INTERNATIONAL STANDARD

ISO 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.

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

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.

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, $c(NaOH) = 5$ 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 [$\rho(CH_3COOH) = 1{,}05$ 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.