
**Water quality — Determination of total
cyanide and free cyanide by continuous
flow analysis**

*Qualité de l'eau — Dosage des cyanures totaux et des cyanures libres par
analyse en flux continu*

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ISO 14403:2002

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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

Annex A forms a normative part of this International Standard. Annexes B and C are for information only.

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Introduction

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

Analysis can be performed by flow injection analysis (FIA) or continuous flow analysis (CFA). In this International Standard the latter is specified. The CFA method shares 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 may be integrated in the manifold. The reaction product is measured in a flow detector (e.g. flow photometer).

It is absolutely essential that the test described in this International Standard be carried out by suitable qualified staff. It should be investigated whether and to what extent particular problems will require the specification of additional marginal conditions.

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Water quality — Determination of total cyanide and free cyanide by continuous flow analysis

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard 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.

1 Scope

This International Standard specifies methods for the determination of cyanide in various types of water (such as ground, drinking, surface, leachate and waste water) with cyanide concentrations usually above 3 µg/l expressed as cyanide ions. The CFA method is applicable to a mass concentration range from 10 µg/l to 100 µg/l. The range of application may be changed by varying the operation conditions.

NOTE Seawater may be analyzed with changes in sensitivity and adaptation of the reagent and calibration solutions to the salinity of the samples.

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2 Normative references

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The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 8466-1:1990, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Terms and definitions

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

3.1

total cyanide

sum of some organically bound cyanides, free cyanide ions, complex compounds and cyanide bound in simple metal cyanides, with the exception of cyanide bound in cobalt complexes and of thiocyanate

3.2

free cyanide

easily liberatable cyanide

sum of cyanide ions and the cyanide bound in simple metal cyanides as determined in accordance with this International Standard

NOTE Organic cyanides are not included.

4 Interferences

4.1 Interferences by oxidizing agents

Oxidizing agents such as chlorine decompose most of the cyanides. If oxidizing agents are suspected, test for their presence as given in clause 8.

4.2 Interferences by sulfides

Sulfide concentrations > 60 mg/l affect the colorimetric procedure. If sulfide is suspected, carry out tests for its presence as given in clause 8.

4.3 Other interferences

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When using in-line distillation for separation of the hydrogen cyanide, salt concentrations higher than 10 g/l can cause clogging of the distillation coil. Dilute these samples prior to measurement in order to overcome this problem.

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Under the given distillation conditions aldehydes can transform cyanide to nitrite. Aldehydes can be removed by adding silver nitrate to the sample.

NOTE The addition of AgNO_3 can alter the ratio of the concentrations of free and total cyanide. The user should evaluate this procedure.

Particulate matter in the sample may lead to clogging of the transport tubes and will interfere with the photometric measurement. Particles $> 0,1$ 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 or from inappropriate distillation procedures (7.1).

5 Principle

5.1 Determination of total cyanide concentration

Complex bound cyanide is decomposed by UV light in a continuous flow at a pH of 3,8. A UV-B lamp (312 nm) and a decomposition spiral of borosilicate glass is used to filter off UV light with a wavelength of 290 nm thus preventing the conversion of thiocyanate into cyanide. Alternatively it is possible to use a long wavelength UV lamp (351 nm), which does not emit light below 290 nm and which is equipped with a decomposition spiral of quartz glass or polytetrafluoroethylene (PTFE). The hydrogen cyanide present at pH 3,8 is separated by on-line distillation at 125°C or by gas diffusion at 30°C across a hydrophobic membrane. The hydrogen cyanide is then determined photometrically by the reaction of cyanide with chloramine-T to cyanogen chloride. This reacts with pyridine-4-carbonic acid and 1,3-dimethylbarbituric acid to give a red dye.

5.2 Determination of free cyanide concentration

The UV lamp is switched off when determining the free cyanide content. During distillation at pH 3,8 for separation of the hydrogen cyanide present, a zinc sulfate solution is added to the sample flow in order to precipitate any iron cyanides present as the zinc-cyanoferrate complex. For detection see 5.1.

6 Reagents

WARNING — KCN, $K_2Zn(CN)_4$, and their 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 according to ISO 3696.

6.2 Hydrochloric acid I, $c(HCl) = 12 \text{ mol/l}$.

6.3 Hydrochloric acid II, $c(HCl) = 1 \text{ mol/l}$.

6.4 Hydrochloric acid III, $c(HCl) = 0,1 \text{ mol/l}$.

6.5 Sodium hydroxide solution I, $c(NaOH) = 2,5 \text{ mol/l}$.

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

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

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

6.9 Surfactant, polyoxyethylene lauryl ether, $OH-(CH_2CH_2-O)_n-C_{18}H_{37}$.

Add 30 g of polyoxyethylene lauryl ether in small quantities to 100 ml of water (6.1) and mix well.

Alternatively use a commercially available solution of the surfactant.

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

6.11 Zinc sulfate heptahydrate, $ZnSO_4 \cdot 7H_2O$.

6.12 Potassium hydrogenphthalate, $KHC_8H_4O_4$.

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 stock solution, KCN , $\rho(CN) = 100 \text{ mg/l}$ (see annex A).

Dissolve $250 \text{ mg} \pm 1 \text{ mg}$ of potassium cyanide, KCN , in sodium hydroxide solution IV (6.8) in a 1 000 ml graduated flask and make up to volume with sodium hydroxide solution IV (6.8).

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

6.18.2 Potassium tetracyanozincate solution, $K_2Zn(CN)_4$, $\rho(CN) = 1\ 000\ mg/l \pm 2\ mg/l$.

Commercially available.

6.18.3 Cyanide solution I, $\rho(CN) = 10\ mg/l$.

Pipette 1 ml of the potassium tetracyanozincate solution I (6.18.2) or 10 ml of the potassium cyanide stock solution (6.18.1) into a 100 ml graduated flask and bring to volume with sodium hydroxide solution IV (6.8).

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

6.18.4 Calibration solutions.

Prepare at least five calibration solutions with cyanide concentrations, equidistantly 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 graduated flask and make up to volume with sodium hydroxide solution IV (6.8).

Pipette, in 100 ml graduated flasks, 1 ml, 3 ml, 5 ml, 6 ml, 8 ml, or 10 ml, respectively, of the above-mentioned 1 mg/l cyanide solution and make up to volume with sodium hydroxide solution IV (6.8).

These solutions contain 10 $\mu g/l$, 30 $\mu g/l$, 50 $\mu g/l$, 60 $\mu g/l$, 80 $\mu g/l$, and 100 $\mu g/l$ of cyanide, respectively (except for corrections in the concentration found on titration of the potassium cyanide solution (6.18.1), (see annex A).

These solutions are stable for 2 days if stored in a refrigerator at 2 °C to 5 °C.

6.19 Reagents for the determination of cyanide [g/standards/sist/48d703b9-e465-441a-bbd5-d1cb785742d4/iso-14403-2002](https://standards.iso.org/standards/sist/48d703b9-e465-441a-bbd5-d1cb785742d4/iso-14403-2002)

6.19.1 Buffer (pH = 3,8) for distillation and gas diffusion method.

Dissolve 50 g of citric acid (6.10) in 350 ml of water (6.1). Add 120 ml of sodium hydroxide solution I (6.5) and, if necessary adjust to pH 3,8 with hydrochloric acid II (6.3) or sodium hydroxide solution II (6.6). Dilute to 500 ml with water.

This solution is stable for 3 months if stored in a refrigerator at 2 °C to 5 °C.

6.19.2 Zinc sulfate solution (only for distillation method).

Dissolve 10 g of zinc sulfate heptahydrate (6.11) in 750 ml of water (6.1), mix and dilute to 1 000 ml with water.

6.19.3 Recipient solution (only for gas diffusion).

Sodium hydroxide solution III (6.7).

6.19.4 Buffer solution for the final photometric determination (pH = 5,2).

Dissolve 2,3 g of sodium hydroxide (NaOH) in 500 ml of water (6.1). Add 20,5 g of potassium hydrogenphthalate (6.12) and dilute to approximately 975 ml with water.

If necessary, adjust the pH of the solution to 5,2 with hydrochloric acid II (6.3) or sodium hydroxide solution II (6.6).

Add 1 ml of surfactant (6.9) and make up to 1 000 ml with water.

This solution is stable for 3 months if stored in a refrigerator at 2 °C to 5 °C.

6.19.5 Chloramine-T trihydrate solution.

Dissolve $2,0 \text{ g} \pm 0,05 \text{ g}$ of chloramine-T trihydrate (6.13) in 1 000 ml of water.

This solution is stable for 3 months if stored in a refrigerator at $2 \text{ }^{\circ}\text{C}$ to $5 \text{ }^{\circ}\text{C}$.

6.19.6 Colour reagent.

Dilute $7,0 \text{ g}$ of sodium hydroxide, NaOH, in 500 ml of water (6.1). Add $16,8 \text{ g} \pm 0,1 \text{ g}$ of 1,3-dimethylbarbituric acid (6.14), and $13,6 \text{ g} \pm 0,1 \text{ g}$ of pyridine-4-carboxylic acid (6.15), and dilute to approximately 975 ml with water (6.1).

If necessary, bring the solution to pH 5,2 with hydrochloric acid II (6.3) or sodium hydroxide solution II (6.6).

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 $30 \text{ }^{\circ}\text{C}$ and then filter over a pleated filter (e.g. hardened ashless paper).

This solution is stable for 3 months if stored in a refrigerator at $2 \text{ }^{\circ}\text{C}$ to $5 \text{ }^{\circ}\text{C}$.

6.20 Standard thiocyanate solution, calculated cyanide concentration: $\rho(\text{CN}) = 100 \text{ mg/l}$.

Dissolve in a 1 000 ml graduated flask $373 \text{ mg} \pm 1 \text{ mg}$ of potassium thiocyanate (6.16) in sodium hydroxide solution IV (6.8), and make up to volume with sodium hydroxide solution IV (6.8).

This solution is stable for 2 months if stored in a refrigerator at $2 \text{ }^{\circ}\text{C}$ to $5 \text{ }^{\circ}\text{C}$.

6.21 Standard potassium hexacyanoferrate(III) solution (red blood alkaline salt).

Calculated cyanide concentration $\rho(\text{CN}) = 10 \text{ mg/l}$.

Dissolve in a 1 000 ml graduated flask $21,1 \text{ mg} \pm 0,1 \text{ mg}$ of potassium hexacyanoferrate(III) (6.17) in sodium hydroxide solution IV (6.8), and make up to volume with sodium hydroxide solution IV (6.8).

This solution is stable for 2 months if stored in a refrigerator at $2 \text{ }^{\circ}\text{C}$ to $5 \text{ }^{\circ}\text{C}$.

6.22 Rinsing solution.

Dissolve 2 ml of surfactant (6.9) in 1 000 ml of water.

6.23 Ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$.**6.24 Powdered lead carbonate**, PbCO_3 .**7 Apparatus**

Usual laboratory apparatus, and

7.1 Continuous flow analysis system for distillation method

A typical system comprises the following components (see Figure 1).

7.1.1 Autosampler, or another device capable of introducing sample reproducibility.

7.1.2 Reagent reservoirs.

7.1.3 Low pulsation pump, having specific chemically inert pump tubes, for flow rates as given in Figure 1 as an example.