



Designation: **D 3868—95 (Reapproved 1999) 3868 – 04**

An American National Standard

Standard Test Method for Fluoride Ions in Brackish Water, Seawater, and Brines¹

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 This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water. Current edition approved ~~Sept. 10, 1995~~; March 1, 2004. Published ~~November 1995~~; April 2004. Originally published as ~~D 3868—79~~; approved in 1979. Last previous edition approved in 1999 as D 3868 – 945 (1999).

1. Scope*

1.1 This test method² 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:*³

D 1129 Terminology Relating to Water

D 1193 Specification of Reagent Water

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water

D 3370 Practices for Sampling Water from Closed Conduits

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

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.

NOTE 1—A specific ion meter that directly reads concentration may be used.

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.

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 For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards*, Vol 11.01, volume information, refer to the standard's Document Summary page on the ASTM website.

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 I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the precision and bias of the test method. Type III water was specified at the time of round robin testing of this test method.

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:

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

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

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

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

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.

12. Precision and Bias ⁶

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

$$\begin{aligned} S_T &= 0.08X + 0.73 \\ S_o &= 0.063X + 0.097 \end{aligned} \quad (3)$$

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 23—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.

⁵ Also available as TISAB II from Orion Research Inc.

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



TABLE 1 Determination of Precision and Bias

Amount Added mg/L	Amount Found mg/L	S _i 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

TABLE 2 Composition of Artificial Brine Samples

Sample No.	mg/L			
	1	2	3	4
F	3.03	19.4	20.5	4.09
Na	9 500	65 000	31 000	75 000
K	300	1 400	2 000	5 000
Ca	550	1 000	700	2 000
Mg	1 200	1 200	500	250
Ba	30	650	300	300
Cl	19 000	107 000	52 000	121 000

12.3 Precision and bias for this test method conforms to Practice D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

13. Quality Control

13.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing fluoride.

13.2 Calibration and Calibration Verification

13.2.1 Determine the slope of the electrode. The slope should meet the manufacturer's specifications.

13.2.2 Verify the electrode by analyzing a sample at the concentration near the mid-range should fall within $\pm 15\%$ of the known concentration.

13.2.3 If calibration cannot be verified, recalibrate the instrument.

13.3 Initial Demonstration of Laboratory Capability

13.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

13.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of fluoride. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. The replicates may be interspersed with samples.

13.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in section Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. If a concentration other than the recommended concentration is used, refer to Test Method D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

13.4 Laboratory Control Sample (LCS)

13.4.1 To ensure that the test method is in control, analyze a LCS containing a mid-range concentration of fluoride with each batch or ten samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every ten samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within $\pm 15\%$ of the known concentration.

13.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.5 Method Blank

13.5.1 Analyze a reagent water test blank with each batch. The concentration of fluoride found in the blank should be less than 1.0 mg/L. If the concentration of fluoride is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.6 Matrix Spike (MS)

13.6.1 Fluoride is not an analyte that can be feasibly spiked into samples.

13.7 Duplicate

13.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

13.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Test Method D 5847 for information on applying the F test.

13.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.8 *Independent Reference Material (IRM)*

13.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

14. Keywords

134.1 analysis; brines; electrode; fluoride

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D 3868 – 95 (1999)) that may impact the use of this standard.

(1) D 5847 was added to 2.1.

(2) A new Note 1 was added.

(3) Section 8.2 was modified to use Type 1 water.

(4) Section 13.4 was added.

(5) Section 13 was added.

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