

---

---

**Water quality — Determination of  
fluoride using flow analysis (FIA and  
CFA) —**

Part 2:

**Method using continuous flow  
analysis (CFA) with automated in-line  
distillation**

(standards.iteh.ai)

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

ISO/TS 17951-2:2016

<https://standards.iteh.org/catalogue/standards/sist/d9d9a8e3-048f-4719-b560-d5610f82368/iso-ts-17951-2-2016>

*Partie 2: Méthode par analyse en flux continu (CFA) avec distillation  
in situ automatique*



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

ISO/TS 17951-2:2016

<https://standards.iteh.ai/catalog/standards/sist/d9d9a8e2-048f-47d9-b560-d5610fc82368/iso-ts-17951-2-2016>



**COPYRIGHT PROTECTED DOCUMENT**

© ISO 2016, Published in Switzerland

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  
Ch. de Blandonnet 8 • CP 401  
CH-1214 Vernier, Geneva, Switzerland  
Tel. +41 22 749 01 11  
Fax +41 22 749 09 47  
copyright@iso.org  
www.iso.org

# Contents

|   | Page      |
|---|-----------|
| Foreword .....  | iv        |
| Introduction .....  | v         |
| <b>1 Scope</b> .....  | <b>1</b>  |
| <b>2 Normative references</b> .....   | <b>1</b>  |
| <b>3 Principle</b> .....  | <b>2</b>  |
| <b>4 Interferences</b> .....  | <b>2</b>  |
| <b>5 Reagents</b> .....   | <b>2</b>  |
| <b>6 Apparatus</b> .....  | <b>5</b>  |
| <b>7 Sampling and sample preparation</b> .....  | <b>5</b>  |
| <b>8 Procedure</b> .....  | <b>5</b>  |
| 8.1 Setting up the system .....   | 5         |
| 8.2 Reagent blank measurement .....   | 5         |
| 8.3 Adjustment of sensitivity .....   | 6         |
| 8.4 Confirmation of repeatability .....   | 6         |
| 8.5 Calibration .....   | 6         |
| 8.6 Measurement of samples .....  | 6         |
| <b>9 Calculation</b> .....  | <b>7</b>  |
| <b>10 Expression of results</b> .....   | <b>7</b>  |
| <b>11 Test report</b> .....   | <b>7</b>  |
| <b>Annex A (informative) Example of continuous flow analysis (CFA) with an in-line distillation unit and spectrometric detection</b> .....        | <b>8</b>  |
| <b>Annex B (informative) Determination of fluoride by automatic distillation continuous flow analysis (CFA) and ion selective detection</b> ..... | <b>9</b>  |
| <b>Annex C (informative) Examples of flow systems</b> .....   | <b>12</b> |
| <b>Annex D (informative) Results of interlaboratory trial</b> .....   | <b>13</b> |
| <b>Annex E (informative) Recovery test for fluoride</b> .....   | <b>14</b> |
| <b>Annex F (informative) Analytical precision of fluoride</b> .....   | <b>15</b> |
| <b>Bibliography</b> .....   | <b>16</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.

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](http://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](http://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 17951 consists of the following parts, under the general title *Water quality — Determination of fluoride using flow analysis (FIA and CFA)*:  
<http://www.iso.org/standard/standard/4710150>  
<https://doi.org/10.31030/15610182368/iso-ts-17951-2-2016>

- *Part 1: Method using flow injection analysis (FIA) and spectrometric detection after off-line distillation* [Technical Specification]
- *Part 2: Method using continuous flow analysis (CFA) with automated in-line distillation* [Technical Specification]

## Introduction

Fluorine compounds in waters and effluents exist in various chemical forms, such as fluoride ion, complexes of iron, aluminium, boron and etc., as well as insoluble forms, such as calcium and magnesium fluorides. Excess fluoride can cause bone damage and fluorosis. In order to ensure conversion of any insoluble fluorides into soluble fluoride for measurement, steam distillation is necessary.

This part of ISO 17951 describes a CFA method for flow analysis of fluoride with integrated in-line distillation and spectrometric detection.

A CFA method with ion-selective detection is described in [Annex B](#).

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

ISO/TS 17951-2:2016

<https://standards.iteh.ai/catalog/standards/sist/d9d9a8e2-048f-47d9-b560-d5610fc82368/iso-ts-17951-2-2016>

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

ISO/TS 17951-2:2016

<https://standards.iteh.ai/catalog/standards/sist/d9d9a8e2-048f-47d9-b560-d5610fc82368/iso-ts-17951-2-2016>

# Water quality — Determination of fluoride using flow analysis (FIA and CFA) —

## Part 2: Method using continuous flow analysis (CFA) with automated in-line distillation

**WARNING** — Persons using this part of ISO 17951 should be familiar with normal laboratory practice. This part of ISO 17951 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 in accordance with this part of ISO 17951 be carried out by suitably qualified staff.

### 1 Scope

This part of ISO 17951 specifies a method for the determination of fluoride in waters, waste waters and effluents by continuous flow analysis (CFA). Any insoluble or complexed fluoride is converted to fluoride ion by an automated continuous flow distillation procedure from sulfuric/phosphoric acid. Fluoride ion in the distillate is measured using flow analysis with lanthanum alizarin complexone and spectrometric detection. This method is applicable to industrial waste waters, effluents, surface waters, ground waters, leachates. When this method is applied to the analysis of drinking water, a heater and a distillation unit is unnecessary. Some drinking water contains high concentration of aluminium and iron. In the case of drinking water this part of ISO 17951 is appropriate to drinking water with low interferences. It is not applicable to samples which contain large amount of suspended matter.

In this part of ISO 17951, two working ranges are described:

- working range I: 0,1 mg/l to 1,0 mg/l;
- working range II: 1,0 mg/l to 10 mg/l.

The specification of the calibration solutions are to be adapted accordingly.

### 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 6353-2, *Reagents for chemical analysis — Part 2: Specifications — First series*

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 Principle

Sample, water and mixture of sulfuric acid and phosphoric acid are gas-segmented and mixed in a reaction coil. The mixture is transported through a heating device and a distillation unit. The distillate is mixed with collection solution and lanthanum alizarin complexone solution. The mixture is transported to a reaction coil and the formed blue colour is measured by spectrometric detection around 620 nm.

### 4 Interferences

Without distillation, lanthanum alizarin complexone spectrophotometric method suffers from the interferences by aluminium, cadmium, cobalt, iron, nickel, beryllium, lead, etc. However, these interferences are removed by the distillation.

In the case of sample containing high chloride, the recovery of fluoride decreases. For example, in a sea water sample, the response decreases to about 70 %. Thus, recovery test is necessary for the analysis of such samples.

### 5 Reagents

Use only reagents of recognized analytical grade. The prepared solution is degassed, if necessary.

5.1 **Water**, grade 1, as specified in ISO 3696.

5.2 **1,2-Dihydroxyanthraquinonyl-3-methylamine-*N,N*-diacetic acid dihydrate (alizarin complexone)**,  $C_{19}H_{15}NO_8 \cdot 2H_2O$ .

5.3 **Ammonia solution I**,  $c(NH_3) = 15 \text{ mol/l}$ , as specified in ISO 6353-2.

5.4 **Hydrochloric acid I**,  $c(HCl) = 12 \text{ mol/l}$ , as specified in ISO 6353-2.

5.5 **Ammonium acetate**,  $CH_3COONH_4$ , as specified in ISO 6353-2.

5.6 **Sodium acetate trihydrate**,  $CH_3COONa \cdot 3H_2O$ , as specified in ISO 6353-2.

5.7 **Acetic acid**,  $CH_3COOH$ , as specified in ISO 6353-2.

5.8 **Lanthanum(III) oxide**,  $La_2O_3$ .

5.9 **Acetone**,  $CH_3COCH_3$ , as specified in ISO 6353-2.

5.10 **Sodium fluoride**, NaF.

5.11 **Ethanol (95)**,  $C_2H_5OH(95)$ .

(95) = volume fraction.

5.12 **Sulfuric acid**,  $c(H_2SO_4) = 18 \text{ mol/l}$ .

5.13 **Imidazole**,  $C_3H_4N_2$ .

5.14 **Poly(oxyethylene)octylphenylether**,  $C_{14}H_{22}O(C_2H_4O)_n$ .



**5.15 Phosphoric acid**,  $c(\text{H}_3\text{PO}_4) = 14,6 \text{ mol/l}$ .

**5.16 Ammonia solution II.**

Mix 10 ml of ammonia solution I (5.3) and 100 ml of water (5.1).

**5.17 Ammonium acetate solution**,  $\rho(\text{C}_2\text{H}_7\text{NO}_2) = 200 \text{ g/l}$ .

Dissolve 200 g of ammonium acetate (5.5) to about 800 ml of water (5.1). Make up to 1 000 ml with water (5.1).

**5.18 Sodium acetate solution.**

Dissolve 41 g of sodium acetate trihydrate (5.6) to 400 ml of water, and add 24 ml of acetic acid (5.7).

**5.19 Hydrochloric acid II**,  $c(\text{HCl}) = 2 \text{ mol/l}$ .

Mix 20 ml of hydrochloric acid I (5.4) and 100 ml of water (5.1).

**5.20 Lanthanum(III) oxide solution**,  $c(\text{La(III)}) = 0,1 \text{ mol/l}$ .

Add 0,163 g of lanthanum(III) oxide (5.8) to 10 ml of hydrochloric acid II (5.19) and dissolve it by heating of the solution.

**5.21 Lanthanum-alizarin complexone solution (solution A).**

Dissolve 0,192 g of alizarin complexone (5.2) to 4 ml of ammonia solution II (5.16) and 4 ml of ammonium acetate solution (200 g/l) (5.17). Add this solution into 425 ml of sodium acetate solution (5.18) with stirring, and add 400 ml of acetone (5.9) gradually. Then, add 10 ml of lanthanum(III) oxide solution (5.20) to the solution and mix it. After cooling, adjust the pH of the solution to 4,7 with acetic acid (5.7) or ammonia solution I (5.3), then make it up to 1 000 ml with water (5.1).

Lanthanum-alizarin complexone solution (solution A) (5.21) can be prepared by using alfusone.<sup>1)</sup> In that case, after dissolving 1,2 g of alfusone to small amount of water (5.1), add 90 ml of acetone (5.9) and mix the solution. Make up the solution to 300 ml with water (5.1). The solution shall be prepared at the time of analysis.

**5.22 Lanthanum-alizarin complexone solution (solution B).**

Dissolve 10 g of imidazole (5.13) to about 200 ml of water (5.1). Add 40 ml of acetic acid (5.7), 45 ml of acetone (5.9) and 0,5 ml of fluoride stock solution I (5.23). Make up the solution to 300 ml with water (5.1). Add 200 ml of lanthanum-alizarin complexone solution (solution A) (5.21) and 5 ml of ethanol solution of poly(oxyethylene)octylphenylether (5.25) and mix the solution.

Lanthanum-alizarin complexone solution (solution B) (5.22) can be prepared with alfusone. In that case, dissolve 2,5 g of alfusone to about 300 ml of water (5.1). Add 40 ml of acetic acid (5.7), 10 g of imidazole (5.13), 125 ml of acetone (5.9) and 0,5 ml of fluoride stock solution I (5.23), and mix the solution. After making up the solution to 500 ml with water (5.1), add 5 ml of ethanol solution of poly(oxyethylene) octylphenylether (5.25) and mix the solution. This solution shall be prepared at the time of analysis.

**5.23 Fluoride stock solution**,  $\rho(\text{F}^-) = 100 \text{ mg/l}$ .

Take sodium fluoride (5.10) in a platinum plate and heat it at 105 °C at least 1 h. Then cool it in a desiccator. Dissolve 0,221 g of NaF (5.10) in water (5.1) and in a 1 000 ml volumetric flask and make up to volume with water (5.1). Store the solution in a polyethylene bottle.

1) Alfusone is a product commercially available. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

This solution is stable for one month at room temperature.

**5.24 Fluoride standard solution,  $\rho(\text{F}^-) = 10 \text{ mg/l}$ .**

Take 10 ml of fluoride stock solution (5.23) to a 100 ml volumetric flask and make up to volume with water (5.1). Store the solution in a polyethylene bottle.

This solution is stable for one week in the dark at 2 °C to 8 °C.

**5.25 Ethanol solution of poly(oxyethylene)octylphenylether.**

Dissolve 50 g of poly(oxyethylene)octylphenylether (5.14) in ethanol (95) (5.11) and make up to 100 ml with ethanol (95) (5.11).

This solution is stable for one month at room temperature.

**5.26 Mixed solution of sulfuric acid and phosphoric acid.**

Add 50 ml of sulfuric acid (5.12), 10 ml of phosphoric acid (5.15) and 3 ml of fluoride stock solution (5.23) into about 800 ml of water (5.1). Make up the solution to 1 000 ml with water (5.1).

This solution is stable for three months at room temperature.

**5.27 Collection solution.**

Add 1 ml of ethanol solution of poly(oxyethylene)octylphenylether (5.25) to 100 ml of water (5.1) and mix the solution.

This solution is stable for one week at room temperature.

**5.28 Calibration solutions.**

Prepare at least five calibration solutions with fluoride concentrations roughly regularly distributed over the working range, by dilution of the appropriate fluoride standard solution (5.24) or the fluoride stock solution (5.23). Examples of calibration solutions for two possible working ranges are given in 5.28.1 and 5.28.2. For other working ranges, prepare calibration solutions appropriate to cover a decade of concentrations, accordingly.

**5.28.1 Calibration solutions for working range I, (0,1 mg/l to 1,0 mg/l).**

For example, six calibration solutions should be prepared as follows.

Pipette, into 100 ml volumetric flasks, 1 ml, 2 ml, 4 ml, 6 ml, 8 ml, 10 ml, respectively, of the fluoride standard solution I (5.24) and make up to volume with water (5.1).

These solutions contain 0,1 mg/l, 0,2 mg/l, 0,4 mg/l, 0,6 mg/l, 0,8 mg/l and 1 mg/l fluoride, respectively.

**5.28.2 Calibration solutions for working range II (1,0 mg/l to 10 mg/l).**

For example, six calibration solutions should be prepared as follows.

Pipette, into 100 ml volumetric flasks, 1 ml, 2 ml, 4 ml, 6 ml, 8 ml, 10 ml, respectively, of the fluoride stock solution (5.23) and make up to volume with water (5.1).

These solutions contain 1 mg/l, 2 mg/l, 4 mg/l, 6 mg/l, 8 mg/l and 10 mg/l fluoride, respectively.

## 6 Apparatus

A suitable example of the continuous flow analysis system contains the components specified in 6.1 to 6.6 (see Figure A.1).

### 6.1 Low pulsation-pump.

Use a multichannel quantitative pump with a low pulsation.

### 6.2 Sample introduction system.

Automatic sample introduction device which can achieve a reproducible sample input.

**6.3 Distiller**, composed of a distillation unit and a heater which is capable of heating at 145 °C.

**6.4 Reaction manifold**, composed of chemically inert tubes with the internal diameter of about 0,5 mm to 2 mm, and glass or plastic parts with a small dead volume.

### 6.5 Detection system.

Use a spectrophotometric detector with flow cell which is capable of measuring at a wavelength of 620 nm ± 5 nm.

UV lamps and the light filter should be calibrated to ensure the repeatability of the results.

**6.6 Recording system**, which is capable of recording signals from the detector.

Usually, peak height signals are measured.

[ISO/TS 17951-2:2016](https://standards.iteh.ai/catalog/standards/sist/d9d9a8e2-048f-47d9-b560-17951-2-2016)

[https://standards.iteh.ai/catalog/standards/sist/d9d9a8e2-048f-47d9-b560-](https://standards.iteh.ai/catalog/standards/sist/d9d9a8e2-048f-47d9-b560-17951-2-2016)

## 7 Sampling and sample preparation

Take the samples in polyethylene bottles which have been washed thoroughly and rinsed with fluoride-free water. Polypropylene, polystyrene and polycarbonate bottles can also be used. No preservative is necessary. Analyse the samples within one month. For further information on sample preservation see ISO 5667-3.

## 8 Procedure

### 8.1 Setting up the system

Set up the analytical apparatus and the detector ready for the analysis. Pump water (5.1) and the mixed solution of sulfuric acid and phosphoric acid (5.26) along the flow path until it is confirmed that water is condensed uniformly on the wall of condenser of the distillation unit. Then, change the water (5.1) to reagent solutions and wait until the base line is stable. Confirm that there is a uniform air bubble pattern in the flows of the CFA. Confirm that the drift of baseline, etc. does not interfere the results and a sufficient signal to noise ratio (S/N) is obtained.

### 8.2 Reagent blank measurement

Set the analysis system in operation by first pumping water through the system. Wait for stabilization of the baseline and zero the baseline. Run mixed solution of sulfuric acid and phosphoric acid (5.26), collection solution (5.27), lanthanum-alizarin complexone (solution B) (5.22), respectively, through the system and measure the increase in absorbance against water. If the absorbance per centimeter