
**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

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).

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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, $c(\text{NaOH}) = 0,1 \text{ mol/l}$.

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

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

6.5 Potassium cyanide, KCN.

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

Dissolve $(2\,503 \pm 1) \text{ mg}$ 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 $(5 \pm 3) \text{ }^\circ\text{C}$, if stored in the dark or brown bottles.

Alternatively, a potassium tetracyanozincate $(2\,380 \text{ mg/l})$ solution [\(6.6.1\)](#) may be used.

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

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 $(5 \pm 3) \text{ }^\circ\text{C}$, 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, $\text{K}_2\text{Zn}(\text{CN})_4$.

6.6.1 Potassium tetracyanozincate solution, $\text{K}_2\text{Zn}(\text{CN})_4$, $\rho(\text{CN}) = (1\,000 \pm 2) \text{ mg/l}$, commercially available.

This solution is stable for six months at $(5 \pm 3) \text{ }^\circ\text{C}$, if stored in the dark.

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

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 $(5 \pm 3) \text{ }^\circ\text{C}$, 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, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

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 $(5 \pm 3)^\circ\text{C}$.

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, $\rho(\text{CN}) = 1\ 000\ \text{mg/l}$.

Weigh 0,270 5 g $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (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 $(5 \pm 3)^\circ\text{C}$

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

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 $(5 \pm 3)^\circ\text{C}$.

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

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, $\rho(\text{CN}) = 1\ 000\ \text{mg/l}$.

Weigh 0,210 9 g of $\text{K}_3\text{Fe}(\text{CN})_6$ (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 $(5 \pm 3)^\circ\text{C}$.

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

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 $(5 \pm 3)^\circ\text{C}$.

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

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), $\text{K}_3\text{Fe}(\text{CN})_6$ **6.8.12 Potassium hexacyanoferrate(II) trihydrate, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.****6.8.13 Sulfuric acid (I), $\rho = 1,84\ \text{g/ml}$, 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, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (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.

6.8.15 Total acid reagent.

Carefully add 55 ml of concentrated sulfuric acid (6.8.13) to about 800 ml of water (6.1) in a 1 000 ml volumetric flask. Cool to room temperature and add 20 ml of hypophosphorous acid (6.8.4). Dilute to volume and mix.

WARNING — This is an exothermic reaction and the solution will become hot when preparing this solution. Use this solution within 48 h of preparation.

6.9 Reagents for sample pre-treatment and preservation

6.9.1 Sodium acetate trihydrate, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$.

6.9.2 Acetic acid, CH_3COOH .

6.9.3 Acetate buffer.

Dissolve 410 g of sodium acetate trihydrate (6.9.1) in 500 ml of water (6.1). Add acetic acid (approximately 500 ml) (6.9.2) to yield a pH of 4,5.

6.9.4 Lead carbonate, PbCO_3 , powder.

Dissolve into a concentrated solution 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.

6.9.5 Lead acetate test paper, commercially available.

6.9.6 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.

6.9.6.1 Sodium arsenite solution, 5 g/l.

Dissolve 0,5 g sodium arsenate on 100 ml of water.

6.9.7 Potassium iodide starch test paper, commercially available.

7 Apparatus

7.1 Segmented flow 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.

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 [Table 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 mm² in contact with acceptor solution.

The gas diffusion membrane should be replaced when the baseline becomes noisy, or every one to two weeks.

7.1.5 UV digester, with a 312 nm lamp and UV transparent digestion coil.

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

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

7.1.8 Recording unit, for example strip chart recorder, integrator or printer/plotter.

As an example, instrument settings are shown in [Table 1](#). 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, 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 Oxidizing agent

Acidify KI starch paper ([6.9.7](#)) by moistening with acetate buffer ([6.9.3](#)). 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 recommended concentrated solution of sodium arsenite ([6.9.6](#)) equivalent to 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 by taking repeated measurements for 1 h, when sodium arsenite ([6.9.6](#)) is used to mitigate the presence of oxidizing agents. Sodium arsenite ([6.9.6](#)) is highly toxic and a potential carcinogen.

Since sodium arsenite ([6.9.6](#)) has a very high water solubility, it should be added as a concentrated solution to reduce risk with solid reagent.

8.2 Sulfide removal

Test for sulfide by moistening lead acetate paper ([6.9.5](#)) with acetate buffer solution ([6.9.3](#)), then add a drop of sample on the lead acetate paper. If the paper turns black, sulfide is present. Add powdered lead carbonate ([6.9.4](#)) (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. The supernatant containing cyanide shall be filtered immediately to avoid the rapid loss of cyanide due to the formation of thiocyanate.

8.3 Preservation

Refer to [Clause 5](#) on interferences and treat samples prior to adjusting pH. Immediately after sampling bring the pH of the water samples to $11 \pm 0,1$ 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 $11 \pm 0,1$ 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 total 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 $0,45 \mu\text{m}$ 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 $(5 \pm 3) ^\circ\text{C}$. if immediate analysis is delayed.

9 Procedure

9.1 Flow system set up

Set up and adjust the flow analysis system in accordance with [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 — Segmented flow analysis parameters

FIA instrument parameter	Recommended method setting
Pump flow rates	0,5 ml/min to 2 ml/min
Cycle period (total)	90 s to 250 s/sample
Sample load period	At least enough time to completely fill the sample loop
Reagent water rinse	At least 15 s time between samples
Peak evaluation	Peak height or area
Working potential	0,0 V vs Ag/AgCl

NOTE 1 The instrument settings in [Table 1](#) are only examples. The analyst can modify the settings as long as performance of the method has not been degraded. Contact the instrument manufacturer for recommended instrument parameters.

Turn on the power to the apparatus and the autosampler (if equipped).

Clamp the pump tube platens in place and start pumping reagents in the flow segmented analysis 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 in accordance with [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 segmented flow analysis system

9.3.1 Cyanide electrode stabilization

Inject the stabilization solution (6.8.3) 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 segmented flow analysis 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., a precision and bias study shall be performed to demonstrate laboratory capability.

This procedure is an example and laboratories should adhere to local requirements.

Analyse seven replicates of an independent reference solution containing 25 µg/l total 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 total 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. Each replicate shall be taken 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

Analyse iron(II) cyanide recovery solution (6.8.7) and iron(III) cyanide recovery solution (6.8.10). Results should fall within the range of 90 µg/l CN⁻ to 110 µg/l CN⁻, before proceeding with analysis of samples.

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 in accordance with 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).

$$y = b \cdot \rho(\text{CN}) + a \quad (1)$$

where

ISO 22066:2020(E)

- y is the measured value for the calibration solutions, in terms of instrument related units (for example peak heights in centimetres or counts);
- b is the slope of the calibration function, expressed in instrument related units / micrograms per litre;
- $\rho(\text{CN})$ are the mass concentrations of the standard solutions, expressed in micrograms per litre, $\mu\text{g/l}$;
- 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

Place 10 ml of test solution in polyethylene tubes, measure as soon as possible,

9.5.1 Cyanide measurement

Analyse the samples, pre-treated, as necessary, in accordance with [Clause 8](#), in the same way as the calibration solutions with the segmented flow analysis system.

Check the validity of the calibration function after each sample series, but at least after the measurement of 10 to 20 samples, using 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 $\rho(\text{CN})$ by using [Formula \(2\)](#):

$$\rho(\text{CN})=(y-a)/b \quad (2)$$

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 $\rho[\text{total CN}] 45 \mu\text{g/l}$.

12 Test report

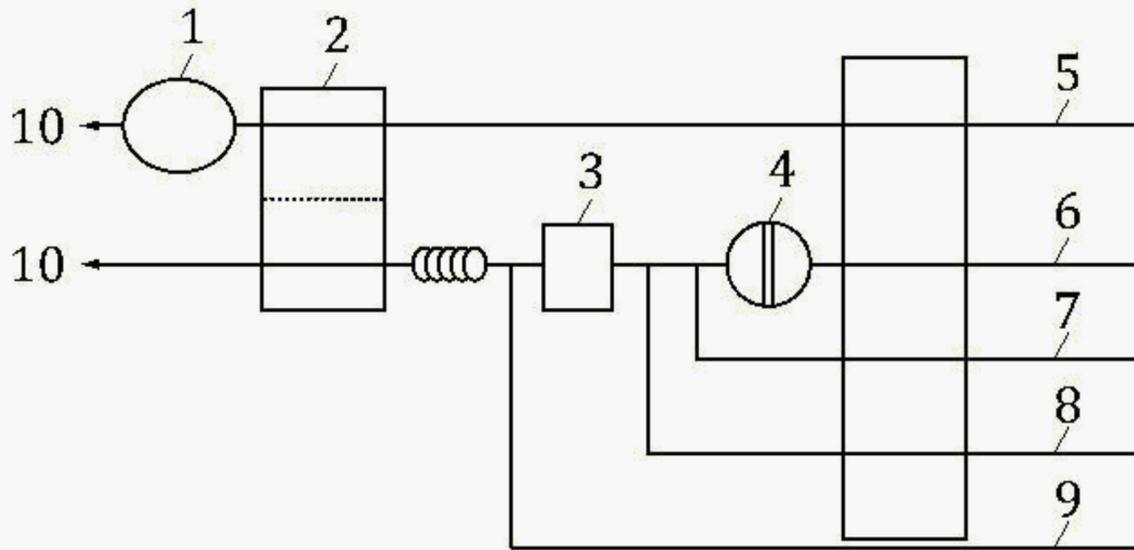
This test report shall contain at least the following information:

- the test method used, together with a reference to this document, i.e. ISO 22066:2020;
- all information necessary for identification of the sample;
- any sample pre-treatment as described in [Clause 8](#) for interferences, filtration or decantation, preservation, elapsed time from sampling to analysis and storage temperature;

- d) the cyanide concentration, total cyanide in micrograms per litre ($\mu\text{g/l}$) 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 etc.);
- g) any deviation from the method or sample validated matrix shall be reported in the test report;
- h) report of all circumstances that may have affected the results.

Annex A (informative)

Example of a segmented flow analysis system



Key

- 1 AMP detector
- 2 gas diffusion module
- 3 UV digester
- 4 sample
- 5 acceptor (sodium hydroxide)
- 6 carrier water ([6.1](#))
- 7 air
- 8 TA 1: total acid reagent ([6.8.15](#))
- 9 TA 2: sulfide removal and acidification reagent ([6.8.14](#))
- 10 to waste

NOTE Range can be extended by reducing sensitivity; there are several options:

- dilute test sample;
- increase depth of channel in gas diffusion module;
- reduce sample introduction time;
- vary tubing length and diameter;
- vary gas diffusion material and thickness.

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

Annex B (normative)

Determination of the real cyanide concentration in the potassium cyanide solution (6.5.1) or potassium tetracyanozincate solution (6.6.1)

If KCN or $K_2Zn(CN)_4$ is used to prepare the cyanide calibration solutions (6.7), proceed as follows:

B.1 Additional reagents

B.1.1 p-dimethylaminobenzylidene rhodanine, $C_{12}H_{12}N_2OS_2$.

B.1.2 Propanone (acetone), C_3H_6O .

B.1.3 Indicator solution

Dissolve 0,02 g of p-dimethylaminobenzylidene rhodanine (B.1.1) in 100 ml of acetone (B.1.2).

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

B.1.4 Silver nitrate solution, $c(\text{AgNO}_3) = 20 \text{ mmol/l}$ or 50 mmol/l .

B.2 Determination of cyanide concentration in potassium cyanide solution (6.5.1)

Pipette into a beaker 10 ml of potassium cyanide solution (6.5.1) or potassium tetracyanozincate solution (6.6.1). Add 0,25 ml of indicator solution (B.1.3). Titrate with the silver nitrate solution (B.1.4) until the colour changes from yellow to yellow-red (consumption V_1).

Calculate the cyanide concentration in the potassium cyanide solution (6.5.1) or potassium tetracyanozincate solution (6.6.1), using Formula (B.1):

$$\rho_{(\text{CN})} = \frac{V_1 c(\text{AgNO}_3) M_{(2\text{CN})}}{V} \quad (\text{B.1})$$

where

$\rho_{(\text{CN})}$ is the cyanide concentration in the potassium cyanide solution (6.5.1) or potassium tetracyanozincate solution (6.6.1), in milligrams per litre, mg/l;

V_1 is the quantity of silver nitrate solution (B.1.4) used in millilitres, ml;

$c(\text{AgNO}_3)$ is the concentration of silver nitrate solution in millimoles per litre, mmol/l;

$M_{(2\text{CN})}$ is the molar mass of 2 CN (= 52 g/mol);

V is the volume of the potassium cyanide solution (6.5.1) in or potassium tetracyanozincate solution (6.6.1), milliliters, ml.

Annex C
(informative)

Performance data

An interlaboratory trial for flow systems as described in [Clause 7](#) was carried out in 2017. The results are shown in [Table C.1](#).

**Table C.1 — Statistical data for the determination of total cyanide by SFA
(in accordance with ISO 5725-2)**

Sample	Matrix ^a	<i>l</i>	<i>n</i>	<i>o</i> %	<i>X</i> µg/ml	\bar{x} µg/ml	η %	<i>S_R</i> µg/ml	<i>C_{V,R}</i> %	<i>s_r</i> µg/ml	<i>C_{V,r}</i> %
1	Drinking water	10	40	9,1	0,223	0,235	105	0,022 8	9,7	0,004 6	2,0
2	Ground water	10	50	9,1	0,025	0,027	110	0,003 2	11,9	0,000 9	3,4
3	Surface water	10	40	9,1	0,504	0,546	108	0,029	5,3	0,001	1,8
4	Tailings decant solution	10	40	9,1	— ^b	0,33		0,033	9,9	0,007 3	2,2
5	Heap Leach Barren	10	40	9,1	— ^b	0,145		0,033	22,6	24,1	1,9
6	Mill tailings slurry filtrate	10	40	9,1	1 262	1 309	104	138	9,8	24,4	1,9
7	Mill leach slurry filtrate	10	40	9,1	72,8	78,6	108	8,98	11,4	1,32	1,7
<i>l</i>	number of laboratories after outlier rejection										
<i>n</i>	number of individual test results after outlier rejection										
<i>o</i>	percentage of outliers										
<i>X</i>	assigned value										
\bar{x}	overall mean of results (without outliers)										
η	recovery rate										
<i>S_R</i>	reproducibility standard deviation										
<i>C_{V,R}</i>	coefficient of variation of reproducibility										
<i>s_r</i>	repeatability standard deviation										
<i>C_{V,r}</i>	coefficient of variation of repeatability										
^a	Origin of the samples: Sample 1 Spiked, Denver Aquifer Exempt Domestic Well, Parker, Colorado. Sample 2, Spiked, Alluvial-Dawson Dual Aquifer Exempt Domestic Well, Parker, Colorado. Sample 3 Spiked, Cherry Creek, Centennial, Colorado. Sample 4 Spiked Metallurgical Process Reclaim Solution, Winnemucca, Nevada. Sample 5 Heap Leach Barren Solution, Carlin, Nevada. Sample 6 Mill Tailings Slurry Filtrate Solution, Battle Mountain, Nevada. Sample 7 Mill Leach Slurry Filtrate Solution, Battle Mountain, Nevada.										
^b	Biased reference value.										

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