

---

---

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

Part 2:

**Method using continuous flow analysis  
(CFA)**

iTeh STANDARD PREVIEW

(standards.iteh.ai)

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

*Partie 2: Méthode par analyse en flux continu (CFA)*

*ISO 14403-2:2012*

<https://standards.iteh.ai/catalog/standards/sist/beadf7d5-8e0a-49de-892c-389de98f86cd/iso-14403-2-2012>



## iTeh STANDARD PREVIEW (standards.iteh.ai)

ISO 14403-2:2012

<https://standards.iteh.ai/catalog/standards/sist/beadf7d5-8e0a-49de-892c-389de98f86cd/iso-14403-2-2012>



### **COPYRIGHT PROTECTED DOCUMENT**

© ISO 2012

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office  
Case postale 56 • CH-1211 Geneva 20  
Tel. + 41 22 749 01 11  
Fax + 41 22 749 09 47  
E-mail [copyright@iso.org](mailto:copyright@iso.org)  
Web [www.iso.org](http://www.iso.org)

Published in Switzerland

<b>Contents</b>	<b>Page</b>
Foreword .....	iv
Introduction .....	v
<b>1 Scope</b> .....	<b>1</b>
<b>2 Normative references</b> .....	<b>1</b>
<b>3 Terms and definitions</b> .....	<b>1</b>
<b>4 Interferences</b> .....	<b>2</b>
<b>4.1 Interferences by oxidizing agents</b> .....	<b>2</b>
<b>4.2 Interferences by sulfide, sulfite, nitrite and carbonyl compounds</b> .....	<b>2</b>
<b>4.3 Other interferences</b> .....	<b>2</b>
<b>5 Principle</b> .....	<b>3</b>
<b>5.1 Determination of total cyanide</b> .....	<b>3</b>
<b>5.2 Determination of free cyanide</b> .....	<b>3</b>
<b>6 Reagents</b> .....	<b>3</b>
<b>7 Apparatus</b> .....	<b>6</b>
<b>8 Sampling and sample preparation</b> .....	<b>8</b>
<b>9 Procedure</b> .....	<b>9</b>
<b>9.1 Flow system set-up</b> .....	<b>9</b>
<b>9.2 Reagent blank measurement</b> .....	<b>9</b>
<b>9.3 Checking the suitability of the flow system</b> .....	<b>10</b>
<b>9.4 Calibration</b> .....	<b>10</b>
<b>9.5 Sample measurement</b> .....	<b>11</b>
<b>10 Calculation</b> .....	<b>11</b>
<b>11 Expression of results</b> .....	<b>11</b>
<b>12 Test report</b> .....	<b>11</b>
<b>Annex A (informative) Examples of flow systems</b> .....	<b>13</b>
<b>Annex B (normative) Determination of the real cyanide concentration in the potassium cyanide solution</b> .....	<b>16</b>
<b>Annex C (informative) Example for the determination of total cyanide and free cyanide by continuous flow analysis (CFA) with gas diffusion and amperometric detection</b> .....	<b>17</b>
<b>Annex D (informative) Performance data</b> .....	<b>19</b>
<b>Bibliography</b> .....	<b>21</b>

## Foreword

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

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

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

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

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

This first edition of ISO 14403-2 cancels and replaces ISO 14403:2002, which has been technically revised.

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

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

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

**iTeh STANDARD PREVIEW**  
**(standards.iteh.ai)**  
ISO 14403-2:2012  
<https://standards.iteh.ai/catalog/standards/sist/beadf7d5-8e0a-49de-892c-389de98f86cd/iso-14403-2-2012>

## Introduction

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

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

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

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

## iTeh STANDARD PREVIEW (standards.iteh.ai)

[ISO 14403-2:2012](https://standards.iteh.ai/catalog/standards/sist/beadf7d5-8e0a-49de-892c-389de98f86cd/iso-14403-2-2012)

<https://standards.iteh.ai/catalog/standards/sist/beadf7d5-8e0a-49de-892c-389de98f86cd/iso-14403-2-2012>

**iTeh STANDARD PREVIEW**  
**(standards.iteh.ai)**

ISO 14403-2:2012

<https://standards.iteh.ai/catalog/standards/sist/beadf7d5-8e0a-49de-892c-389de98f86cd/iso-14403-2-2012>

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

## Part 2: Method using continuous flow analysis (CFA)

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

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

### 1 Scope

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

In this method, a suitable mass concentration range from 10 µg/l to 100 µg/l is described.

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

<https://standards.iteh.ai/catalog/standards/sist/beadf7d5-8e0a-49de-892c-389de98f86cd/iso-14403-2-2012>

### 2 Normative references

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

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

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

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

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

### 3 Terms and definitions

For the purpose of this part of ISO 14403, the following definitions apply:

#### 3.1

##### **free cyanide**

##### **easily liberatable cyanide**

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

### 3.2 total cyanide

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

NOTE 1 Thiocyanate, organically bound cyanide and cyanate are not included in this definition of total cyanide.

NOTE 2 Distillation methods may recover some organic cyanide. Use the diffusion method when organic cyanide complexes are suspected to be present.

## 4 Interferences

### 4.1 Interferences by oxidizing agents

Oxidizing agents such as chlorine decompose most of the cyanides. If the presence of oxidizing agents cannot be excluded, treat the sample immediately after sampling. Test a drop of the sample with potassium iodide–starch test paper (KI starch paper); a blue colour indicates the need for treatment. Add sodium thiosulfate, a few crystals at a time, until a drop of sample produces no colour on the indicator paper. Then add an additional portion of 0,6 g of ascorbic acid (6.9) for each 1 000 ml of sample volume.

Do not add ascorbic acid unless samples will be analysed within 24 h.

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

Interferences by sulfide start at 100 mg/l. It affects the colorimetric procedure, especially the gas diffusion method, and the amperometric procedure (see Annex C). If a drop of the sample on lead acetate test paper indicates the presence of sulfide, treat an additional 25 ml of the stabilized sample (pH >12) to that required for the cyanide determination with powdered lead carbonate.

Lead sulfide precipitates if the sample contains sulfide.

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

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

If the amperometric method (Annex C) is applied, it is necessary systematically to add lead carbonate to samples during the analysis (a few milligrams for a 10 ml sample), followed by filtration or decantation performed before the filtered sample aliquot is placed on the sample tray of the continuous flow analyser.

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

Under the given distillation conditions, aldehydes can transform cyanide to nitrite. Aldehydes can be removed by adding silver nitrate to the sample. The addition of AgNO<sub>3</sub> can alter the ratio of the concentrations of free and total cyanide. The user should evaluate this procedure.

Interference by nitrite above concentrations of 5 mg/l can be avoided by addition of sulfamic acid (6.10) to the buffer (pH 3,8) for the distillation and gas diffusion method (6.21.1).

Sulfite interferes above concentrations of 1 mg/l.

### 4.3 Other interferences

Samples containing particulate matter can lead to losses if the particles clog the transport tubes and are not transported completely into the UV unit. This effect can be minimized by homogenizing (e.g. stirring) the sample immediately prior to analysis to ensure that a representative sample is taken and to reduce the particle size. Remaining particles with diameters >0,1 mm should be removed by filtration.



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

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

Complex-bound cyanide is decomposed by UV light at pH 3,8. An UV-B lamp (312 nm to 400 nm) and a digestion coil of borosilicate glass, quartz glass or polytetrafluorethylene (PTFE) is used. The UV unit shall ensure that UV light with a wavelength of <290 nm is filtered off thus preventing the conversion of thiocyanate into cyanide.

The hydrogen cyanide present at pH 3,8 is separated by online distillation at 125 °C or by gas diffusion at 30 °C to 40 °C across a hydrophobic membrane. Using gas diffusion, hydrogen cyanide is absorbed in a sodium hydroxide solution.

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

### 5.2 Determination of free cyanide

During the procedure specified in 5.1, the UV-B lamp is switched off when determining the free cyanide content. 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.

When using the gas diffusion method for the liberation of cyanide from the nickel complex, 50 µl tetraethylenepentamine solution (6.12) per 30 ml sample is added prior to the analysis (see Reference [11]).

For detection see 5.1.

Alternatively, free and total cyanide can be determined after gas diffusion using an amperometric detector (see Annex C).

## 6 Reagents

**WARNING — KCN, K<sub>2</sub>Zn(CN)<sub>4</sub>, their solutions, and wastes are toxic. Waste containing these substances shall be removed appropriately.**

Use only reagents of recognized analytical grade.

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

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

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

**6.3 Sodium hydroxide solution I**,  $c(\text{NaOH}) = 0,4 \text{ mol/l}$ .

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

**6.5 Sodium hydroxide solution III**,  $c(\text{NaOH}) = 0,2 \text{ mol/l}$ .

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

**6.7 Surfactant, polyoxyethylene laurylether**,  $\text{HO}-(\text{CH}_2\text{CH}_2-\text{O})_n-\text{C}_{18}\text{H}_{37}$ .

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

Alternatively use a commercially available solution of the surfactant.

**6.8 Citric acid monohydrate**,  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ .

**6.9 Ascorbic acid**,  $\text{C}_6\text{H}_8\text{O}_6$ .

**6.10 Sulfamic acid**,  $\text{H}_3\text{SO}_3\text{N}$ .

**6.11 Tetraethylenepentamine**,  $\text{C}_8\text{H}_{23}\text{N}_5$ .

**6.12 Tetraethylenepentamine solution** (for free cyanide only).

Dissolve 0,75 g of tetraethylenepentamine (6.11) in 250 ml of water.

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

**6.13 Zinc sulfate heptahydrate**,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .

**6.14 Potassium hydrogenphthalate**,  $\text{KHC}_8\text{H}_4\text{O}_4$ .

**6.15 Chloramine-T trihydrate**,  $\text{C}_7\text{H}_7\text{ClNNaO}_2\text{S} \cdot 3\text{H}_2\text{O}$ .

**6.16 1,3-Dimethylbarbituric acid**,  $\text{C}_6\text{H}_8\text{N}_2\text{O}_3$ .

**6.17 Pyridine-4-carboxylic acid**,  $\text{C}_6\text{H}_5\text{NO}_2$ .

**6.18 Potassium thiocyanate**,  $\text{KSCN}$ .

**6.19 Potassium hexacyanoferrate(III)**,  $\text{K}_3\text{Fe}(\text{CN})_6$ .

**6.20 Cyanide standards.**

**6.20.1 Potassium cyanide**,  $\text{KCN}$ .

**6.20.2 Potassium cyanide solution**,  $\text{KCN}$ ,  $\rho_{\text{CN}} = 1\,000 \text{ mg/l}$ , (see Annex B).

Dissolve  $2\,500 \text{ mg} \pm 1 \text{ mg}$  of potassium cyanide,  $\text{KCN}$  (6.20.1), in sodium hydroxide solution IV (6.6) in a 1 000 ml volumetric flask, and make up to volume with sodium hydroxide solution IV (6.6).

A commercially available and certified 1 000 mg/l  $\text{KCN}$  stock solution may be used.

The solution is stable for 3 months at  $1\text{ }^\circ\text{C}$  to  $8\text{ }^\circ\text{C}$ .

Alternatively, a potassium tetracyanozincate solution (6.20.3) can be used:

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

The solution is stable for 3 months at  $1\text{ }^\circ\text{C}$  to  $8\text{ }^\circ\text{C}$ .

#### 6.20.4 Cyanide solution I, $\rho_{\text{CN}} = 10 \text{ mg/l}$ .

Pipette 1 ml of the potassium tetracyanozincate solution I (6.20.3) or 1 ml of the potassium cyanide solution (6.20.2) into a 100 ml volumetric flask, and make up to volume with sodium hydroxide solution IV (6.6).

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

#### 6.20.5 Calibration solutions

Prepare at least five calibration solutions with cyanide concentrations, roughly regularly distributed over the working range, by appropriate dilution of the cyanide solution I (6.20.4). If, for example, six calibration standards should be prepared, proceed as follows.

Pipette 10 ml of the cyanide solution I (6.20.4) into a 100 ml volumetric flask, and make up to volume with sodium hydroxide solution IV (6.6). This solution contains 1mg/l cyanide.

Pipette, into 100 ml volumetric flasks, 1 ml, 3 ml, 5 ml, 6 ml, 8 ml, or 10 ml, respectively, of the previously mentioned 1 mg/l cyanide solution and make up to volume with sodium hydroxide solution IV (6.6).

These solutions contain 10 µg/l, 30 µg/l, 50 µg/l, 60 µg/l, 80 µg/l, and 100 µg/l of cyanide, respectively [except for corrections in the concentration found on titration of the potassium cyanide solution (6.20.2), (see Annex B)].

These solutions are stable for 2 d if stored in a refrigerator at 1 °C to 5 °C.

#### 6.21 Reagents for the determination of cyanide

##### 6.21.1 Buffer, pH 3,8, for distillation and gas diffusion method (R1 in Figures A.1, A.2 and C.1).

Dissolve, in about 350 ml water (6.1), 10 g of citric acid (6.8). Add 50 ml of sodium hydroxide solution I (6.3) and, if necessary, adjust to pH 3,8 with hydrochloric acid (6.2) or sodium hydroxide solution IV (6.6). Add 12,5 ml of hydrochloric acid (6.2). Dilute to 500 ml with water.

NOTE Due to the addition of HCl, the pH of this buffer is about 3,4. After mixing with the sample a pH of 3,8 is achieved.

This solution is stable for 3 months if stored in a refrigerator at 1 °C to 5 °C.

##### 6.21.2 Zinc sulfate solution, only for distillation method (R2 in Figure A.1).

Dissolve 10 g of zinc sulfate heptahydrate (6.13) in 750 ml of water (6.1), mix and dilute to 1 000 ml with water.

##### 6.21.3 Recipient solution, only for gas diffusion (R3 in Figure A.2).

Sodium hydroxide solution III (6.5).

##### 6.21.4 Buffer solutions for the final photometric determination (R4 in Figures A.1 and A.2)

###### 6.21.4.1 For the distillation method (R4a in Figure A.1).

Dissolve 2,3 g of sodium hydroxide (NaOH) in 500 ml of water. Add 20,5 g of potassium hydrogenphthalate (6.14) and dilute to approximately 975 ml with water.

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

Add 1 ml of surfactant (6.7) and make up to 1 000 ml with water.

For best results this solution is stable for 1 month if stored in an amber bottle in a refrigerator at 1 °C to 5 °C.