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STANDARD

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10359-1

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Water quality — Determination of fluoride —

Part 1:
Electrochemical probe method for potable and lightly polluted water

Qualité de l'eau — Dosage des fluorures —

Partie 1: Méthode de la sonde électrochimique pour l'eau potable et faiblement polluée

Reference number
ISO 10359-1:1992(E)

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.

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.

International Standard ISO 10359-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 2, *Physical, chemical, biochemical methods*.

ISO 10359 consists of the following parts, under the general title *Water quality — Determination of fluoride*:

— *Part 1: Electrochemical probe method for potable and lightly polluted water*

— *Part 2: Determination of inorganically bound total fluoride after digestion and distillation*

Annex A of this part of ISO 10359 is for information only.

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Introduction

Fluoride ions occur in almost all ground and surface waters. Their concentration depends primarily on the hydrogeological conditions and is generally below 1 mg/l.

Certain industrial waste waters may also contain fluoride ions in higher concentrations.

The fluoride value is also dependant on the type and concentration of cations present at the same time in water, such as Ca^{2+}, Mg^{2+}, Al^{3+} or Fe^{3+}, which may form sparingly soluble compounds with fluoride ions or complexes of low dissociation constant.

Apart from these compounds, stable boron-fluoride complexes exist.

Several different methods are available for determining fluoride and the choice of method depends on the type of problem posed as follows.

a) Direct measurement using fluoride ion selective electrodes. This method is suitable for the determination of fluoride in potable and surface water.

   It is specified in this part of ISO 10359.

b) Determination of the total inorganically bound fluoride using decomposition, distillation and potentiometric measurement.

   This method will be specified in ISO 10359-2.

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Water quality — Determination of fluoride —

Part 1:
Electrochemical probe method for potable and lightly polluted water

1 Scope

1.1 Field of application

This part of ISO 10359 specifies a method for the determination of dissolved fluoride in fresh, potable and low contaminated water, and some surface waters, using an electrochemical technique.

The method is directly suitable for measuring fluoride concentrations from 0,2 mg/l to 2,0 g/l.

After the addition of a known amount of fluoride, concentrations as low as 0,02 mg/l can be detected (see 7.3).

The method is not suitable for waste waters and industrial effluents; this determination will be the subject of ISO 10359-2.

1.2 Interferences

The electrode will respond directly to hydroxide ions. The formation of HF under acidic conditions will reduce the measured fluoride concentration. Therefore, buffer all test aliquots to a pH between 5 and 7 to prevent such interference. Cations such as calcium, magnesium, iron and aluminium form complexes with fluoride or precipitates to which the electrode does not respond. Therefore the buffer solution also contains *trans*–1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid (CDTA) as a decomplexing agent to free bound fluoride. The boron tetrafluoride anion, BF_4^-, is not decomplexed by the addition of buffer.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this part of ISO 10359. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this part of ISO 10359 are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-3:—[1], *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

3 Principle

When a fluoride ion-selective electrode comes into contact with an aqueous solution containing fluoride ions, a potential difference develops between the measuring electrode and the reference electrode. The value of this potential difference is proportional to the logarithm of the value of the fluoride ion activity in accordance with the Nernst equation.

Temperature and ionic strength may influence the potential difference. Accordingly, these parameters shall be the same during calibration and measurement and shall be kept constant throughout the procedure.

The activity of the fluoride ions is also pH-dependant. Values of pH between 5 and 7 have proved favorable for measurement. Special buffer solutions are used to fix the pH and the activity coefficient.

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1) To be published. (Revision of ISO 5667-3:1985)

On these assumptions, this method will no longer refer to activities, but to fluoride ion concentrations.

Fluoride ion-selective electrodes operate between 0,2 mg/l and 2 000 mg/l, and show a linear relationship between the potential and the logarithm of the numerical value of the fluoride activity.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 **Sodium hydroxide**, $c(\mathrm{NaOH}) = 5$ mol/l.

Dissolve cautiously 100 g ± 0,5 g of sodium hydroxide in water, cool and dilute to 500 ml.

4.2 Total ionic strength adjustment buffer (TISAB).

Add 58 g of sodium chloride (NaCl) and 57 ml of glacial acetic acid [$\rho(\mathrm{CH_3COOH}) = 1{,}05$ g/ml] to 500 ml of water in a 1 litre beaker. Stir until dissolved. Add 150 ml of the sodium hydroxide solution (4.1) and 4 g of CDTA (*trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid). Continue stirring until all the solids have dissolved and adjust the solution to pH 5,2 with sodium hydroxide solution using a pH meter. Transfer to a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix.

The solution is stable for about 6 months, but do not use it if a precipitate forms.

NOTE 1 This solution is commercially available.

4.3 **Fluoride**, stock solution, 1 000 mg/l.

Dry a portion of sodium fluoride (NaF) at 150 °C for 4 h and cool in a desiccator.

Dissolve 2,210 g ± 0,001 g of the dried material in water contained in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

Store the solution in a screw-capped polyethylene container.

4.3.1 **Fluoride**, working standard solution I, 10 mg/l.

Pipette 10 ml of the fluoride stock solution (4.3) into a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

All standard solutions should be stored in plastic bottles and are usable for one month.

4.3.2 **Fluoride**, working standard solution II, 5 mg/l.

Pipette 5 ml of the fluoride stock solution (4.3) into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

4.3.3 **Fluoride**, working standard solution III, 1 mg/l.

Pipette 100 ml of the working standard solution I (4.3.1) into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

4.3.4 **Fluoride**, working standard solution IV, 0,5 mg/l.

Pipette 100 ml of the working standard solution II (4.3.2) into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

4.3.5 **Fluoride**, working standard solution V, 0,2 mg/l.

Pipette 20 ml of the working standard solution I (4.3.1) into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

5 Apparatus

Usual laboratory apparatus and

5.1 Meter, a millivolt meter with an impedance of not less than 10^{12} Ω, capable of resolving potential differences of 0,1 mV or better.

5.2 Fluoride ion-selective electrode, which shall give stable readings. The e.m.f response, using standard solutions, shall not be less than 55 mV per decade change in fluoride concentration at 25 °C.

5.3 Reference electrode, either a calomel electrode, filled with saturated potassium chloride (KCl) solution, or a silver/silver chloride electrode shall be used.

NOTE 2 Single junction, sleeve-type electrodes which reduce the liquid-liquid junction potential are preferable.

5.4 Measuring cells, of capacity 100 ml, made of polypropylene and fitted with a thermostatted jacket.

5.5 Water bath, capable of supplying water to the jacket of the measuring cell (5.4) at a temperature of 25 °C ± 0,2 °C.

5.6 Magnetic stirrer, with a polytetrafluoroethylene (PTFE)-coated stirring bar.

5.7 Polyethylene beaker, of capacity 100 ml.

5.8 Membrane filtration device, with membrane filters of pore size 0,45 µm.

6 Sampling and sample preservation

Samples shall be taken in polyethylene bottles which have been washed thoroughly and rinsed with fluoride-free water. No preservative is normally necessary, but the analysis should be performed as soon as possible, preferably within 3 days. (See also ISO 5667-3.)

7 Procedure

7.1 Preparation for measurement

Since the electrode characteristics of a fluoride ion-selective electrode generally vary with time, check the calibration curve on the day of use.

To accelerate the establishment of the equilibrium potential, condition the electrode prior to measurement in the following way.

Prior to measurement, immerse the electrode for 1 h in the cell (5.4) which contains the reference solution 5 (see table 1).

After rinsing with the first solution to be measured, the electrode is ready for use.

7.2 Measurement

Filter the solution through a membrane filter (5.8).

NOTE 3 Measurement without filtration is also possible, however this should be stated with the result.

Pipette 25 ml of the buffer solution (4.2), followed by 25 ml of the water sample, into a measuring cell (5.4).

Ensure that the pH is 5,2 ± 0,2; if necessary, adjust the pH with hydrochloric acid or sodium hydroxide solution, using as little as possible.

NOTES

4 If a precipitate is formed, perform the analysis with a diluted sample.

5 Any dilution of the sample should be taken into account during the calculation of the results.

For a series of determinations, start the measurement with the lowest concentration and finish with the highest following the anticipated concentration of the samples.

After measuring the high concentrations, recondition the electrode before measuring the low concentrations (see 7.1).

Measure all the solutions according to the following procedure.

Wait until constant temperature (e.g. 25 °C ± 0,5 °C) is reached and carry out all the measurements at this temperature.

Put a stirring bar into the measuring cell (5.4) and place it on the magnetic stirrer (5.6).

Insert the electrodes (5.2) into the solution and fix them in place.

Adjust the stirring rate to about 180 min^{-1} to 200 min^{-1}.

When the potential does not change by more than 0,5 mV in 5 min, switch off the stirrer. After at least 15 s, record the value obtained.

Rinse the stirring bar and the electrodes with the next solution to be measured, before starting the next measurement.

7.3 Measurement after concentration enhancement

If a water sample contains less than 0,2 mg/l F^-, proceed as follows:

— to 25 ml of the sample, add 500 µl of the fluoride standard solution I (4.3.1) using a piston pipette, and 25 ml of the buffer solution (4.2) with a volumetric pipette;

— continue as described in 7.2;

— when calculating the result, subtract the amount of fluoride ions added from the total result.

7.4 Calibration

Establish a calibration function using the five reference solutions in the corresponding concentration range.

For the range 0,2 mg/l to 10 mg/l, proceed as follows:

— pipette 25,0 ml of the buffer solution (4.2) into each of five measuring cells (5.4);

— pipette the respective volumes of the working standard fluoride solutions specified in table 1 into the measuring flasks.

Table 1 — Preparation of reference solutions

Reference solution No.	Buffer solution ml	Working standard solution No.[2]	 ml	Fluoride concentration[1] mg/l
1	25	I	25	10
2	25	II	25	5
3	25	III	25	1
4	25	IV	25	0,5
5	25	V	25	0,2

[1] The term "concentration" refers to the concentration of the working standard solutions and the sample solutions but not to the concentration of the measuring solutions after addition of the buffer.

[2] See 4.3.1 to 4.3.5.

For the establishment of the calibration function proceed step by step from the most dilute solution to the most concentrated solution, rinsing after each measurement with the solution of the next highest concentration.

After the above measurements have been completed, recondition the electrode for 5 min to 10 min, using the reference solution 5 (see table 1) in order to eliminate memory effects.

Use the following order of measurement (the numbers refer to the reference solutions in table 1):

> 5 — rinse — 4 — rinse — 3 — rinse — 2 — rinse — 1 — rinse with 5 — recondition — repeat measuring run.

If the individual values of the parallel series vary from the first series by more than ± 0,5 mV, repeat the measuring run.

Regular checking of the calibration graph is essential. Ensure that the slope is not less than 55 mV, otherwise check the equipment and establish a new calibration graph.

8 Calculation and expression of results

Plot the calibration values on semi-logarithmic paper, with the fluoride concentrations, in milligrams per litre, on the abscissa and the cell potential, in millivolts, on the ordinate and establish the regression line.

Read the value for the samples by using the regression line and express the mass concentration of fluoride in milligrams per litre.

NOTE 6 The evaluation may also be calculated using the Nernst equation (see for example [1]).

9 Precision

An interlaboratory trial, carried out in Germany in 1982, gave the results shown in table 2.

10 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) the date and place of testing;

c) a precise identification of the sample;

d) the results and the method of expression used;

e) a description of the electrode pair used;

f) any deviation from the procedure specified or any other circumstances that may have affected the results.

Table 2 — Precision data

No.	**Sample**	l	n	ρ mg/l	$\bar{x}$ mg/l	WFR %	σ_r mg/l	VC_r %	σ_R mg/l	VC_R %
1	Drinking water	12	48	0,275	0,283	—	0,021	7,4	0,0068	2,4
2	Drinking water + F^-	13	52	2,4 + 0,275	2,596	—	0,103	4,0	0,0395	1,5
3	Drinking water + F^- + 15 mg Al 100 mg Mg 500 mg Ca	13	52	5,0 + 0,275	4,340	—	0,110	2,5	0,0559	1,3
4[1]	Distilled water + F^- + 100 mg Fe 15 mg Al 100 mg Mg 500 mg Ca	11	43	0,6	0,531	88,5	0,024	4,5	0,0116	2,2
5[1]	Distilled water + F^- + 100 mg Fe 15 mg Al 100 mg Mg 500 mg Ca	12	48	8,6	6,864	79,8	0,195	2,8	0,0701	1,0
6[1]	Same as 5 + F^-	12	48	60,6	46,351	76,5	1,560	3,4	0,6433	1,4

l	Number of laboratories
n	Number of values
ρ	Mass concentration
$\bar{x}$	Mean value
WFR	Recovery rate
σ_r	Repeatability standard deviation
VC_r	Repeatability variation coefficient
σ_R	Reproducibility standard deviation
VC_R	Reproducibility variation coefficient

[1] In samples 4, 5 and 6, the fluoride content is based only on different mass concentrations achieved by adding.