
**Water quality — Determination of
available free cyanide (pH 6) using
flow injection analysis (FIA), gas-
diffusion and amperometric detection**

*Qualité de l'eau — Dosage des cyanures libres disponibles (pH 6)
par analyse avec injection en flux (FIA), diffusion de gaz et détection
ampérométrique*

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 17690:2015

<https://standards.iteh.ai/catalog/standards/sist/8a86c115-2dc1-4d4c-93f4-39f5a16c739f/iso-17690-2015>



iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 17690:2015

<https://standards.iteh.ai/catalog/standards/sist/8a86c115-2dc1-4d4c-93f4-39f5a16c739f/iso-17690-2015>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2015

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested 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
Web 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	2
7 Apparatus	4
8 Sampling and sample preparation	5
9 Procedure	5
9.1 Flow system set up	5
9.2 Reagent blank measurement	6
9.3 Checking the suitability of the flow injection system	6
9.3.1 Electrode stabilization	6
9.3.2 Recovery rates	6
9.4 Calibration	7
9.5 Sample measurement	7
10 Calculations	7
11 Expression of results	8
12 Test report	8
Annex A (informative) Example of a flow injection system	9
Annex B (normative) Determination of the real cyanide concentration in the potassium cyanide solution (6.5.1)	10
Annex C (informative) Performance data	11
Bibliography	12

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 meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword - Supplementary information](#)

The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

ISO 17690:2015

<https://standards.iteh.ai/catalog/standards/sist/8a86c115-2dc1-4d4c-93f4-39f5a16c739f/iso-17690-2015>

Introduction

Methods using flow analysis automate wet chemical procedures and 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 reacts with the reagent solutions on their way through the manifold. The sample preparation can be integrated in the manifold. The reaction product is measured by a flow detector (e.g. amperometer).

iTeh STANDARD PREVIEW (standards.iteh.ai)

[ISO 17690:2015](https://standards.iteh.ai/catalog/standards/sist/8a86c115-2dc1-4d4c-93f4-39f5a16c739f/iso-17690-2015)

<https://standards.iteh.ai/catalog/standards/sist/8a86c115-2dc1-4d4c-93f4-39f5a16c739f/iso-17690-2015>

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 17690:2015

<https://standards.iteh.ai/catalog/standards/sist/8a86c115-2dc1-4d4c-93f4-39f5a16c739f/iso-17690-2015>

Water quality — Determination of available free cyanide (pH 6) using flow injection analysis (FIA), gas-diffusion and amperometric detection

WARNING — Persons using this International Standard should be familiar with the 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 including neutralization and proper disposal of waste solutions.

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

1 Scope

This International Standard specifies methods for the determination of available free cyanide at pH 6 in various types of water (such as ground, drinking, surface, leachate, waste water, and metallurgical processing waste water) with cyanide concentrations from 5 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 using a different injection volume (Figure A.1).

NOTE 1 ISO 2080:2008, 3.105, the concentration of available free cyanide as determined by a specified analytical method.

NOTE 2 The detection limit for this method was determined by interlaboratory testing at the national level using ASTM International D6512 Practice for Interlaboratory Quantitation Estimate.

NOTE 3 Free cyanides according to ISO 14403 and ISO 17690 are not equivalent.

In this method, two suitable mass concentration ranges from 5 µg/l to 50 µg/l and from 50 µg/l to 500 µg/l are described.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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.

3.1 available free cyanide (pH 6)

sum of HCN, cyanide ions, and cyanide bound in the metal-cyano complexes that are easily dissociated into HCN/CN⁻ at the pH of 6 determined in accordance with this International Standard

4 Interferences

4.1 Interferences by oxidizing agents

Test for the presence of oxidizing agents. Acidify KI starch paper by moistening with acetate buffer (6.7.1). Add a drop of the sample to the test paper as soon as the sample is collected; a blue colour indicates the need for treatment. If oxidizing agents are present, add powdered sodium arsenite (6.9) (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.

4.2 Interferences by sulfide

Sulfide will diffuse through the gas diffusion membrane and can be detected in the amperometric flow cell. Oxidized products of sulfide can also rapidly convert CN⁻ to SCN⁻ at a high pH. Test for sulfide by moistening lead acetate paper with acetate buffer solution (6.7.1) and then add a drop of sample on the lead acetate paper. If the paper turns black, sulfide is present. Add powdered lead carbonate (6.8) (0,1 g/l of sample). 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.

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 should be performed to remove sulfide.

5 Principle

The sample is introduced into a carrier solution of the flow injection analysis (FIA) system through an injection valve and confluence downstream with a phosphate buffer solution at pH 6 to measure available free 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.

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

6.3 Sodium hydroxide solution II, $c(\text{NaOH}) = 1,0$ 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 $2\,500 \text{ mg} \pm 1 \text{ mg}$ of potassium cyanide, KCN, in sodium hydroxide solution III ([6.4](#)) in a $1\,000 \text{ ml}$ graduated flask and make up to volume with sodium hydroxide solution III ([6.4](#)).

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 solution ([6.6.1](#)) can be used.

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

Pipette $1,00 \text{ ml}$ 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.

6.5.3 Calibration solutions.

Prepare at least five and up 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](#)).

If, for example, six calibration solutions should be prepared to cover the range of $5 \text{ } \mu\text{g/l}$ to $50 \text{ } \mu\text{g/l}$, proceed as follows.

Pipette 25 ml of the cyanide solution I ([6.5.2](#)) in a 500 ml graduated flask and make up to volume with sodium hydroxide solution III ([6.4](#)). This solution contains $0,5 \text{ mg/l}$ 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 $0,5 \text{ mg/l}$ cyanide solution and make up to volume with sodium hydroxide solution III ([6.4](#)). These solutions contain nominally $5 \text{ } \mu\text{g/l}$, $15 \text{ } \mu\text{g/l}$, $25 \text{ } \mu\text{g/l}$, $35 \text{ } \mu\text{g/l}$, $45 \text{ } \mu\text{g/l}$, and $50 \text{ } \mu\text{g/l}$ 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 given in [Annex B](#) by multiplying the nominal value by $\rho(\text{CN})/1\,000$ and round to the nearest $\mu\text{g/l}$, or, for example, if six calibration solutions should be prepared to cover the range of $50 \text{ } \mu\text{g/l}$ to $500 \text{ } \mu\text{g/l}$, proceed as follows.

Pipette 25 ml of the cyanide solution I ([6.5.2](#)) 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 $50 \text{ } \mu\text{g/l}$, $150 \text{ } \mu\text{g/l}$, $250 \text{ } \mu\text{g/l}$, $350 \text{ } \mu\text{g/l}$, $450 \text{ } \mu\text{g/l}$, and $500 \text{ } \mu\text{g/l}$ 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 $\rho(\text{CN})/1\,000$ and round to the nearest $\mu\text{g/l}$.

6.5.4 Electrode stabilization solution, approximately 5 mg/l as CN^- .

Pipette $500 \text{ } \mu\text{l}$ of potassium cyanide solution ([6.5.1](#)) into a 100 ml volumetric flask containing $1,0 \text{ ml}$ of sodium hydroxide solution I ([6.2](#)). Dilute to volume with water.

This solution is stable for one week if stored at $(5 \pm 3) \text{ }^\circ\text{C}$.

NOTE Lower cyanide concentrations can be used provided the detector signal is near saturation.

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

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

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

6.7 Reagents for the determination of available free cyanide.

6.7.1 Acetate buffer.

Dissolve 410 g of sodium acetate trihydrate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) in 500 ml of water. Add glacial acetic acid (approximately 500 ml) to yield a pH of 4,5.

6.7.2 Buffer solution A, 2 mol/l sodium phosphate monobasic solution.

Weigh 276 g dihydrogen phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) in a 1 l volumetric flask. Dissolve and dilute to volume with water.

6.7.3 Buffer solution B, 1 mol/l sodium phosphate di-basic solution.

Weigh 142 g disodium hydrogen phosphate (Na_2HPO_4) in a 1 l volumetric flask. Dissolve and dilute to volume with water. If necessary, warm to approximately 40°C on a hot plate and stir to completely dissolve the sodium phosphate dibasic into the water. Allow the solution to cool prior to use.

6.7.4 1 mol/l phosphate buffer pH 6,0 stock solution.

Add 219,25 ml buffer solution A (6.7.2) and 61,5 ml of buffer solution B (6.7.3) to a 500 ml volumetric flask. Dilute to volume with water.

6.7.5 0,2 mol/l phosphate buffer pH 6,0.

In a 1 l volumetric flask, add 200 ml 1 mol/l phosphate buffer solution pH 6,0 stock solution (6.7.4) and dilute to volume with water. The pH should be $6,0 \pm 0,1$. Verify the pH and adjust if necessary with sodium hydroxide solution III (6.4) or dilute sulfuric acid solution (6.7.6).

6.7.6 Dilute sulfuric acid solution, $c(\text{H}_2\text{SO}_4) = 0,005\ \text{mol/l}$.

6.8 Lead carbonate, PbCO_3 , powder.

6.9 Sodium arsenite, NaAsO_2 , powder.

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.

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 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 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, an 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 Lead acetate test paper, commercially available.

7.2.2 Potassium iodide starch test paper, commercially available.

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

7.2.4 pH meter and electrode, capable of measuring $\pm 0,1$ pH units.

8 Sampling and sample preparation

Refer to [Clause 4](#) 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 (one to two pellets per 500 ml). Avoid excess preservation as it can result in problems with a low recovery and/or poor peak shape of available free cyanide during analysis.

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

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

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.

9 Procedure

9.1 Flow system set up

Set up and adjust the flow analysis system according to [Table 1](#).