

METHOD 9214

POTENTIOMETRIC DETERMINATION OF FLUORIDE IN AQUEOUS SAMPLES WITH ION-SELECTIVE ELECTRODE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring total solubilized fluoride in drinking waters, natural surface waters, groundwaters, domestic and industrial wastewaters, and in soil extracts (ASTM methods D4646-87, D5233-92 or D3987-85).

NOTE: This method is for the analysis of simple fluoride ion rather than total fluoride, as analysis using the ion-selective electrode is not preceded by a distillation step.

1.2 The method detection limit is 0.5 mg/L. Fluoride concentrations from 0.025 to 500 mg/L may be measured. However, using a linear calibration, results less than 0.5 mg/L may be biased up to approximately 160% high.

1.3 ISEs must be used carefully and results must be interpreted cautiously, since an ISE may be affected by numerous analytical interferences which may either increase or decrease the apparent analyte concentration, or which may damage the ISE. Effects of most interferences can be minimized or eliminated by adding appropriate chemical reagents to the sample. Obtaining the most accurate results, therefore, requires some knowledge of the sample composition.

NOTE: ISE manufacturers usually include a list of interferences in the instruction manual accompanying an ISE, along with recommended methods for minimizing or eliminating effects of these interferences.

2.0 SUMMARY OF METHOD

2.1 Total solubilized fluoride is determined potentiometrically using a fluoride ion-selective electrode (ISE) in conjunction with a standard single-junction reference electrode, or a fluoride combination ISE, and a pH meter with an expanded millivolt scale or an ISE meter capable of being calibrated directly in terms of fluoride concentration.

2.2 Standards and samples are mixed 1:1 with a total ionic strength adjustment buffer (TISAB). TISAB adjusts ionic strength, buffers pH to 5-5.5, and contains a chelating agent to break up metal-fluoride complexes. Calibration is performed by analyzing a series of standards and plotting mV vs. fluoride concentration on semilog paper or by calibrating the ion meter directly in terms of fluoride concentration.

3.0 INTERFERENCES

3.1 Polyvalent cations (e.g., Fe^{+3} and Al^{+3}) interfere by forming complexes with fluoride which are not measured by the fluoride ISE. (See Table 1.) The results in Table 1 are in agreement with the fact that aluminum-fluoride complex ions are approximately ten times more stable than corresponding iron(III)-fluoride complex ions. As the aluminum concentration increases, more fluoride is consumed to form the metal-fluoride complex. Adding TISAB, which contains a strong chelating agent, eliminates this interference by complexing polyvalent cations.

3.2 Sample pH is critical. Hydroxide is a significant interferant at concentrations ten times the fluoride concentration. This interference is avoided by adding TISAB which buffers the sample at a pH of 5-5.5. At low pH values, fluoride forms bifluoride (HF_2^-) which is not detected by the fluoride ISE. Again, adding TISAB prevents this interference by buffering the pH.

3.3 Temperature changes affect electrode potentials. Using an ISE calibrated at 22°C, a 20.0 mg/L fluoride solution was measured as 20.3 mg/L at 22°C and 13.6 mg/L at 32°C (see Ref. 4). Therefore, standards and samples must be equilibrated at the same temperature ($\pm 1^\circ\text{C}$).

3.4 The user should be aware of the potential of interferences from colloidal substances and that, if necessary, the samples may be filtered.

4.0 APPARATUS AND MATERIALS

4.1 pH/mV meter capable of reading to 0.1 mV or an ISE meter.

4.2 Combination fluoride ISE (Orion 9609 or equivalent), or separate fluoride ISE (Orion 9409 or equivalent) and reference electrode (Orion 9001 or equivalent) prepared for use as described in owner's manual.

4.3 Thermally isolated magnetic stirrer, polytetrafluoroethylene (PTFE)-coated stir bar, and stopwatch.

4.4 Volumetric flask, 1,000 mL.

4.5 Polyethylene labware.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. 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.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (5M NaOH): Dissolve 200 g of NaOH in sufficient reagent water to make 1 L of solution. Store in a tightly sealed polyethylene bottle.

CAUTION: This solution is extremely corrosive.

5.4 Glacial acetic acid ($\text{CH}_3\text{CO}_2\text{H}$).

5.5 Sodium chloride (NaCl).

5.6 CDTA or 1,2-cyclohexanedinitrilo-tetraacetic acid ($\text{C}_6\text{H}_{10}[\text{N}(\text{CH}_2\text{CO}_2\text{H})_2]_2 \cdot \text{H}_2\text{O}$).

5.7 TISAB solution

5.7.1 To approximately 500 mL of reagent water add 57.0 mL of glacial acetic acid, 58.0 g of sodium chloride, and 4.00 g of CDTA. Stir to dissolve and cool to room temperature. Adjust the solution pH to between 5.0 and 5.5 with 5M NaOH (about 150 mL will be required). Transfer the solution to a 1,000 mL volumetric flask and dilute to the mark with reagent water. Transfer the solution to a clean polyethylene bottle.

5.7.2 Alternatively, TISAB solution is available commercially (Orion 940999 or equivalent).

5.8 Fluoride calibration stock solution (1,000 mg/L F⁻): Dissolve 0.2210 g of sodium fluoride (NaF, dried two hours at 110°C and stored in a desiccator) in reagent water and dilute to 100 mL in a polyethylene volumetric flask. Store in a clean polyethylene bottle.

5.9 Fluoride standard solution (100 mg/L F⁻): Dilute 10.0 mL of 1,000 mg/L fluoride calibration stock solution to 100 mL with reagent water in a polyethylene volumetric flask.

5.10 Fluoride calibration standards: Prepare a series of calibration standards by diluting the 100 mg/L fluoride standard. A suitable series is given in the table below.

mL of 100 mg/L F ⁻ Solution	Concentration when Diluted to 50.0 mL (mg/L F ⁻)
0.0500	0.100
0.150	0.300
0.500	1.00
1.50	3.00
5.00	10.0
15.0	30.0

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples must be stored and handled in polyethylene containers. Samples should be stored at 4°C.

7.0 PROCEDURE

7.1 Calibration

7.1.1 If using a fluoride combination ISE, ensure that the ISE is filled with the solution recommended by the manufacturer. Change the solution if the ISE has not been used for a week. If using a fluoride ISE and a separate reference electrode, ensure that the reference electrode is filled with the solution recommended by the manufacturer. In either case, equilibrate the electrodes for 24 hours in a 10.0 mg/L fluoride standard before use.

7.1.2 Calibrate the fluoride ISE using standards that narrowly bracket the expected sample concentration. If the sample concentration is unknown, calibrate with 1.00 mg/L and 10.0 mg/L fluoride standards. Add 20.0 mL of standard and 20.0 mL of TISAB to a 50 mL

polyethylene beaker. Add a PTFE-coated magnetic stir bar, place the beaker on a magnetic stir plate, and stir at slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. If using an ISE meter, calibrate the meter in terms of fluoride concentration following the manufacturer's instructions. If using a pH/mV meter, record the meter reading (mV) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of fluoride concentration. The slope must be 54-60 mV per decade of fluoride concentration. If the slope is not acceptable, the ISE may not be working properly. For corrective action, consult the ISE operating manual.

NOTE: Use only plasticware (polyethylene) when preparing and analyzing fluoride samples.

7.2 Allow samples and standards to equilibrate to room temperature.

7.3 Prior to and between analyses, rinse the electrode thoroughly with reagent water and gently shake off excess water. Low-level measurements are faster if the electrode tips are first immersed for five minutes in reagent water.

7.4 Add 20.0 mL of sample and 20.0 mL of TISAB to a 50 mL polyethylene beaker. Add a PTFE-coated magnetic stir bar. Place the beaker on a magnetic stir plate and stir at a slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. Record the meter reading (mV or concentration) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. If reading mV, determine fluoride concentration from the calibration curve.

7.5 When analyses have been completed, rinse the electrodes thoroughly and store them in a 10.0 mg/L fluoride standard solution. If the electrodes will not be used more than one day, drain the internal filling solution, rinse with reagent water, and store dry.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Initial Calibration Verification standard (ICV): After performing the calibration step (7.1), verify calibration by analyzing an ICV. The ICV contains a known fluoride concentration at mid-range of the calibration standards and is from an independent source. ICV recovery must be 90-110 percent. If not, the error source must be found and corrected. An acceptable ICV must be analyzed prior to sample analysis. The ICV also serves as a laboratory control sample.

8.3 Continuing Calibration Verification standard (CCV): After every 10 samples, and after the final sample, a CCV must be analyzed. The CCV contains a known fluoride concentration at mid-calibration range. CCV recovery must be 90-110 percent. If not, the error source must be found and corrected. If ISE calibration has changed, all samples analyzed since the last acceptable CCV must be re-analyzed.

8.4 Reagent blank: After the ICV and after every CCV, a reagent blank must be analyzed. A reagent blank is reagent water mixed 1:1 with TISAB. The indicated reagent blank concentration must be less than 0.1 mg/L fluoride. If not, the contamination source must be found and corrected. All samples analyzed since the last acceptable reagent blank must be re-analyzed.

8.5 Matrix spike: Follow the matrix spike protocols presented in Chapter One. The spike concentration must be 10 times the detection limit and the volume added must be negligible (less than or equal to one-thousandth the sample aliquot volume). Spike recovery must be 75-125 percent. If not, samples must be analyzed by the method of standard additions.

9.0 METHOD PERFORMANCE

9.1 In a single-laboratory evaluation, a series of standards with known fluoride concentrations was analyzed with a fluoride ISE. Measurements were conducted over three consecutive days using an Orion 9609 fluoride combination ISE connected to an Orion 940 ISE meter. A two-point calibration (1.00 and 10.0 mg/L fluoride) was performed prior to analysis. The results are listed in Table 2.

9.2 In the same study, 12 groundwater samples and six extraction procedure (EP, Method 1310) soil leachate samples were spiked with fluoride at four different concentrations and were measured with the fluoride ISE. (The groundwater samples initially contained 0.1-2 mg/L fluoride and the EP leachates initially contained 0.1-8 mg/L fluoride.) Each spiked sample was analyzed at each concentration and the mean recoveries and RSDs are listed in Table 3.

10.0 REFERENCES

1. Franson, Mary Ann H., Ed. Standard Methods for the Examination of Water and Wastewater, 18th Edition. American Public Health Association, Washington, DC, 1992.
2. Model 96-09 Fluoride Combination Electrode Instruction Manual. Orion Research, Inc., Boston, MA, 1988.
3. Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency, Cincinnati, Ohio, 1983.
4. Miller, E.L., Waltman, D.W., and Hillman, D.C. Single-Laboratory Evaluation of Fluoride, Chloride, Bromide, Cyanide, and Nitrate Ion-Selective Electrodes for Use in SW-846 Methods. Lockheed Engineering and Sciences Company for Environmental Monitoring Systems Laboratory, U.S. EPA. September 1990. EPA/600/X-90/221.
5. Cotton, F. Albert, and Geoffrey Wilkinson; *Advanced Inorganic Chemistry, 2nd Edition*; Interscience Publishers, New York, NY; 1966.
6. Weast, Robert C., Ed.; *CRC Handbook of Chemistry and Physics, 58th Edition*; CRC Press, Inc., Cleveland, Ohio; 1977.

TABLE 1
FLUORIDE ISE INTERFERENCES

Analyte Concentration (mg/L)	Interference	Measured Concentration (mg/L)	RSD (%)
1.00	None	0.95	2.0
1.00	1 mg/L Al ⁺³	0.97	3.1
1.00	5 mg/L Al ⁺³	0.86	3.9
1.00	25 mg/L Al ⁺³	0.51	*
1.00	50 mg/L Al ⁺³	0.41	4.9
1.00	1 mg/L Fe ⁺³	1.00	3.9
1.00	5 mg/L Fe ⁺³	1.02	3.8
1.00	50 mg/L Fe ⁺³	0.92	3.2
* Single measurement			

TABLE 2
RESULTS FROM A SINGLE-LABORATORY ACCURACY
EVALUATION OF A FLUORIDE ISE

Fluoride Concentration (mg/L)	Fluoride Detected (mg/L)	Fluoride Recovery (%)	Rel. Std. Deviation (%)
0.0250	0.066	264	19
0.0500	0.085	170	11
0.125	0.164	131	10
0.250	0.31	125	7
0.500	0.51	103	2
2.50	2.43	97	2
5.00	5.0	101	2
25.0	25.2	101	2
50.0	53.	105	3
250.	260.	105	3
500.	530.	107	3

TABLE 3
 MEAN SPIKE RECOVERIES FOR TWELVE GROUNDWATER SAMPLES AND
 SIX EP LEACHATE SAMPLES

Spike	Groundwater		EP Leachate	
Fluoride Added (mg/L)	Fluoride Recovered (%)	Rel. Std. Deviation (%)	Fluoride Recovered (%)	Rel. Std. Deviation (%)
0.5	92	5.3	100	20
1.5	92	3.3	92	9.7
3.5	93	3.0	91	5.5
8.5	96	2.6	91	4.1

METHOD 9214

POTENTIOMETRIC DETERMINATION OF FLUORIDE
IN AQUEOUS SAMPLES WITH ION-SELECTIVE ELECTRODE

