Fluoride in Drinking Water

DOC316.53.01237

USEPA[1] Direct Measurement ISE Method **Method 8323**

0.1 to 10.0 mg/L F^- **Powder Pillow or TISAB Solution**

Scope and Application: Drinking water

[1] USEPA equivalent method

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 447 Instrument-specific information

Meter	Electrode
sension™ 4 meters	5192800
sension™ 2 meters[1]	5192800

[1] The user must construct the calibration curve with the *sension* 2 meter.

Before starting the test:

Refer to the meter user manual for meter operation. Refer to electrode manual for electrode maintenance and care.
For USEPA reporting, replace the standards in step 1 with a 0.5-mg/L, 1.0-mg/L and 2.0-mg/L fluoride standard solution to calibrate the electrode.
Prepare the electrode. Refer to *Electrode assembly* and *Condition the electrode* in this procedure.

Collect the following items:

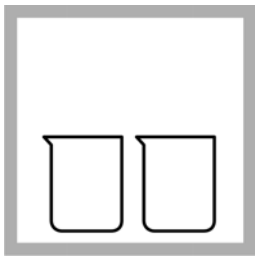
Description	Quantity
Fluoride ISA buffer pillows (TISAB)	1
OR	
Fluoride ISA solution, concentrated (TISAB)	5.0 mL
Sodium acetate, ACS	varies
Fluoride standard solutions:	
1.00-mg/L F	varies
2.00-mg/L F or	varies
0.5 mg/L F (USEPA)	varies
Potassium chloride reference electrolyte gel cartridges	varies
Water, deionized	varies

Collect the following items: (continued)

Description	Quantity
Beaker, 50-mL, polypropylene	3 or 4 (USEPA)
Bottle, wash, 500-mL	1
Cylinder, graduated, 25-mL, polypropylene	3
Platinum series fluoride combination electrode, BNC	1
sension™2 Portable pH/ISE Meter. or *sension*™4 Laboratory pH/ISE Meter	1
Stir Bar, 7/8 X 3/16 in. (22.2 x 4.8 cm)	2 or 3 (USEPA)
Stirrer, electromagnetic with stand and stir bar	1

See *Consumables and replacement items* for reorder information.

Fluoride in drinking water, powder pillows method

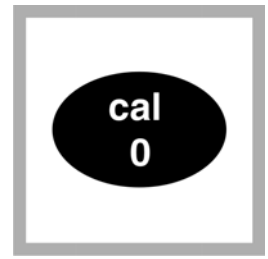


1. In 50-mL beakers, prepare two 25-mL standard solutions of 1-mg/L and 10-mg/L F^-.

2. Add the contents of one Fluoride Total Ionic Strength Adjustment Buffer (TISAB) Powder Pillow to each standard. Stir to dissolve.

3. Turn the meter on. Set the electrode type to BNC. Set the units to mg/L. Press **CAL**.

Refer to the meter user manual for details.



4. Place the beaker with the 1-mg/L standard on a magnetic stirrer. Stir at a moderate rate.

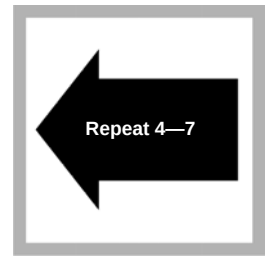
5. Place the electrode into the standard.

6. Edit the display to show the concentration of the standard.

Press **ENTER** to accept the concentration.

7. The display will show **Stabilizing** until the measurement is complete.

Remove the electrode from the standard solution Rinse with deionized water and blot dry.



8. Repeat steps 4–7 for the 10-mg/L and 0.5 mg/L (USEPA) standard.

After the last standard is measured, store the calibration in the meter. Refer to the meter user manual for details.

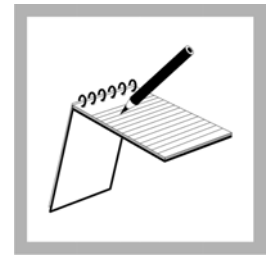
Fluoride in drinking water, powder pillows method (continued)

9. Transfer 25 mL of the sample to a 50-mL beaker. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.

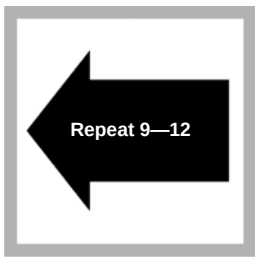
10. Remove the electrode from the standard solution. Rinse it with deionized water and blot dry. Place it into the sample.

The sample should be the same temperature as the standards, ±1 °C.

11. Add the contents of one TISAB Powder Pillow. Stir to dissolve.



12. After the measurement is stable, record or store the measurement value.

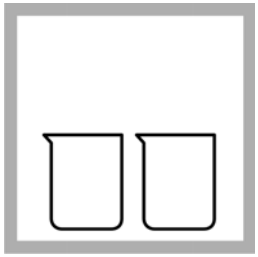


13. Repeat steps 9 through 12 for each sample.

14. Remove the electrode after reading the last sample. Rinse the electrode. Store in a fluoride standard of similar concentration to the sample that will be analyzed next.

Refer to the electrode manual for more information on electrode storage.

Fluoride in drinking water, liquid TISAB solution method

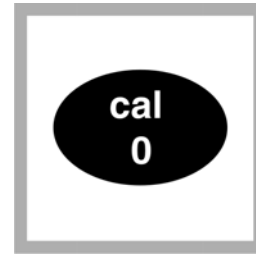


1. In 50-mL beakers, prepare two 25-mL standard solutions of 1-mg/L and 10-mg/L F^-.

2. Add the contents of 5 mL concentrated Fluoride Total Ionic Strength Adjustment Buffer (TISAB) per 25 mL of standard. Stir to mix.

3. Turn the meter on. Set the electrode type to BNC. Set the units to mg/L. Press **CAL**.

Refer to the meter user manual for details.



4. Place the beaker with the 1-mg/L standard on a magnetic stirrer. Stir at a moderate rate.

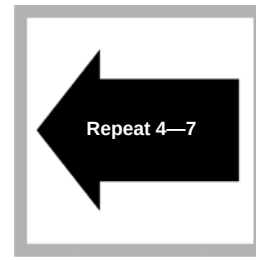
5. Place the electrode into the standard.

6. Edit the display to show the concentration of the standard.

Accept the concentration.

7. The display will show **Stabilizing** until the measurement is complete.

Remove the electrode from the standard solution Rinse with deionized water and blot dry.



8. Repeat steps 4–7 for the 10-mg/L standard.

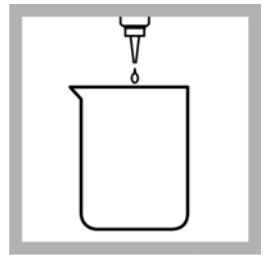
After the last standard is measured, store the calibration in the meter. Refer to the meter user manual for details.

Fluoride in drinking water, liquid TISAB solution method (continued)

9. Transfer 25 mL of the sample to a 50-mL beaker. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.

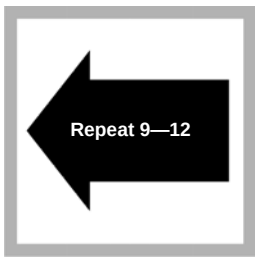
10. Remove the electrode from the standard solution. Rinse it with deionized water and blot dry. Place it into the sample.

The sample should be the same temperature as the standards, ±1 °C.



11. Add 5 mL concentrated liquid TISAB to the sample. Stir to mix.

12. After the measurement is stable, record or store the measurement value.



13. Repeat steps 9 through 12 for each sample.

14. Remove the electrode after reading the last sample. Rinse the electrode. Store in a fluoride standard of similar concentration to the sample that will be analyzed next.

Refer to the electrode manual for more information on electrode storage.

Electrode assembly

1. Remove the cap from the electrolyte cartridge.
2. Visually inspect the Luer tip of the electrolyte cartridge. If air is present, rotate the feed-screw counter-clockwise until gel expels the air and fills the tip.
3. Fit the cartridge outlet tube firmly onto the inlet tube of the electrode body (Figure 28).

Figure 28 Attach the outlet tube

4. Place the dispenser unit over the electrolyte cartridge. Screw the dispenser unit onto the electrode body until reaching the stop. Do not over tighten.
5. Dispense the electrolyte gel by pressing the pump button. Repeat this procedure until gel is visible at the reference outlet (Figure 29).

Figure 29 Dispense the electrolyte gel

6. Rinse the electrode with deionized water. Do not scratch the crystal.
7. To remove an empty cartridge, unscrew the dispenser unit and rotate the cartridge counterclockwise while gently pulling it out of the electrode.

8. Connect the BNC connector of the electrode to the BNC connector on the meter (Figure 30).

Figure 30 BNC connector

Note: *One BNC and one 5-pin connector are on the back of the meter. Choose the BNC for the fluoride electrode. Disconnect the pH electrode from the 5-pin connector when using the BNC connector.*

Condition the electrode

Condition and store the electrode in 1 mg/L Fluoride standard storage with Ionic Strength Adjuster for 15 to 30 minutes.

For electrode storage procedures, refer to the Fluoride Electrode Instruction Manual.

Clean the Lanthanum Fluoride Crystal

It may be necessary to clean the LaF crystal on the sensing tip of the probe if it becomes covered with organic film or buildup.

1. 1. Put a small amount of fluoride toothpaste on a soft toothbrush or cloth.
2. Gently rub the LaF crystal with the toothpaste using a circular motion. Rub until the film is removed.
3. Thoroughly rinse the probe with deionized water and blot dry. Verify the crystal is clean. If not, repeat cleaning and rinsing until it is clean.
4. If the crystal becomes contaminated by oil, grease, or fingerprints, soak for a few minutes in isopropyl alcohol then rinse with deionized water.

Interferences

Table 448 Interfering substances

Interfering substance	Interference level
Cations	Do not interfere
Cl^-, Br^-, SO_4^{2-}, HCO_3^-, PO_4^{3-}, acetate	Do not interfere
OH^- (Hydroxyl ions)	Interferes: refer to
CO_3^{2-} or PO_4^{3-}	Make the sample more basic and increase OH^-

pH Effects

In solutions with a pH below 5, hydrogen ion complexes some of the fluoride ions, forming the undissociated acid HF and the ion HF_2^-. Figure 31 shows the proportion of free fluoride ion in acid solutions.

If the background ionic strength is high and constant in comparison with the ion being measured, the activity coefficient is constant and activity is directly proportional to ion concentration. Total ionic strength adjustor is added to standards and samples to make the background ionic strength high, decomplex fluoride, and adjust the solution pH to 5.0–5.5.

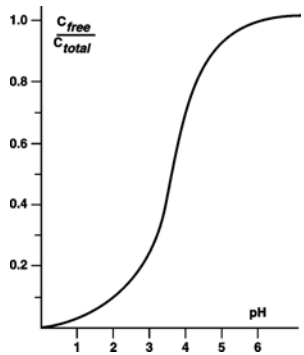


Figure 31 Ratio of free F^- in acid solutions

Sample collection, preservation and storage

- Collect samples in plastic bottles.
- Samples may be stored up to 28 days.

Accuracy check

Checking electrode response

To verify measurement accuracy, measure the electrode potential of two fluoride standard solutions that are one decade apart in concentration. For example, use 1-mg/L and 10-mg/L standards to bracket an expected sample concentration of 3 mg/L. The two standards should have mV potentials that are 58 ± 3 mV apart at 25 °C. Both solutions must be greater than 0.2 mg/L F^-.

Checking calibration accuracy

To verify calibration accuracy, measure the concentration of a known standard (e.g., 2.00 mg/L) within the calibration range.

Checking the accuracy of the sample reading

To verify sample measurement accuracy, add a spike of standard fluoride solution with a TenSette® or volumetric pipet. Use the *Spike Volumes* table and the formulas in.

Table 449 Spike Volumes

Measured sample Concentration	Volume & Concentration of F^- Standard to Add		C x V
	V	C	
0.6–1 mg/L	0.3 mL of...	...100-mg/L	30
1–2 mg/L	0.5 mL of...	...100-mg/L	50
3–6 mg/L	1.0 mL of...	...10-mg/L	100

Percent recovery

To calculate the percent recovery (only applicable if sample volume is 25 mL):

$$M = S \times 25 + C \times V$$

$$E = \frac{M}{25 + V}$$

$$R = \frac{A}{E} \times 100\%$$

Where:

M = calculated mass of fluoride present after the spike (micrograms)
S = mg/L of F^- in sample (before spike)
C = concentration of standard used for spiking (mg/L)
V = spike volume from the *Spike Volumes* table (mL)
E = expected concentration after spiking (mg/L)
R = percent recovery (should be 95–100%)
A = actual reading on meter after spike (mg/L F^-)

Method performance

Instrument	Standard	Precision 95% Confidence Limits of Distribution
*sens**ion*** 4	1.6 mg/L	1.595–1.605 mg/L
*sens**ion*** 2		

Summary of method

The fluoride electrode consists of a sensing Lanthanum Fluoride element bonded into an epoxy body. When the sensing element contacts fluoride ions in a solution, a potential develops across the sensing element. The potential is proportional to the level of fluoride ions present. The potential is measured against a constant reference potential with a pH/mV meter or ISE meter.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Fluoride ISA buffer pillows	1	100/pkg	258999
OR			
Fluoride ISA solution	5 mL	3.78 L	2829017
Fluoride Standard Solutions:			
1.00-mg/L	varies	500 mL	29149
2.00-mg/L	varies	500 mL	40520
10.0-mg/L	varies	500 mL	35949
Potassium Chloride Reference Electrolyte Gel Cartridges	varies	2/pkg	2546902
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/Test	Unit	Catalog number
Beaker, 50-mL, polypropylene	3	each	108041
Bottle, wash, 500-mL	1	each	62011
Cylinder, graduated, 25-mL, poly	3	each	108140
Fluoride Combination Electrode, BNC, w/ filling solution	1	each	5192800
*sens**ion*** 2 Portable pH/ISE Meter	1	each	5172500
OR			
*sens**ion*** 4 Laboratory pH/ISE Meter	1	each	5177500
Stir Bar, 7/8 x 3/16 in. (22.2 x 4.8 cm)	1	each	4531500
Select one based on available voltage:			
Stirrer, electromagnetic, 115 VAC, with stand and stir bar	1	each	4530001
Stirrer, electromagnetic, 230 VAC, with stand and stir bar	1	each	4530002

Optional apparatus

Description	Unit	Catalog number
Electrode Washer	each	2704700
Pipet, TenSette, 0.1 to 1. 0 mL	each	1970001
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	2185696

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