

# Fluoride, electrometric, ion-selective electrode, automated segmented flow

## Parameters and Codes:

Fluoride, dissolved, I-2327-85 (mg/L as F): 00950  
Fluoride, total, I-4327-85 (mg/L as F): 00951  
Fluoride, suspended total, I-7327-85 (mg/L as F): 82299

## 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 0.1 to 3.0 mg/L of fluoride with conductivities less than 20,000 uS/cm. Samples with higher conductivities need to be distilled.

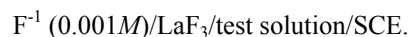
1.2 Suspended total fluoride is calculated by subtracting dissolved fluoride from total fluoride

1.3 Total fluoride in water-suspended sediment is determined after each sample is shaken vigorously and a suitable aliquot of well-mixed sample is rapidly withdrawn and then distilled.

## 2. Summary of method

2.1 Fluoride is determined potentiometrically in a buffered sample with use of an ion-selective (fluoride) electrode in conjunction with a standard calomel reference electrode (SCE) and with a pH meter having an expanded millivolt scale (Frant and Ross, 1968; Harwood, 1969; Bellack, 1958).

2.2 The fluoride electrode consists of a lasertype, doped lanthanum fluoride crystal, across which a potential is developed by fluoride ions. The cell may be represented by:



This electrode deteriorates in time and must be replaced when results become erratic.

2.3 The method includes a distillation step to decompose organic fluoride compounds and attack minerals such as fluorspar in watersuspended sediment. A fixed volume of sample is added to a

sulfuric acid solution having a specific boiling point and is distilled until an identical volume is recovered (Bellack, 1958). The fluoride is distilled as fluosilicic acid.

## 3. Interferences

3.1 The ion-selective electrode measures fluoride-ion activity; thus, high concentrations of dissolved solutes (which lower the ion-activity coefficient) cause an error in the determination. Addition of a buffer solution that contains a high concentration of dissolved solutes effectively masks minor variations in the salt content of the samples and, therefore, minimizes this error.

3.2 The optimum pH for measurement is between 5.0 and 8.5. Below this range, hydrofluoric acid is only slightly dissociated, and above a pH of 8.5, hydroxyl ion interferes. The addition of the buffer solution will adjust the pH of most samples to between 5.0 and 5.5.

3.3 Several polyvalent cations capable of complexing fluoride ion interfere. These include iron(III), aluminum(III), and silicon dioxide. The extent of their interference is proportional to their concentration, so that dilution of the sample with an equal volume of buffer solution reduces the interference. The (1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA) in the buffer solution complexes up to 10,000 µg iron(III), 2,000 µg aluminum(III), and 100 mg silicon dioxide.

3.4 Orthophosphate-phosphorus concentrations of 25 mg/L and sulfate and chloride concentrations of 3,000 mg/L do not interfere (Harwood, 1969).

#### 4. Apparatus

4.1 *Distillation assembly*, (fig. 1), consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer (250°C).

4.2 *Technicon AutoAnalyzer II*, consisting of a sampler, proportioning pump, cartridge manifold, heating bath, recorder, potentiometer, and printer.

4.3 *Fluoride ion-selective electrode*.

4.4 *Reference electrode*, standard calomel.

4.5 With this equipment a 40/h (2/1) cam has been found satisfactory for the range from 0.1 to 3.0 mg/L.

#### 5. Reagents

5.1 *Brij-35 solution*: 30-percent aqueous solution (Baker Cat. No. C 706 or equivalent).

5.2 *Buffer solution*, 0.33 mg/L, pH 5.0 to 5.5: To approx 500 mL demineralized water in a 1-L beaker, add 57 mL glacial  $\text{HC}_2\text{H}_3\text{O}_2$ , 58 g NaCl, and 4.5 g (1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA). Stir to dissolve and cool to room temperature. Adjust the pH of the solution between 5.0 and 5.5 with 5M NaOH (about 170 mL will be required). Filter if necessary and add 33 mL of fluoride standard solution II and 0.5 mL of Brij-35 solution. Dilute to 1,000 mL with demineralized water.

5.3 *Fluoride standard solution I*, 1.00 mL = 1.00 mg F: Dissolve 2.2101 g NaF in demineralized water and dilute to 1,000 mL.

5.4 *Fluoride standard solution II*, 1.00 mL = 0.01 mg F: Dilute 10.0 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.5 *Fluoride working standards*: Prepare a blank and 500 mL each of a series of fluoride working standards by appropriate quantitative dilution of fluoride standard solution II as follows:

Fluoride standard solution (mL)	Fluoride concentration (mg/L)
0.0	0.0
10.0	.20
25.0	.50
50.0	1.00
75.0	1.50
100.0	2.00
125.0	2.50
150.0	3.00

5.6 *Silver sulfate*, powder.

5.7 *Sulfuric acid*, concentrated (sp gr 1.84).

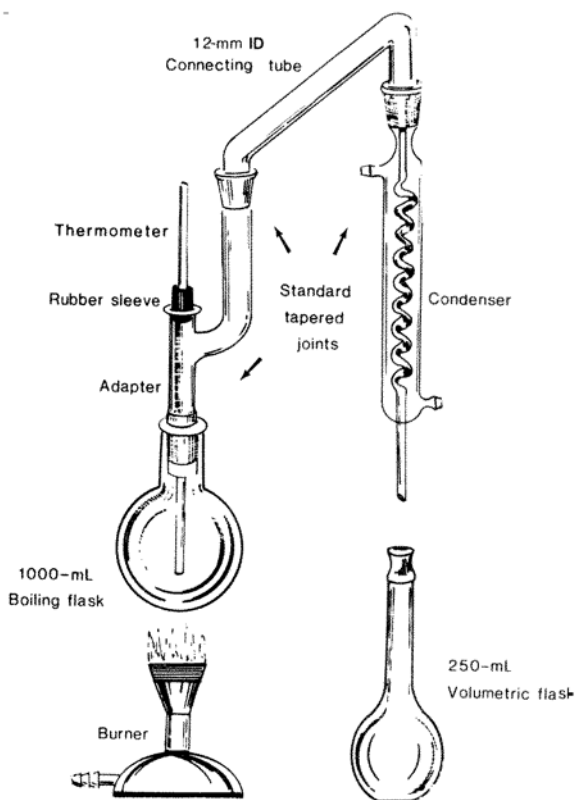


Figure 1.-Fluoride, distillation assembly

#### 6. Procedure

6.1 *Distillation procedure*: Water-suspended sediment needs to be distilled. The distillation may be omitted for samples for determining dissolved fluoride if the specific conductance is less than 20,000  $\mu\text{S}/\text{cm}$ .

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously*, and with constant swirling, add 200 mL concentrated  $\text{H}_2\text{SO}_4$ . Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180°C. At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously*, and with constant swirling, add 250 mL of well-mixed sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL distillate has been collected and the temperature of the acid mixture

has returned to 180°C. When the temperature of the acid mixture at the completion of the distillation exceeds 183°C, add 50 mL distilled water and distill the mixture until the temperature again reaches 180°C. After distilling a high fluoride sample (3 mg/L or more), clean the apparatus by distilling 250 mL water. This prevents a carryover of fluoride in subsequent samples. When samples with high chloride content are to be distilled, AgSO<sub>4</sub> should be added to the distilling flask in proportion of 5 mg per milligram of Cl<sup>-</sup>.

## 6.2 Electrometric procedure:

6.2.1 Set up manifold (fig. 2).

6.2.2 Allow potentiometer, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 37°C.

6.2.3 Calibrate the potentiometer according to the manufacturer's instructions.

6.2.4 Adjust the baseline to read 10 scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.2.5 Place a complete set of standards in the first positions of the first sample tray, beginning with the most concentrated working standard (the first two

positions should both contain 3-mg/L standards). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.2.6 Begin analysis. When the peak from the second 3-mg/L standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads 100 scale divisions.

## 7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective fluoride concentration. This curve should be linear or very nearly linear.

7.2 Compute the concentration of dissolved or total fluoride in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 To determine milligrams per liter of suspended total fluoride, subtract dissolved-fluoride concentration from total-fluoride concentration.

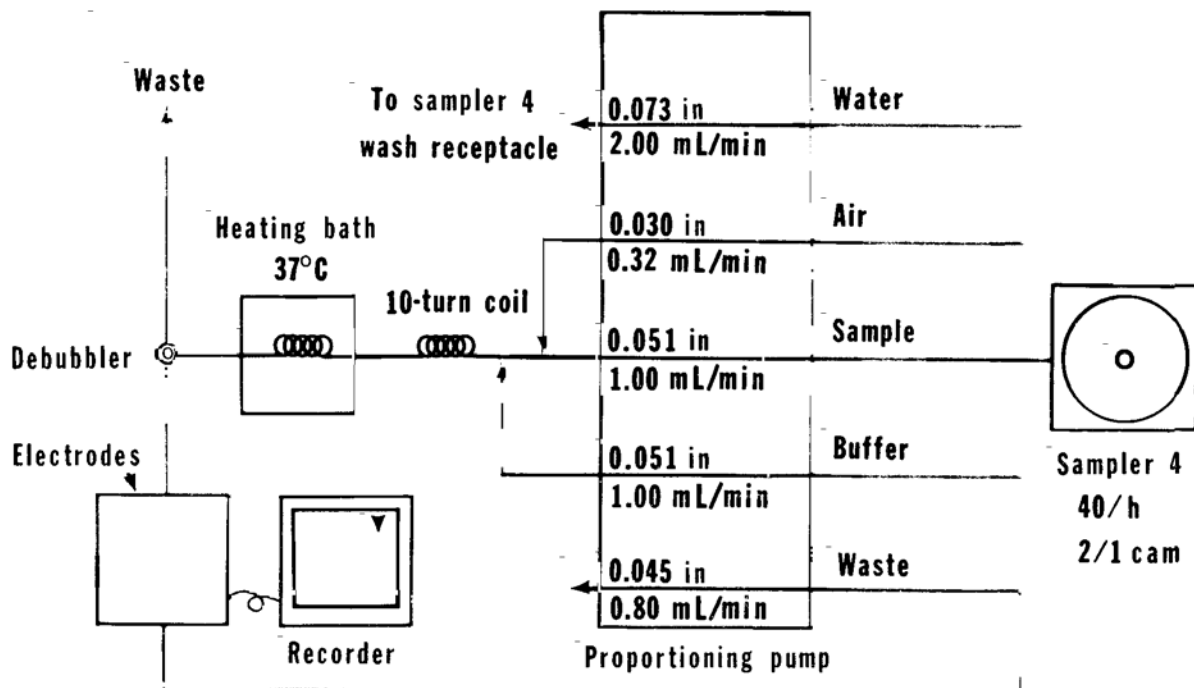


Figure 2.-Fluoride, ion-selective electrode manifold

## 8. Report

Report fluoride, dissolved (00950), total (00951), and suspended-total (82299), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

## 9. Precision

9.1 The standard deviation for dissolved fluoride within the range of 0.33 to 1.28 mg/L for nine samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.07 mg/L ranged from 0.05 to 0.09 mg/L.

9.2 Precision for dissolved fluoride for three of the nine samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.33	18
8	1.09	6
4	1.28	7

9.3 It is estimated that the percent relative standard deviation for total and suspended total fluoride will be greater than that reported for dissolved fluoride.

## References

- Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530-5.
- Erdmann, D.E., 1975, Automated ion-selective method for determining fluoride in natural waters: Environmental Science and Technology, v. 9, p. 252-3.
- Frant, M. S., and Ross, J. W., Jr., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies: Analytical Chemistry, v. 40, p. 1169-71.
- Harwood, J. E., 1969, The use of an ion-selective electrode for routine fluoride analysis on water samples: Water Research, v. 3, p. 273-80.