Designation: D 3868 – 95 (Reapproved 1999)

An American National Standard

Standard Test Method for
Fluoride Ions in Brackish Water, Seawater, and Brines[1]

This standard is issued under the fixed designation D 3868; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method[2] covers the determination of soluble fluoride ions in brackish water, seawater and brines by use of a fluoride selective electrode.

1.2 Samples containing from 1.0 to 25 mg/L can be analyzed by this test method.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]
D 1193 Specification of Reagent Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[3]
D 3370 Practices for Sampling Water from Closed Conduits[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

4. Summary of Test Method

4.1 A fluoride selective electrode, reference electrode, and millivoltmeter are used to determine fluoride in brine samples by a standard addition method.

4.2 The fluoride selective electrode consists of a lanthanum fluoride crystal that develops an electrode potential corresponding to the level of fluoride ion in solution.

5. Significance and Use

5.1 Identification of a brackish water, seawater, or brine is determined by comparison of the concentrations of their dissolved constituents. The results are used to evaluate the origin of the water, determine if it is a possible pollutant, or if it is related to a potential source of a valuable mineral. For example, in geochemical studies some correlation data indicate that fluoride is an indirect indicator of the presence of lithium.

6. Interferences

6.1 Metal ions such as aluminum and iron (III) interfere with the fluoride determination by forming complexes with fluoride ions. The buffer solution contains a complexing agent that preferentially complexes these metal ions. This solution also contains a pH buffer to reduce electrode interference from hydroxide ions and to prevent the formation of HF. Sodium chloride is added as ionic strength adjustor. Increasing amounts of aluminum, iron (III), and borate ions were added to 1.5 mg/L fluoride solutions and were found not to interfere up to 5, 350, and 250 mg/L (as boron), respectively.

7. Apparatus

7.1 *Millivoltmeter* (accurate to ± 0.1 mV), specific ion meter.

7.2 *Fluoride Selective Electrode*, reference electrode.

7.3 *Microlitre Pipets*.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommitee D19.05 on Inorganic Constituents in Water.

Current edition approved Sept. 10, 1995. Published November 1995. Originally published as D 3868 – 79. Last previous edition D 3868 – 94.

[2] Additional information is contained in the following references: Hoke, S. H., Fletcher, G. E., and Collins, A. G., "Fluoride and Iodide Selective Electrodes Applied to Oilfield Brine Analysis," U.S. Department of Energy, Report of Investigations, BETC/RI-78/7.

Rix, C. J., Bond, A. M., and Smith, J. D., "District Determination of Fluoride in Sea Water with a Fluoride Selective Ion Electrode by a Method of Standard Additions," *Analytical Chemistry*, Vol 48, 1976, p. 1236.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

8.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type III.

8.3 *Buffer Solution*[5]—Dissolve 58 g of NaCl, 4 g of CDTA complexing agent (cyclohexylene dinitrilo tetraacetic acid), and 57 mL of glacial acetic acid in 500 mL of water. Slowly add NaOH solution (200 g/L) to adjust the pH of the solution to 5.0 to 5.5 while cooling in a water bath. Transfer solution to a 1-L volumetric flask and dilute to the mark with water.

8.4 *Fluoride Solution*, *Standard* (1 mL = 2 mg F^-)—Dissolve 4.420 g of NaF in water and dilute to 1 L and store in a polyethylene bottle. This solution will contain 2000 mg of F^-/L.

9. Sampling

9.1 Collect the sample in accordance with Practices D 3370.

10. Procedure

10.1 Pipet an aliquot of a brine sample containing 0.01 to 0.03 mg of fluoride into a 125-mL polyethylene beaker and if necessary add water to make the total volume equal 40 mL. Add 40 mL of buffer solution. Place electrodes in the solution to a depth of 30 mm. Stir solution for 5 min or until equilibrium is reached. Stop the stirrer and record the potential. Add 20 µL of the standard fluoride solution, stir solution for 3 min, and record the second potential under quiet conditions. Repeat the above step for the second addition.

11. Calculation

11.1 Calculate the slope of the electrode as follows:

$$\text{Slope} = \frac{E_B - E_A}{\log [B] - \log [A]} \tag{1}$$

where:

A and B = two fluoride solutions of known concentration, mg/L,
E_A = electrode potential of Solution *A* mV, and
E_B = electrode potential of Solution *B*, mV.

NOTE 1—The slope of the electrode should meet the manufacturer's specifications.

11.2 Calculate the concentration of fluoride in the sample as follows:[2]

$$A = \text{mg/L} = \frac{Xf}{\text{antilog}\left(\frac{\Delta E}{\text{slope}}\right) - 1} \times 1000 \tag{2}$$

where:

X = change in concentration upon addition of standard. (mg F^- added per 80 mL of solution),
f = dilution factor (80 mL/mL of sample), and
ΔE = change in potential resulting from addition of standard.

From the above procedure, two *A* values can be calculated and averaged for each sample.

TABLE 1 Determination of Precision and Bias

Amount Added mg/L	Amount Found mg/L	S_t mg/L	S_o mg/L	Bias%
3.03	3.68	1.051	0.439	+ 21.4
4.09	5.89	1.208	0.253	+ 44.1
19.4	12.14	1.596	0.972	−37.4
20.5	23.42	2.383	1.570	+ 14.2

12. Precision and Bias [6]

12.1 The precision of the test method within its designated range may be expressed as follows:

$$S_T = 0.08X + 0.73 \tag{3}$$
$$S_c = 0.063X + 0.097$$

where:

S_T = overall precision,
S_o = single-operator precision, and
X = concentration of fluoride determined, mg/L.

12.2 The bias of the test method determined from recoveries of known amounts of fluoride in a series of prepared standards as shown in Table 1.

NOTE 2—The above precision and bias estimates are based on an interlaboratory study on four artificial brine samples containing various amounts of fluoride and interfering ions as shown in Table 2. One analyst in each of three laboratories and two analysts in each of four laboratories performed duplicate determinations on each of two days. Practice D 2777 was used in developing these precision and bias estimates.

13. Keywords

13.1 analysis; brines; electrode; fluoride

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[5] Also available as TISAB II from Orion Research Inc.

[6] Supporting data are available from ASTM Headquarters. Request RR:D19-1060.