INTERNATIONAL STANDARD

ISO 20950-1

First edition
2018-05

Water quality — Determination of available weak and dissociable (WAD) cyanide —

Part 1: Method using ligand exchange, flow injection analysis (FIA), gas-diffusion and amperometric detection

Qualité de l'eau — Détermination du cyanure à acide faible dissociable (WAD) disponible —

Partie 1: Méthode par échange de ligand, analyse par injection en flux (FIA), diffusion gazeuse et détection ampérométrique

Reference number
ISO 20950-1:2018(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword ..... **iv**
Introduction ..... **v**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **1**
4 Interferences **2**
4.1 Interferences by oxidizing agents 2
4.2 Interferences by sulfide 2
5 Principle **2**
6 Reagents **3**
7 Apparatus **7**
8 Sampling and sample preparation **7**
8.1 General 7
8.2 Oxidizing agents 7
8.3 Sulfide removal 8
8.4 Preservation 8
9 Procedure **8**
9.1 Flow system set up 8
9.2 Reagent blank measurement 9
9.3 Checking the suitability of the flow injection system 9
9.3.1 Cyanide electrode stabilization 9
9.3.2 Performance verification of the system 9
9.4 Calibration 9
9.5 Sample measurement 10
9.5.1 General 10
9.5.2 Manual ligand addition options 10
9.5.3 Automated ligand addition 11
9.5.4 Cyanide measurement 11
10 Calculations **11**
11 Expression of results **11**
12 Test report **11**
Annex A (informative) **Examples of flow injection systems** **13**
Annex B (normative) **Determination of the real cyanide concentration in the potassium cyanide solution (6.5.1) or potassium tetracyanozincate solution (6.6.1)** **15**
Annex C (informative) **Performance data** **16**
Bibliography **17**

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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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*.

Introduction

Methods using flow analysis automate 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 flow injection analysis (FIA) using the feature of an automatic dosage of the sample into a flow system (manifold) where the analytes in the sample react with the reagent solutions on their way through the manifold. The sample preparation can be integrated into the manifold. The reaction product is measured by a flow detector (e.g. amperometer).

Water quality — Determination of available weak and dissociable (WAD) cyanide —

Part 1: Method using ligand exchange, flow injection analysis (FIA), gas-diffusion and amperometric detection

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.

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 available WAD cyanide in various types of water such as drinking, ground, and surface, waters, and metallurgical processing tailings reclaim, heap leach barren, mill slurry tailings 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 changed by varying the operation conditions, e.g. by using a different injection volume, thicker membrane, detector response, etc.

NOTE ISO 2080:2008, 3.105, defines free cyanide. The concentration of available WAD cyanide includes free cyanide and some of the metals complexed in solution as determined by a specified analytical method but not all of the metal complexes present in total cyanide (3,191).

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
available WAD cyanide
sum of HCN, cyanide ions and cyanide bound in the metal-cyano complexes that are dissociated, using ligand reagents, if necessary, and sulfuric acid into HCN/CN^- in accordance with this document

4 Interferences

4.1 Interferences by oxidizing agents

Test for the presence of oxidizing agents, which can continue to oxidize the cyanide, leading to low results.

4.2 Interferences by sulfide

Sulfide will diffuse through the gas diffusion membrane and can be detected in the amperometric flow cell, causing high results. 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 stage should be carried out as soon as possible. Lead acetate test strips might not be sensitive enough to detect low levels of sulfide; therefore, treatment should be performed on samples where sulfide is suspected. Interference can be confirmed by analysing the sample with or without treatment.

If the measured cyanide in the untreated sample is significantly higher than in the treated sample, sulfide is likely present and treatment shall be performed to remove sulfide. In addition, the use of the sulfide removal and acidification reagent (6.8.4) is specified in this method. Its use will ensure removal of sulfide interference up to 50 mg/l of sulfide. This shall be applied within 24 h of taking the sample (see Clause 8).

NOTE USEPA method OIA-1677[7] uses of 0,1 mol/l HCl as acidification reagent, in the absence of sulfide in the samples.

5 Principle

The analytical procedure employed for determination of available WAD cyanide is divided into two parts: sample pre-treatment and cyanide detection. In the pre-treatment step, proprietary or non-proprietary ligand exchange reagents are added at room temperature to the sample, if needed to release the cyanide ions from mercury and nickel cyanide complexes. The ligand-exchange reagents form thermodynamically stable complexes with the transition metal ions, including: zinc, copper, cadmium, mercury, nickel and silver resulting in the release of bound cyanide ion from some metal-cyano complexes. Cyanide is not released from the more stable iron, gold and cobalt cyanide complexes.

The sample is treated with ligand exchange reagents, if necessary, and introduced into a carrier solution of the flow injection analysis (FIA) system via an injection valve and confluence downstream with a sulfuric acid solution containing sulfide removal reagent to measure available WAD cyanide. Ligand exchange reagents are needed to release cyanide from mercury cyanide and nickel cyanide complexes when the concentrations of mercury or nickel cyanides, relative to the weak and dissociable cyanide, will increase the result by more than 5 % relative. 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 (Eapp = 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 this document has to be followed strictly to assure comparable results as the actual method conditions used can affect the result obtained.

6 Reagents

WARNING — Cyanide solutions and wastes are toxic. Waste containing these substances shall be removed appropriately.

Use only reagents of recognized analytical grade.

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

6.2 Sodium hydroxide solution I, acceptor solution, c(NaOH) = 0,1 mol/l.

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

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

6.5 Potassium cyanide, KCN.

6.5.1 Potassium cyanide solution, KCN, ρ(CN) = 1 000 mg/l, (see Annex B).

Dissolve (2 500 ± 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).

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

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

Alternatively, a potassium tetracyanozincate solution (6.6.1) may be used.

6.5.2 Cyanide solution I, ρ(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.

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

6.6.1 Potassium tetracyanozincate solution, $K_2Zn(CN)_4$, ρ(CN) = (1 000 ± 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, ρ(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, or 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 on the concentration found on titration of the potassium cyanide solution (6.5.1) or potassium tetracyanozincate solution (6.6.1) used, following the procedure in Annex B by multiplying the nominal value by ρ(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, or 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 on the concentration found on titration of the potassium cyanide solution (6.5.1), following the procedure in Annex B by multiplying the nominal value by ρ(CN)/1 000 and round to the nearest µg/l.

NOTE Use of calibration solutions less than or equal to 500 µg/l for samples with cyanide concentrations < 500 µg/l improved accuracy and precision during interlaboratory testing.

6.8 Reagents for the determination of available WAD 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 Sulfuric acid (I), ρ = 1,84 g/ml; 95 % to 97 % (mass fraction).

6.8.4 Sulfide removal and acidification reagent.

Weigh 1 g bismuth nitrate pentahydrate, $Bi(NO_3)_3 \cdot 5H_2O$ and add it to a 500 ml beaker. Add 55 ml of water (6.1), then carefully add 55 ml of concentrated sulfuric acid (6.8.3) to the 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 when preparing this solution.

6.8.5 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.

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

6.9 Ligand-exchange reagents.

6.9.1 Ligand-exchange reagent A[1)], optional proprietary organic amine reagent for nickel, follow manufacturers' instruction for preparation.

6.9.2 Ligand-exchange reagent B[2)], optional proprietary specially purified organic sulfide reagent for mercury, follow manufacturers' instruction for preparation.

6.9.3 Mixed ligand exchange reagent, for automated ligand addition as shown in Figure A.2.

Transfer 0,125 ml of WAD reagent A (6.9.1) and 0,250 ml of WAD reagent B (6.9.2) into a 100 ml volumetric flask containing 50 ml water (6.1). Dilute to volume with water (6.1) and mix. The solution should be stored at room temperature.

6.9.4 Tetraethylenepentamine, $(NH_2CH_2CH_2NHCH_2CH_2)_2NH$.

6.9.5 Ligand exchange reagent 1 (tetraethylenepentamine (TEP) solution).

Weigh 0,10 g tetraethylenepentamine (TEP) (6.9.4) into a 100 ml volumetric flask. Dilute to volume with water (6.1). The solution should be stored at room temperature. Commercially prepared or alternative ligand exchange reagents can be used if equivalent results can be demonstrated. Commercial reagents should be used in accordance with manufacturer's instructions.

6.9.6 Dithizone, $C_6H_5NHNHOSN = NC_6H_5$.

6.9.7 Ligand exchange reagent 2 (dithizone solution)

Weigh 0,010 g of dithizone (6.9.6) into a 100 ml volumetric flask containing 1 ml of 1 mol/l NaOH (6.3). Dilute to volume with water (6.1). Sonicate if necessary until all of the dithizone has dissolved. The solution should be stored at room temperature. Commercially prepared or alternative ligand exchange reagents can be used if equivalent results can be demonstrated. Commercial reagents should be used in accordance with manufacturer's instructions.

6.10 Reagents for ligand addition quality control.

6.10.1 Mercury(II) cyanide, $Hg(CN)_2$.

6.10.2 Mercury(II) cyanide stock solution.

Weigh 0,485 4 g $Hg(CN)_2$ (6.10.1) into a 100 ml volumetric flask. Place 1 ml of 1 mol/l NaOH (6.3) in the flask and dilute to volume with water (6.1). $Hg(CN)_2$ as $\rho(CN)$ = 1 000 mg/l. Store the solution in an amber glass bottle under refrigeration at (5 ± 3) °C.

1) OI Analytical WAD Reagent A, PN A001416 has been found to be suitable for this analysis.

2) OI Analytical WAD Reagent B, PN A001417 has been found to be suitable for this analysis.

6.10.3 Mercury(II) cyanide intermediate solution.

Pipette 10 ml of the mercury(II) cyanide stock solution (6.10.2) into a 100 ml volumetric flask containing 1 ml of 1 mol/l NaOH (6.3). Dilute to volume with water (6.1). $Hg(CN)_2$ as CN^- = 100 mg/l. Store the solution in an amber glass bottle under refrigeration at (5 ± 3) °C.

6.10.4 Mercury(II) cyanide recovery solution.

Pipette 100 µl of mercury(II) cyanide intermediate solution (6.10.3) into a 100 ml volumetric flask containing 1 ml of 1 mol/l NaOH (6.3). Dilute to volume with water (6.1). $Hg(CN)_2$ as $\rho(CN)$ = 100 µg/l. Prepare fresh daily.

6.10.5 Potassium nickel(II) cyanide, $K_2Ni(CN)_4 \cdot H_2O$.

6.10.6 Potassium nickel cyanide stock solution.

Weigh 0,248 8 g of $K_2Ni(CN)_4 \cdot H_2O$ (6.10.5) into a 100 ml volumetric flask. Place 1 ml of 1 mol/l NaOH (6.3) in the flask and dilute to volume with water (6.1). $K_2Ni(CN)_4$ as $\rho(CN)$ = 1 000 mg/l. Store the solution in an amber glass bottle under refrigeration at (5 ± 3) °C.

6.10.7 Potassium nickel cyanide intermediate solution.

Pipette 10 ml of the potassium nickel cyanide stock solution (6.10.6) into a 100 ml volumetric flask containing 1 ml of 1 mol/l NaOH. Dilute to volume with water (6.1). $K_2Ni(CN)_4$ as $\rho(CN)$ = 100 mg/l. Store the solution in an amber glass bottle under refrigeration at (5 ± 3) °C.

6.10.8 Potassium nickel cyanide recovery solution.

Pipette 100 µl of potassium nickel cyanide intermediate solution (6.10.7) into a 100 ml volumetric flask containing 1 ml of 1 mol/l NaOH (6.3). Dilute to volume with water (6.1). $K_2Ni(CN)_4$ as $\rho(CN)$ = 100 µg/l. Prepare fresh daily.

6.11 Reagents for sample pre-treatment and preservation.

6.11.1 Sodium acetate trihydrate, $NaC_2H_3O_2 \cdot 3H_2O$.

6.11.2 Acetic acid, CH_3COOH.

6.11.3 Acetate buffer solution.

Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) (6.11.1) in 500 ml of water (6.1). Add acetic acid (approximately 500 ml) (6.11.2) to yield a pH of 4,5.

6.11.4 Lead carbonate, $PbCO_3$, powder, dissolving 50 g/l concentration in solution is recommended prior to use.

DANGER — Harmful if swallowed or if inhaled, may cause cancer, may damage fertility or the unborn child, may cause damage to organs through prolonged or repeated exposure, very toxic to aquatic life with long lasting effects. Handle carefully using personal protective equipment and dispose properly.

6.11.5 Lead acetate test paper, commercially available.

6.11.6 Sodium arsenite, $NaAsO_2$, powder.

DANGER — Fatal if swallowed or in contact with skin; toxic if inhaled; may cause cancer; very toxic to aquatic life with long lasting effects. Handle carefully using personal protective equipment and dispose properly.

6.11.7 Potassium iodide starch test paper, commercially available.

7 Apparatus

7.1 Flow injection analysis system

A suitable example of the system is shown in Figure A.1. Alternative systems are also applicable if the requirements in Clause 9 are achieved (see Annex A for examples of flow injection systems and Annex C for the results of an interlaboratory trial for flow systems).

7.1.1 Autosampler or another device, allowing a reproducible introduction of the sample.

7.1.2 Reagent reservoirs.

7.1.3 Low pulsation pump, with specific chemically inert pump tubes, for flow rates as shown in Figure A.1 as an example.

7.1.4 Gas diffusion cell, with hydrophobic semipermeable membrane from e.g. polypropylene or PTFE, typical thickness 90 µm to 200 µm, pore size 0,1 µm to 1 µm, and minimum area of 150 mm^2 in contact with acceptor solution. The gas diffusion membrane should be replaced when the baseline becomes noisy, or every 1 to 2 weeks.

7.1.5 Manifold with highly reproducible dosing of sample and reagents, with appropriate transport systems and connection assemblies made of chemically inert polymers.

7.1.6 Amperometric detector, with flow cell, to include a silver working electrode, a Ag/AgCl reference electrode, and a Pt or stainless steel counter electrode.

7.1.7 Recording unit (e.g. strip chart recorder, integrator or printer/plotter).

In general, signal peak height is measured. Use the computer hardware and software recommended by the instrument manufacturer to control the apparatus and to collect data from the detector.

7.2 Additional apparatus, materials and measuring device.

7.2.1 Syringe membrane filter assembly, with membrane filters having a pore size 0,45 µm.

7.2.2 pH meter and electrode, capable of measuring ±0,1 pH units.

8 Sampling and sample preparation

8.1 General

Refer to Clause 4 on interferences and treat samples prior to adjusting pH.

8.2 Oxidizing agents

Acidify KI starch paper (6.11.7) by moistening with acetate buffer solution (6.11.3). Add a drop of the sample to the test paper as soon as the sample is collected; a blue color indicates the need for treatment.

If oxidizing agents are present, add powdered or a concentrated solution of sodium arsenite (6.11.6) (0,1 g/l sample) to the sample to avoid degradation of cyanide and mix well. Repeat this test until a drop of treated sample no longer produces a blue colour on the acidified KI starch test paper. Check the sample holding time of treated samples for new sampling points when sodium arsenite (6.11.6) is used to mitigate the presence of oxidizing agents. Sodium arsenite (6.11.6) is highly toxic and a potential carcinogen.

Since sodium arsenite (6.11.6) has a very high water solubility, it should be added as a concentrated solution to reduce risk with solid reagent

8.3 Sulfide removal

Test for sulfide by moistening lead acetate paper (6.11.5) with acetate buffer solution (6.11.3), then add a drop of sample on the lead acetate paper. If the paper turns black, sulfide is present. Add powdered lead carbonate (6.11.4) (0,1 g/l of sample) and mix. Repeat this test until a drop of treated sample no longer darkens the acidified lead acetate test paper. Immediately filter the supernatant containing cyanide to avoid the rapid loss of cyanide due to the formation of thiocyanate.

8.4 Preservation

Immediately after sampling bring the pH of the water samples to 11 ± 0,1 with sodium hydroxide solutions I to III (6.2 to 6.4) such that the quantity of added alkaline yields a negligible dilution of the sample. Alternatively, bring the pH of the water samples to 11 ± 0,1 by adding sodium hydroxide pellets (1 to 2 pellets per 500 ml). Avoid excess preservation, as it can result in problems with a low recovery and/or poor peak shape of available WAD cyanide during analysis.

If sodium hydroxide pellets are used, take care not to raise the pH above 11,1.

If sample appears turbid, remove particles by filtration at 0,45 µm or decantation at the laboratory and record the method used.

Analyse the sample in accordance with Clause 9 as soon as possible after sampling, at the latest within 6 d, but as specified in ISO 5667-3, no longer than 1 d if sulfide is present. Collect and store samples in containers which protect the samples from UV light. Refrigerate at (5 ± 3) °C if immediate analysis is delayed.

9 Procedure

9.1 Flow system set up

Set up and adjust the flow analysis system according to Table 1. When working at the higher ranges of the method, thicker gas permeable membranes, smaller sample loops, and dilutions may be used and the detector sensitivity may be reduced.

Table 1 — Adjustment of flow injection analysis system

FIA instrument parameter	Recommended method setting
Pump flow rates	0,5 ml/min to 2,0 ml/min
Cycle period (total)	120 s maximum
Sample load period	At least enough time to completely fill the sample loop prior to injection
Injection valve rinse time between samples	At least enough time to rinse the sample loop and achieve baseline resolution between peaks
Peak evaluation	Peak height or area
Working potential	0,0 V vs. Ag/AgCl

Turn on the power to the apparatus and the auto-sampler (if equipped).

Clamp the pump tube platens in place and start pumping reagents in the flow injection system.

Start the data acquisition system.

Pump reagents for 10 min to 30 min to establish a steady baseline. The analyser is ready for use when the baseline is stable.

Proceed according to 9.2 to 9.5.

9.2 Reagent blank measurement

Pump reagents through all the tubes and verify that there are no leaks and no air in the sample or reagent tubing. Adjust the detector to 0,0 V.

Wait for a steady baseline and ensure that the baseline noise is low enough to attain a minimum 2:1 Signal to Noise ratio for the lowest calibration standard. Use the sodium hydroxide solution III (6.4) as the reagent blank solution.

9.3 Checking the suitability of the flow injection system

9.3.1 Cyanide electrode stabilization

Inject the stabilization solution (6.8.5) into the apparatus and record the amperometric response (current value) after the cycle period has been completed.

Repeat this procedure until the peak responses are less than 2 % RSD. This process will ensure that the electrode system has stabilized.

After the electrode system has stabilized, aspirate the highest working standard (6.7) into the flow injection apparatus.

Follow the instrument manufacturer's instructions to store the retention time window for cyanide using the data acquisition software.

9.3.2 Performance verification of the system

If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., perform a precision and bias study to demonstrate laboratory capability.

Analyse seven replicates of an independent reference solution containing 25 µg/l available WAD cyanide as CN^- in the low range of 5 µg/l to 50 µg/l. Analyse seven replicates of an independent reference solution containing 250 µg/l available WAD cyanide as CN^- in the higher range from 50 µg/l to 500 µg/l. The matrix of the solution should be equivalent to the solution samples to be analysed. Take each replicate through the complete analytical procedure. The replicates may be interspersed with samples.

Calculate the mean and standard deviation of the seven values.

— The mean should range from 22 µg/l CN^-, to 28 µg/l CN^-, and the standard deviation should be less than 2 µg/l CN^-, in the low range of 5 µg/l to 50 µg/l.

— The mean should range from 237 µg/l CN^-, to 263 µg/l CN^-, and the standard deviation should be less than 6,3 µg/l CN^-, in the high range of 50 µg/l to 500 µg/l, otherwise the study should be repeated until these criteria are met.

9.4 Calibration

Select the working mode of the flow system and calibrate by sequentially applying the calibration solutions (6.7) and the sodium hydroxide solution III (6.4) as the blank. Select calibration solutions most appropriate for the samples to be measured.

Prior to the calibration, establish a steady baseline according to 9.1 and 9.2.

Determine the detector response values from the calibration solutions.

The test conditions for the calibration and the measurement of samples (9.5) are the same. The magnitude of the measuring signal is proportional to the mass concentration of cyanide. Establish the regression line for the measuring series obtained.

Calibrate the flow system as specified in ISO 8466-1. The following general Formula (1) is appropriate (ISO 8466-1).

$$y = b \cdot \rho(\mathrm{CN}) + a \tag{1}$$

where

y is the measured value for the calibration solutions, in terms of instrument-related units (e.g. peak heights in centimetres or counts);

b is the slope of the calibration function, expressed in instrument-related units / micrograms per litre;

ρ(CN) is the mass concentration of an individual standard solution, expressed in micrograms per litre, µg/l;

a is the ordinate intercept, expressed in instrument-related units.

If the linearity test described in ISO 8466-1 shows that the calibration curve is not linear, calculate the calibration curve as specified in ISO 8466-2.

9.5 Sample measurement

9.5.1 General

Add ligand exchange reagents to the prepared samples and mixed, prior to measurements, if needed. If high concentrations of WAD cyanide are present, compared to nickel and mercury concentrations, ligands addition are not needed. Ligands are only needed when release of the WAD cyanide from nickel and mercury increases the WAD cyanide concentration significantly (>5 % relative). Compare results with and without ligands for verification.

Samples shall be diluted when using optional ligand exchange reagents A (6.9.1) and B (6.9.2) to maintain nickel concentrations < 0,5 mg/l and mercury concentrations < 10 mg/l. Ligand exchange reagents may be omitted if the nickel content is < 2,5 % of ρ(CN) and mercury concentration < 10 % of the ρ(CN). If needed, proceed in accordance with 9.5.2.1, 9.5.2.2 or 9.5.3; otherwise, it is permissible to proceed with cyanide measurement (9.5.4) without ligand exchange reagents.

9.5.2 Manual ligand addition options

9.5.2.1 General

Add ligand exchange reagents to the prepared samples and mix, prior to measurements of the cyanide, unless nickel and mercury concentrations are known to fall within the ranges for omission (9.5.1).

9.5.2.2 Ligand exchange reagent A and B option

Place 10 ml of test solution in polyethylene tubes and add 20 µl of ligand exchange reagents A (6.9.1) as required to release cyanide from nickel. Add 20 µl of ligand exchange reagent B (6.9.2) as required to release cyanide from mercury. Mix and measure as soon as possible. Verify the reagent effectiveness

by processing the mercury(II) cyanide recovery solution (6.10.4) and the potassium nickel cyanide recovery solution (6.10.8) in the same way as the samples. Proceed with cyanide measurement (9.5.4).

9.5.2.3 Ligand exchange reagent 1 and 2 option

Place 10 ml of test solution in polyethylene tubes and add 100 µl of ligand exchange reagent 1 TEP (6.9.5) and ligand exchange reagent 2 dithizone (6.9.7) as required to release cyanide from mercury or nickel, mix and measure as soon as possible. Verify the reagent effectiveness by processing the mercury(II) cyanide recovery solution (6.10.4) and the potassium nickel cyanide recovery solution (6.10.8) in the same way as the samples. Proceed with cyanide measurement (9.5.4).

9.5.3 Automated ligand addition

If using the optional mixed ligand exchange reagent (see 6.9.3) and the configuration shown in Figure A.2, step 9.5.2 is not necessary. Inject the mixed ligand reagent (6.9.3) into a mixed ligand solution to achieve a sample ratio of at least 1:10, as required to release cyanide from mercury or nickel; measure as soon as possible. Verify reagent effectiveness by processing the mercury(II) cyanide recovery solution (6.10.4) and the potassium nickel cyanide recovery solution (6.10.8) in the same way as the samples.

9.5.4 Cyanide measurement

Analyse the samples (pre-treated, as necessary, according to Clause 8) in the same way as the calibration solutions with the flow injection system.

Check the validity of the calibration function after each sample series, but at least after the measurement of 10 to 20 samples, using at least one calibration solution each for the lower and upper part of the working range.

Make a new calibration, if necessary.

10 Calculations

Determine the mass concentrations of the samples using the measured values, obtained as described in 9.4 for the calibration solutions.

Calculate $\rho(\mathrm{CN})$ using Formula (2):

$$\rho(\mathrm{CN}) = \frac{y - a}{b} \tag{2}$$

For an explanation of symbols, see 9.4, Formula (1).

If the linearity test described in ISO 8466-1 shows that the calibration curve is not linear, calculate the calibration curve as specified in ISO 8466-2.

11 Expression of results

Report the results to two significant figures at most.

EXAMPLE ρ [available weak and dissociable (WAD) CN] 45 µg/l.

12 Test report

The test report shall contain at least the following information.

a) the test method used, together with a reference to this document, i.e. ISO/FDIS 20950-1:2018;

b) all information necessary for identification of the sample;

c) any sample pre-treatment as described in Clause 4 for interferences, filtration or decantation, preservation, elapsed time from sampling to analysis and storage temperature;

d) the cyanide concentration, available weak and dissociable (WAD) cyanide in micrograms per litre (µg/l) or milligrams per litre (mg/l), in accordance with Clause 10;

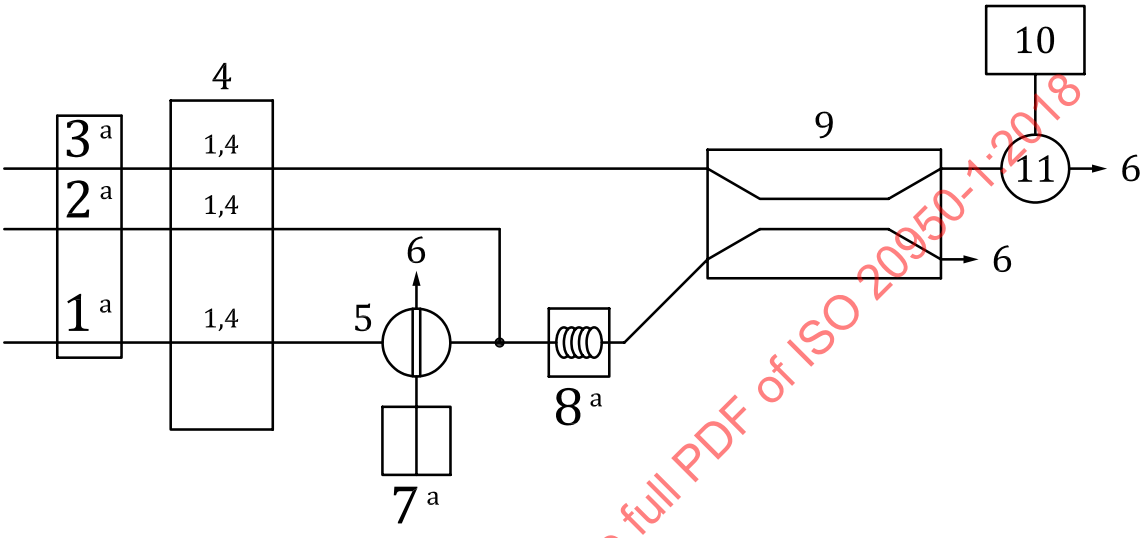
e) any special observations noted during the determination;

f) documentation framework (e.g. date of the test, operator);

g) any deviations from this document, which could have affected the result.

Annex A
(informative)

Examples of flow injection systems



Key

1 carrier water (6.1)
2 sulfide removal and acidification reagent (6.8.4)
3 acceptor solution (0,1 mol/l NaOH) (6.2)
4 peristaltic pump (flow rates in ml/min)
5 injection valve (200 µl sample loop)
6 waste flows
7 sample
8 mixing coil (30 cm to 60 cm × 0,5 mm to 0,8 mm i.d.) positioned in optional constant temperature
9 gas-diffusion cell
10 potentiostat/data collection device running data acquisition software
11 amperometric flow cell
a t = constant

Figure A.1 — Example of a flow injection analysis system