TECHNICAL SPECIFICATION

ISO/TS 17951-2

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

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

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

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

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Foreword

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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 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)*:

— *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.

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 mol/l, as specified in ISO 6353-2.

5.4 Hydrochloric acid I, $c(HCl)$ = 12 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 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, $c(H_3PO_4)$ = 14,6 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, $\rho(C_2H_7NO_2)$ = 200 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, $c(HCl)$ = 2 mol/l.

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

5.20 Lanthanum(III) oxide solution, $c(La(III))$ = 0,1 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.[1)] 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, $\rho(F^-)$ = 100 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.

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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, $\rho(F^-)$ = 10 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.

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

changes by more than 0,000 3 cm^{-1} of cell path length, it is possible that either the water or the reagent solutions are contaminated. Take appropriate measures to eliminate the interference.

NOTE If the photometric detector does not give absorbance readings, the absorbance can be determined with an external absorbance-measuring spectrometer.

8.3 Adjustment of sensitivity

Adjust the sensitivity of detector to be appropriate for the response by analytical species in the sample.

An appropriate path length should be used to achieve a minimum absorbance of 0,005 (absolute value) for a fluoride solution with the concentration of the lower end (0,1 mg/l) of the working range.

8.4 Confirmation of repeatability

Analyse a standard solution five times at a concentration in the middle of the using working curve and confirm that repeatability coefficient of variation is not greater than 10 %.

8.5 Calibration

Prepare the calibration solutions for the working ranges I and II by diluting the stock solution (5.23) or the standard solution (5.24) with water (5.1). At least five calibration solutions per working range are prepared. Measure each standard solution by the analytical conditions to be used for the analysis of samples.

Select the working mode of the flow system and calibrate by sequentially applying the calibration solutions (5.28) and the blank solution.

Prior to the calibration, zero the instrument, following the manufacturer's instructions, as long as they are in accordance with the specifications of this part of ISO 17951.

Determine the measured values from the calibration solutions.

The test conditions for the calibration and the measurement of samples (8.6) are the same. The magnitude of the measuring signal is proportional to the mass concentration of fluoride. Establish the regression line for the measuring series obtained.

Calibrate the flow system as specified in ISO 8466-1. In general, Formula (1) is appropriate (ISO 8466-1). 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.

The measured value for the calibration solutions, y, in terms of instrument related units (e.g. peak heights in centimetres or counts), is given by Formula (1):

$$y = b\rho + a \tag{1}$$

where

b is the slope of the calibration function, expressed in instrument-related units per milligram per litre, mg/l;

ρ is the mass concentration of the calibration solutions, expressed in milligrams per litre, mg/l;

a is the ordinate intercept, expressed in instrument-related units.

8.6 Measurement of samples

Measure samples by using the same conditions as the preparation of the calibration graphs. When the measurement value exceeds the range of the working curve, dilute the samples appropriately. In order

to confirm the adequacy of the measurements, measure the calibration solutions for the working curve at the minimum and the maximum concentrations at an interval of 10 to 20 samples. In order to confirm that there is no hindrance to the results of the measurement, compare the response of the calibration solutions at this time with the response of the calibration solutions at the time of the preparation of the calibration graph. In addition, confirm that when each sample is measured, there is no abnormality in the peak shape and confirm that the variation of the baseline is within acceptable limits.

Analyse the samples in the same way as the calibration solutions with the CFA system.

Make a new calibration, if necessary.

9 Calculation

For the calculation of concentration, use the working curve given in 8.5. Do not extrapolate the working curve.

Determine the mass concentrations of the samples using the measured values, obtained as specified in 8.5 for the calibration solutions.

Calculate ρ using Formula (2):

$$\rho = \frac{y - a}{b} \tag{2}$$

where, ρ, is the mass concentration of the sample, expressed in milligram per litre.

For an explanation of the symbols a and b, see 8.5.

10 Expression of results

Describe the concentration of fluoride determined in Clause 9 by using the unit of mg/l as F^-.

Report the results to two significant figures at most.

EXAMPLE 1 $\rho(F^-)$ 0,24 mg/l.

EXAMPLE 2 $\rho(F^-)$ 6,9 mg/l.

11 Test report

This test report shall contain at least the following information:

a) the test method used, together with a reference to this part of ISO 17951, i.e. ISO/TS 17951-2:2016;

b) all information necessary for identification of the sample;

c) the type of sample pretreatment;

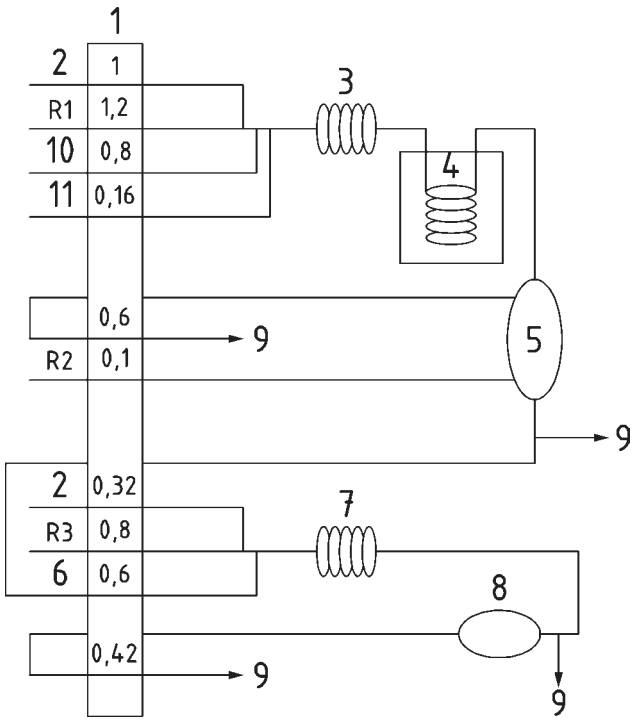
d) the fluoride concentration in milligrams per litre, expressed in accordance with Clause 10;

e) any special observations noted during the determination;

f) any deviations from this part of ISO 17951, which could have affected the result.

Annex A
(informative)

Example of continuous flow analysis (CFA) with an in-line distillation unit and spectrometric detection



Key

1	low pulsation-pump, flow rate ml/min
2	air; (segmentation gas)
3	reaction coil (internal diameter 2 mm, length 0,5 m)
4	heater (145 °C)
5	distillation unit (internal diameter 1,6 mm, length 2 m, made of glass)
6	distillate
7	reaction coil (internal diameter 2 mm, length 2 m)
8	detector (absorption cell, optical length 3 cm, wavelength 620 nm) and recording system
9	waste
10,11	sample or water: in the case of determination range 0,1 mg/l to 1,0 mg/l: 10 = sample, 11 = water in the case of determination range 1,0 mg/l to 10 mg/l: 10 = water, 11 = sample
R1	mixed solution of sulfuric acid and phosphoric acid
R2	collection solution
R3	lanthanum-alizarin complexone solution (solution B)

Figure A.1 — Example of a continuous flow analysis system (CFA) with an in-line distillation unit for the determination of 0,1 mg/l to 1,0 mg/l and 1,0 mg/l to 10 mg/l

Annex B
(informative)

Determination of fluoride by automatic distillation continuous flow analysis (CFA) and ion selective detection

B.1 Principle

Sample, water and a 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 a TISAB buffer solution and measured with an ion selective electrode (ISE) for fluoride and a reference electrode.

B.2 Interferences

High alkalinity concentrations ($CaCO_3$ > 7 000 mg/l) will disturb ISE measurement but are removed by distillation.

B.3 Additional reagents

Use only reagents of recognized analytical grade.

B.3.1 Sulfuric acid, H_2SO_4 18 mol/l.

B.3.2 di-Ammonium hydrogen citrate, $(NH_3)_2C_6H_8O_7$.

B.3.3 Sodium chloride, NaCl.

B.3.4 1,2-Cyclohexylenedinitrilotetraacetic acid (CDTA), $C_{14}H_{22}N_2O_8{\cdot}H_2O$.

B.3.5 Sodium hydroxide, c(NaOH) = 1 mol/l.

B.3.6 Hydrochloric acid, c(HCl) = 1 mol/l.

B.3.7 Distillation reagent, (Key R1 in Figure C.1).

Add 50 ml of sulfuric acid (B.3.1) to 800 ml of water (5.1) and mix. Dilute to 1 000 ml with water (5.1) and mix.

This solution is stable for two weeks.

B.3.8 TISAB buffer, (Key R3 in Figure C.1).

Dissolve in about 500 ml water (5.1) 115 g of di-Ammonium hydrogen citrate (B.3.2). Add 40 g of sodium chloride (B.3.3) and add 5 g of 1,2-Cyclohexylenedinitrilotetraacetic acid (CDTA) (B.3.4). Adjust to pH 4,5 with sodium hydroxide (B.3.5) or hydrochloric acid (B.3.6). Add 1,0 ml of fluoride stock solution (5.23). Dilute to 1 000 ml with water (5.1). Add 1 ml of ethanol solution of poly(oxyethylene) octylphenylether (5.25) and mix.

This solution is stable for three months.

B.3.9 Calibration solutions.

Prepare at least five calibrations solutions with fluoride concentrations regularly distributed over the working ranges, by appropriate dilution of the fluoride stock solution (5.23) or the fluoride standard solution (5.24).

EXAMPLE Six calibration standards could be prepared as follows: Pipette, in 100 ml graduated flasks, 0,5 ml, 1 ml, 2 ml, 4 ml, 8 ml, or 10 ml respectively, of the above mentioned 100 mg/l fluoride stock solution (5.23) and make up to volume with water (5.1). These solutions contain 0,5 mg/l, 1,0 mg/l, 2,0 mg/l, 4,0 mg/l, 8,0 mg/l and 10,0 mg/l of fluoride.

Prepare solutions fresh daily.

A similar set-up can be used for the lower range: six calibration standards could be prepared as follows: Pipette, in 100 ml graduated flasks, 0,2 ml, 0,5 ml, 1 ml, 2 ml, 4 ml, or 5 ml respectively, of the above mentioned 10 mg/l fluoride standard solution (5.24) and make up to volume with water (5.1). These solutions contain 0,02 mg/l, 0,05 mg/l, 0,10 mg/l, 0,20 mg/l, 0,40 mg/l and 0,50 mg/l of fluoride.

Prepare solutions fresh daily.

B.4 Apparatus

Usual laboratory apparatus.

B.4.1 Continuous flow analysis system for distillation method.

A suitable example of the system configuration contains the following components (see Figure C.1). Alternative system configurations are also applicable.

B.4.2 Autosampler, or another device capable of introducing sample reproducibility.

B.4.3 Reagent reservoirs.

B.4.4 Low pulsation pump, having specific chemically inert pump tubes, for flow rates as given in Figure C.1 as an example.

B.4.5 In-line distillation device, adjustable to a temperature of 145 °C ± 1 °C with a distillation coil of glass or polymer material, length of coil, e.g. 80 cm, internal diameter, e.g. 1,5 mm.

B.4.6 Manifold, capable of highly reproducible dosing of gas bubbles, sample and reagents, and having appropriate transport systems and connection assemblies of chemically inert glass, polymer, or metal.

B.4.7 Ion selective detector, with a flow cell, measuring electrode and reference electrode.

Use a lanthanum fluoride measuring electrode and an Ag/AgCl reference electrode.

B.4.8 Recording unit (e.g. strip chart recorder, integrator or printer/plotter, or a computer data system).

In general, peak height signals are measured.

B.5 Calibration

As the range of the ISE is quite big, it can be necessary to produce a calibration curve for the lower range and for the upper range of the system. Generally, the ranges are split into a lower range of 0,02 mg/l to

0,5 mg/l fluoride and an upper range of 0,5 mg/l to 5,0 mg/l fluoride. This is necessary because the calculations for both ranges are different due to the behaviour of the ISE.

a) For the lower range (0,02 mg/l to 0,5 mg/l), a second degree curve can be used as specified in ISO 8466-2:

$$y = c\rho^2 + b\rho + a \tag{B.1}$$

b) For the upper range (0,5 mg/l to 5,0 mg/l), an inverse logarithmic function shall be used:

$$y = d \lg \rho + e \tag{B.2}$$

where

y is the measured value, in terms of instrument-related units;

ρ is the mass concentration, in milligrams per litre, of fluoride in the calibration solutions;

a is the ordinate intercept of the calibration function, in terms of instrument-related units;

b is the parameter of the calibration function in terms of instrument-related units (l/mg);

c second-order parameter of the calibration function in terms of instrument-related units (l^2/mg^2);

d is the slope of the logarithmic calibration curve;

e is the ordinate intercept of the calibration function, in terms of instrument-related units.

B.6 Calculation of results

Determine the mass concentration of fluoride in the measuring solution using the measured value obtained as described in B.5 from the calibration function given in Formula (B.1) or (B.2).

For the calculation, use the appropriate calibration function. Do not extrapolate beyond the working range selected.

For the lower range (0,02 mg/l to 0,5 mg/l), calculate ρ from Formula (B.3):

$$\rho = \left(-b / 2c\right) - \left[\left(b / 2c\right)^2 - \left(a - y\right) / c\right]^{1/2} \tag{B.3}$$

or the higher range (0,5 mg/l to 5,0 mg/l), calculate ρ from Formula (B.4):

$$\lg \rho = \left(y - e\right) / d$$

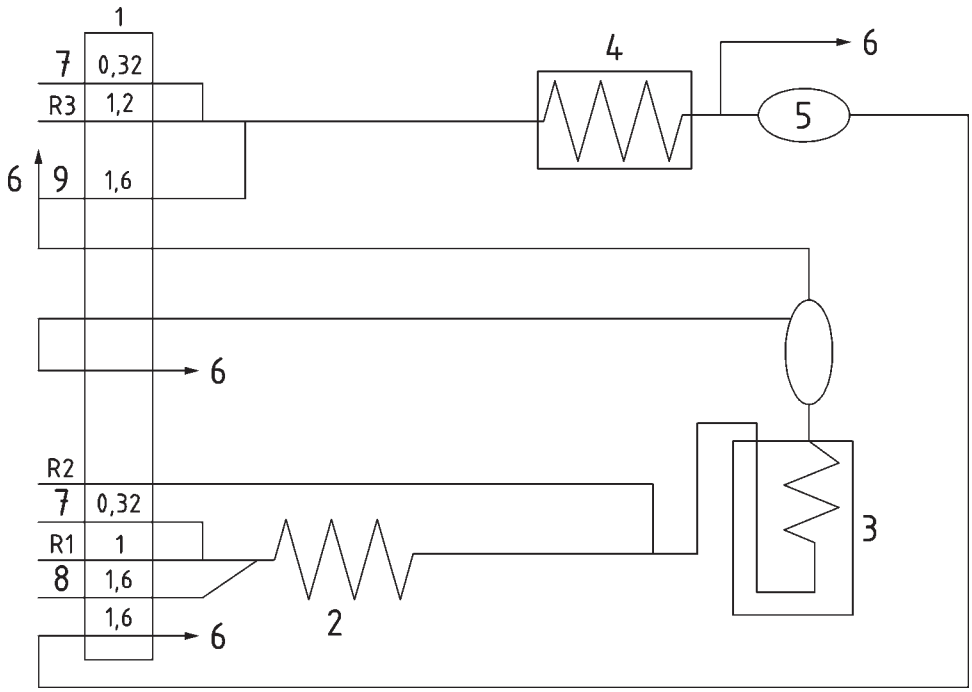
or

$$\rho = 10^{(y-e)/d} \tag{B.4}$$

For the explanation of the symbols in these formulae, see B.5. All dilution steps shall be taken into account in the calculation.

Annex C
(informative)

Examples of flow systems



Key

1 pump (flow rates in ml/min)
2 reaction coil l length 50 cm/ internal diameter 1,5 mm
3 distillation unit, 145 °C
4 heating bath, 60 °C, l length 100 cm/ internal diameter 2 mm
5 ion selective detector with electrodes
6 waste
7 air, segmentation gas
8 sample
9 resample
R1 distillation reagent (B.3.7)
R2 distillation gas, f.e. N_2, flow rate 20 l/h
R3 TISAB buffer (B.3.8)

Figure C.1 — Example of a CFA system for the determination of fluoride (0,10 mg/l to 10,0 mg/l) with an in-line distillation unit and ISE detector

Annex D
(informative)

Results of interlaboratory trial

Table D.1 — Results of interlaboratory trial

No	Analyst	Sample	Results	Detection
1	Korea, Rural organization	Hot spring water	1,03 mg/l ± 0,030 mg/l, (n = 7), RSD 2,9 %	Colourimetric
2	Korea, Rural organization	River water	0,94 mg/l ± 0,013 mg/l, (n = 7), RSD 1,4 %	Colourimetric
3	Netherlands, CFA company	Effluent of research institute	7,27 mg/l ± 0,115 mg/l, (n = 16), RSD 1,6 %	Ion selective electrode
4	Netherlands, CFA company	Synthetic sample 1	1,22 ± 0,055 mg/l, (n = 16), RSD 4,5 %	Ion selective electrode
5	Netherlands, CFA company	Synthetic sample 2	1,01 mg/l ± 0,025 mg/l, (n = 16), RSD 2,5 %	Ion selective electrode
6	Belgium, Scientific institute	Synthetic sample 1	0,92 mg/l ± 0,026 mg/l, (n = 3), RSD 2,8 %	Colourimetric
7	Belgium, Scientific institute	Synthetic sample 2	0,79 mg/l ± 0,010 mg/l, (n = 3), RSD 1,3 %	Colourimetric
8	Germany, Analysis company	Hot spring water	1,07mg/l ± 0,020 mg/l (n = 3), RSD 1,9 %	Colourimetric
9	Germany, Analysis company	Lake water	0,84 mg/l ± 0,014 mg/l, (n = 3), RSD 1,7 %	Colourimetric
10	Japan, University	Hot spring water	1,01 mg/l ± 0,0071 mg/l, (n = 6), RSD 0,70 %	Colourimetric
11	Japan, University	Lake water	0,81 mg/l ± 0,0056 mg/l, (n = 6), RSD 0,70 %	Colourimetric
12	Japan, Analysis company	River water	0,99 mg/l ± 0,034 mg/l, (n = 5), RSD 3,4 %	Colourimetric
13	Japan, Analysis company	Lake water	0,81 mg/l ± 0,0028 mg/l, (n = 5), RSD 0,35 %	Colourimetric
14	Japan, CFA company	Effluent of research institute	7,3 mg/l ± 0,13 mg/l, (n = 3), RSD 1,8 %	Colourimetric
15	Japan, CFA company	Synthetic sample 1	1,15 mg/l ± 0,067 mg/l, (n = 3), RSD 5,8 %	Colourimetric
16	Japan, Analysis company	River water	0,99 mg/l ± 0,012 mg/l, (n = 3), RSD 1,2 %	Colourimetric
17	Japan, Analysis company	Lake water	0,78 mg/l ± 0,0009 mg/l, (n = 6), RSD 0,12 %	Colourimetric
18	Japan, Research institute	Effluent of research institute	7,34 mg/l ± 0,15 mg/l, (n = 5), RSD 2,0 %	Colourimetric
19	Japan, Research institute	River water	0,97 mg/l ± 0,010 mg/l, (n = 5), RSD 1,0 %	Colourimetric
20	Japan, Research institute	Synthetic sample 2	0,85 mg/l ± 0,011 mg/l, (n = 5), RSD 1,3 %	Colourimetric

Annex E
(informative)

Recovery test for fluoride

NOTE The recoveries in Table E.1 were calculated from mean values (n = 5); the results are quoted from Reference [5].

Table E.1 — Recovery test for fluoride

Compound	**Concentration added** (mg/l)	**Recovery** (%) (Vxo/%)
Fluoride	0	—
	0,2	94,5(2,3)
	0,5	97,8(2,0)
	0,8	99,2(2,1)

Annex F
(informative)

Analytical precision of fluoride

Table F.1 — Analytical precision of fluoride

Compound	**Linearity**				**Detection limit** 3σ/mg l^{-1}	**LOQ** 10σ /mg l^{-1}
	Range (mg/l)	r^2[a]	Vxo[b] (%)	Absorbance (at 1,0 mg/l)	36 (mg/l)	106 (mg/l)
Fluoride	0,1 to 1,0	0,998 9	0,89	0,134	0,014	0,045

NOTE From Reference [5].

[a] r^2: coefficient of correlation (n = 5).

[b] Vxo: relative standard deviation at 0,5 mg^{-1}.

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