho(\mathrm{CN}) = 10$ mg/l.

Pipette 1,00 ml of the potassium tetracyanozincate solution (6.6.1) in a 100 ml graduated flask and bring to volume with sodium hydroxide solution III (6.4).

This solution is stable for one week at (5 ± 3) °C, if stored in the dark or brown bottles.

6.7 Calibration solutions

Prepare five to ten calibration solutions with cyanide concentrations, equidistantly distributed over the working range, either by appropriate dilution of the cyanide solution I (6.5.2) or potassium tetracyanozincate solution I (6.6.2).

If, for example, six calibration solutions should be prepared to cover the range of 5 µg/l to 50 µg/l, proceed as follows:

Pipette 25 ml of the cyanide solution I (6.5.2) or potassium tetracyanozincate solution I (6.6.2), in a 500 ml graduated flask and make up to volume with sodium hydroxide solution III (6.4). This solution contains 0,5 mg/l cyanide.

Pipette, in 100 ml graduated flasks, 1 ml, 3 ml, 5 ml, 7 ml, 9 ml, and 10 ml, respectively, of the above mentioned 0,5 mg/l cyanide solution and make up to volume with sodium hydroxide solution III (6.4). These solutions contain nominally 5 µg/l, 15 µg/l, 25 µg/l, 35 µg/l, 45 µg/l, and 50 µg/l of cyanide, respectively. Correct calibration solution concentrations based the concentration found on titration of the potassium cyanide solution (6.5.1) or potassium tetracyanozincate solution (6.6.1) used, following the procedure given in Annex B by multiplying the nominal value by $\rho(\text{CN})/1\,000$ and round to the nearest µg/l. Or, for example, if six calibration solutions should be prepared to cover the range of 50 µg/l to 500 µg/l proceed as follows:

Pipette 25 ml of the cyanide solution I (6.5.2) or potassium tetracyanozincate solution I (6.6.2), in a 50 ml graduated flask and make up to volume with sodium hydroxide solution III (6.4). This solution contains 5 mg/l cyanide.

Pipette, in 100 ml graduated flasks, 1 ml, 3 ml, 5 ml, 7 ml, 9 ml, and 10 ml, respectively, of the above mentioned 5 mg/l cyanide solution and make up to volume with sodium hydroxide solution III (6.4). These solutions contain nominally 50 µg/l, 150 µg/l, 250 µg/l, 350 µg/l, 450 µg/l, and 500 µg/l of cyanide, respectively. Correct calibration solution concentrations based the concentration found on titration of the potassium cyanide solution (6.5.1), following the procedure given in Annex B by multiplying the nominal value by $\rho(\text{CN})/1\,000$ and round to the nearest µg/l.

Use calibration solutions less than or equal to 500 µg/l for samples with cyanide concentrations <500 µg/l.

6.8 Reagents for the determination of total cyanide

6.8.1 Ag/AgCl reference electrode filling solution.

Fill the reference electrode as recommended by the instrument manufacturer.

6.8.2 **Bismuth nitrate pentahydrate**, $Bi(NO_3)_3 \cdot 5H_2O$.

6.8.3 **Cyanide electrode stabilization solution**, approximately 5 mg/l as CN^-.

Pipette 500 µl of potassium cyanide solution (6.5.1) or potassium tetracyanozincate solution (6.6.1), into a 100 ml volumetric flask containing 1,0 ml of sodium hydroxide solution I (6.2). Dilute to volume with water (6.1).

This solution is stable for one week if stored at (5 ± 3) °C.

Lower cyanide concentrations can be used, provided the detector signal is near saturation and sharp, repeatable peaks are produced.

6.8.4 **Hypophosphorous acid**, H_3PO_2, 50 % solution.

6.8.5 Iron(II) cyanide stock solution, $\rho(\text{CN}) = 1\,000$ mg/l.

Weigh 0,270 5 g $K_4Fe(CN)_6 \cdot 3H_2O$ (6.8.12) into a 100 ml volumetric flask. Place 1,0 ml of 1,00 mol/l NaOH (see 6.3) in the flask and dilute to volume with water (6.1).

The solution shall be stored in an amber glass bottle under refrigeration at (5 ± 3) °C

6.8.6 Iron(II) cyanide intermediate solution, $\rho(\text{CN}) = 100$ mg/l,

Pipette 10,0 ml of the iron(II) cyanide stock solution (6.8.5) into a 100 ml volumetric flask containing 1,0 ml of 1,00 mol/l NaOH (6.3). Dilute to volume with water (6.1).

The solution shall be stored in an amber glass bottle under refrigeration at (5 ± 3) °C.

6.8.7 Iron(II) cyanide recovery solution, $\rho(\text{CN}) = 100$ µg/l.

Pipette 100 µl of iron(II) cyanide intermediate solution (6.8.6) into a 100 ml volumetric flask containing 1,0 ml of 1,00 mol/l NaOH (6.3). Dilute to volume with water (6.1). Prepare fresh daily.

6.8.8 Iron(III) cyanide stock solution, $\rho(\text{CN}) = 1\,000$ mg/l.

Weigh 0,210 9 g of $K_3Fe(CN)_6$ (6.8.11) in a 100 ml volumetric flask. Place 1,0 ml of 1,00 mol/l NaOH (6.3) in the flask and dilute to volume with water (6.1).

The solution shall be stored in an amber glass bottle under refrigeration at (5 ± 3) °C.

6.8.9 Iron(III) cyanide intermediate solution, $\rho(\text{CN}) = 100$ mg/l.

Pipette 10,0 ml of the iron(III) cyanide stock solution (6.8.8) into a 100 ml volumetric flask containing 1,0 ml of 1,00 mol/l NaOH (6.3). Dilute to volume with water (6.1).

The solution shall be stored in an amber glass bottle under refrigeration at (5 ± 3) °C.

6.8.10 Iron(III) cyanide recovery solution, $\rho(\text{CN}) = 100$ µg/l.

Pipette 100 µl of iron(III) cyanide intermediate solution (6.8.9) into a 100 ml volumetric flask containing 1,0 ml of 1,00 mol/l NaOH (6.3). Dilute to volume with water. Prepare fresh daily.

6.8.11 Potassium hexacyanoferrate(III), $K_3Fe(CN)_6$

6.8.12 Potassium hexacyanoferrate(II) trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$.

6.8.13 Sulfuric acid (I), $\rho = 1{,}84$ g/ml, mass fraction 95 % to 97 %.

6.8.14 Sulfide removal and acidification reagent.

Add 55 ml of water (6.1), to a 500 ml beaker, then carefully add 55 ml of concentrated sulfuric acid (6.8.13) to the beaker. Weigh 1 g of bismuth nitrate pentahydrate, $Bi(NO_3)_3 \cdot 5H_2O$ (6.8.2) and add it to the 500 ml beaker. Gently, stir the beaker until the bismuth nitrate pentahydrate has dissolved in the acid solution. Carefully, add approximately 250 ml of water (6.1) to the beaker with stirring and allow to cool. Then quantitatively transfer the beaker contents to a 1 l volumetric flask and fill to volume with water (6.1).

CAUTION — This is an exothermic reaction and the solution will become hot during preparation.