

## Direct ISE Method

Method 8323

0.1 to 10.0 mg/L F<sup>-</sup>

Fluoride ISE

**Scope and application:** For drinking water<sup>1</sup> and wastewater<sup>2</sup>.

<sup>1</sup> The equipment that is specified in this method meets the requirements of the approved EPA Reference Method for NPDWR reporting. Users with NPDWR permits must follow and make a reference to the EPA Reference Method.

<sup>2</sup> This method is USEPA Equivalent for wastewater and can be used for NPDES reporting.



## Test preparation

### Instrument-specific information

This procedure is applicable to the meters and probes that are shown in [Table 1](#). Procedures for other meters and probes can be different.

**Table 1 Instrument-specific information**

Meter	Probe
HQ30d portable single input, multi-parameter HQ40d portable dual input, multi-parameter HQ430d benchtop single input, multi-parameter HQ440d benchtop dual input, multi-parameter	IntelliCAL ISEF121 combination fluoride ISE
sensION™ + MM340 lab dual input, pH/mV/ISE	sensION+ 9655C combination fluoride ISE
sensION™ + MM374 lab dual input, pH/mV/EC/ISE	sensION+ 9655 half-cell fluoride ISE with sensION+ 5044 double junction reference electrode
sensION™ + MM378 lab dual input, pH/ISE/EC/DO	

### Before starting

Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information.

Prepare the probe before initial use. Refer to probe documentation.

When an IntelliCAL™ probe is connected to an HQd meter, the meter automatically identifies the measurement parameter and is prepared for use.

Condition the probe before use. To condition the probe, put the probe in 100 mL of the lowest concentration standard solution for a maximum of 1 hour.

Calibrate the probe before initial use. Refer to [Calibration procedure](#) on page 3.

During calibration, measure the standard solutions from lowest to highest concentration for best results.

For USEPA reporting, use fluoride standard solutions of 0.5-mg/L, 1.0-mg/L and 2.0-mg/L to calibrate the electrode.

Make sure that the calibration solutions and the samples are at the same temperature ( $\pm 2\text{ }^{\circ}\text{C}$  ( $\pm 3.6\text{ }^{\circ}\text{F}$ )) for best results.

Stir the standards and samples at a slow and constant rate to prevent the formation of a vortex.

Air bubbles under the sensor tip can cause slow response or measurement errors. To remove the bubbles, carefully shake the probe.

Small differences in concentration between samples can increase the stabilization time. Make sure to condition the probe correctly. Try different stir rates to see if the stabilization time decreases.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

This procedure is specified for the HQd meters. The sensION+ meters can be used, but the menus and navigation will be different.

## Items to collect

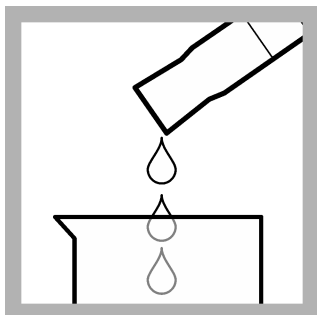
Description	Quantity
Fluoride ISA (TISAB)—powder pillow or solution (1 pillow or 5.0 mL per 25 mL solution)	1
Fluoride Standard Solutions, 1.00 and 10.0 mg/L or 0.5, 1.00 and 2.00 mg/L (USEPA)	varies
Beaker, polypropylene, 50 mL, low form	3 or 4 (USEPA)
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	3 or 4 (USEPA)
Stirrer, magnetic	1
Wash bottle with deionized water	1
Lint-free cloth	1

Refer to [Consumables and replacement items](#) on page 6 for order information.

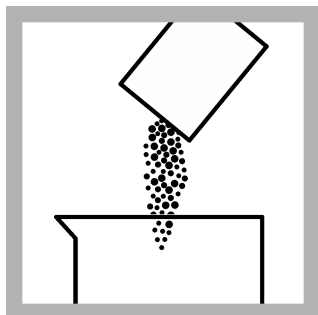
## Sample collection

- Collect samples in clean polyethylene bottles.
- If immediate analysis is not possible, keep the samples at room temperature for a maximum of 28 days.

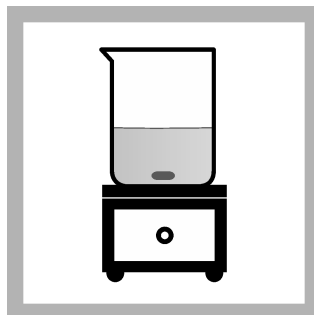
## Test procedure



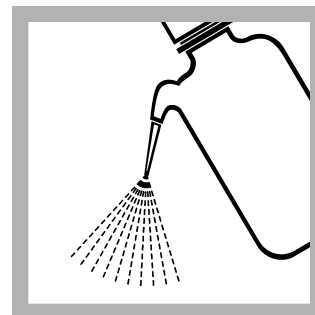
1. Add 25 mL of sample to a beaker.



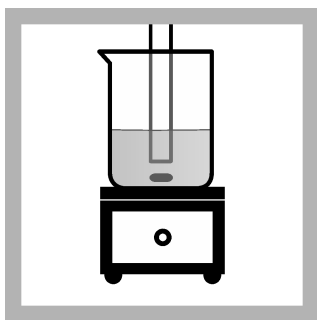
2. Add the contents of one Fluoride ISA Powder Pillow. **Note:** As an alternative, add 5 mL of Fluoride ISA Solution.



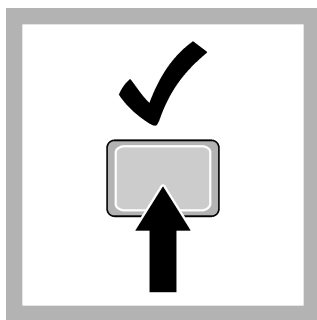
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



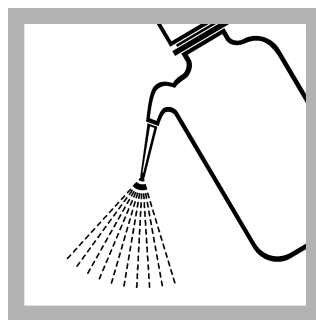
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



5. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.

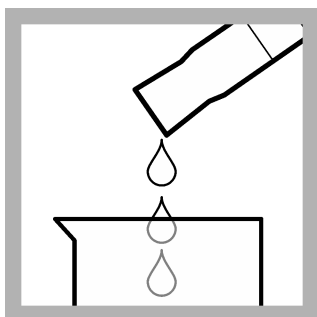


6. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.

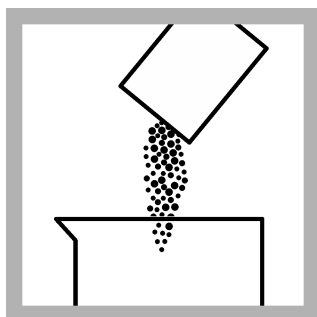


7. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

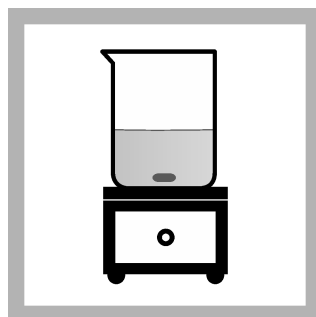
### Calibration procedure



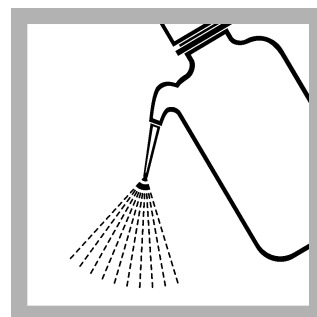
1. Add 25 mL of the lowest concentration standard solution to a beaker.



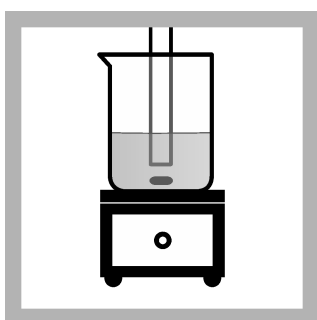
2. Add the contents of one Fluoride ISA Powder Pillow. **Note:** As an alternative, add 5 mL of Fluoride ISA Solution.



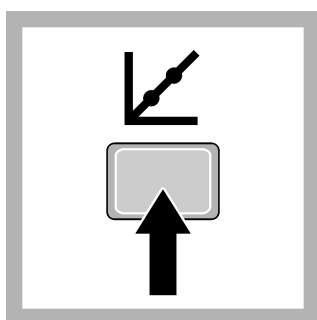
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



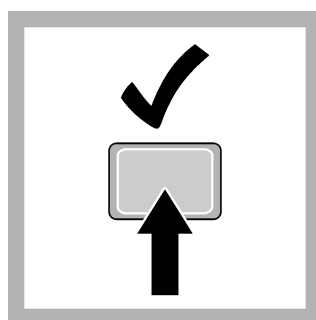
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



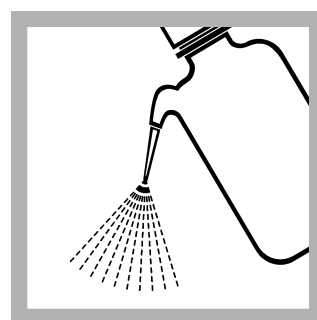
5. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.



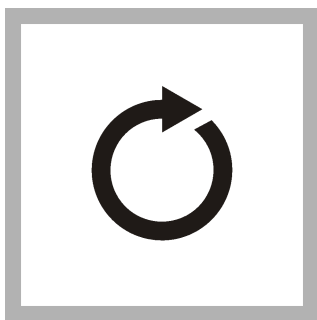
6. Push **Calibrate**. The standard solution value is shown.



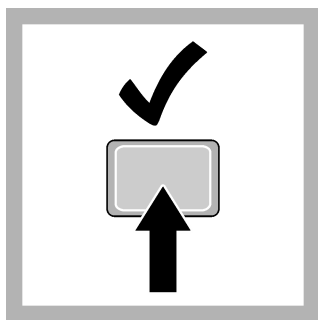
7. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



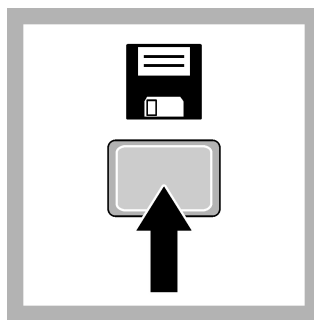
8. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



9. Measure the remaining standard solutions.



10. Push **Done**. A calibration summary is shown when the minimum number of calibration standards are measured.



11. Push **Store** to accept the calibration.

## Low-level measurements

Use the techniques that follow for measurements at low concentrations (<1 mg/L).

- Use plastic containers during calibration and measurements. Glass containers can cause inaccurate measurements.
- Clean the probe regularly. Refer to [Clean the probe](#) on page 5.
- Soak the probe in the lowest concentration standard solution for a maximum of 1 hour before calibration and measurement.
- Set the stability criteria in the settings menu to a low value (for applicable meters and probes).
- Use a dilute ionic strength adjustor (ISA) solution for calibration and measurements:
  1. Dissolve the contents of one ionic strength adjustor powder pillow in 50 mL of deionized water.
  2. Add 5 mL of this solution to every 25 mL of standard or sample that is used.

**Note:** The use of the ISA is optional when the conditions that follow are true:

- The sample does not contain interferences.
- The sample pH is in the range that is given in the electrode specifications.
- Omission of the ISA is accepted by the regulatory reporting agency (if applicable).

## Interferences

Interfering substance	Interference level
Cations	Do not interfere.
Cl <sup>-</sup> , Br <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , acetate	Do not interfere.
OH <sup>-</sup> (hydroxyl ions)	Interferes when the sample pH is 8 or more. The ISA adjusts the sample pH to 5.0–5.5.
CO <sub>3</sub> <sup>2-</sup> or PO <sub>4</sub> <sup>3-</sup>	Do not interfere but can increase the OH <sup>-</sup> interference.

## Accuracy check

### Slope method

Use the slope method to validate the electrode response.

1. Prepare two standard solutions that are one decade apart in concentration (e.g., 1 mg/L and 10 mg/L or 10 mg/L and 100 mg/L). The minimum concentration is 0.2 mg/L.
2. Use the test procedure to measure the mV value of each standard solution.
3. Compare the mV value of each standard solution. The expected difference is 58 (± 3) mV at 25 °C (77 °F).

### Standard solution method

Use the standard solution method to validate the test procedure, the reagents (if applicable) and the instrument.

Items to collect:

- Standard solution within the test range
1. Use the test procedure to measure the concentration of the standard solution.
  2. Compare the expected result to the actual result.

### Standard additions method

Use the standard additions method to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Fluoride Standard Solution, 100-mg/L
  - Graduated cylinder, 25-mL, polypropylene
  - TenSette pipet
  - Pipet tips
1. Use a graduated cylinder to measure 25 mL of sample into a beaker.
  2. Use the test procedure to measure the concentration of the sample.
  3. Use the TenSette pipet to add 0.5 mL of the standard solution to the sample.
  4. Measure the concentration of the spiked sample.
  5. Compare the results before and after the standard solution addition. The concentration should increase by 1.96 mg/L F<sup>-</sup>.

### Temperature check

For probes that do not have a temperature sensor, measure the temperature of the standard solutions and samples. Make sure that the calibration solutions and the samples are at the same temperature ( $\pm 2$  °C ( $\pm 3.6$  °F)) for best results.

### Clean the probe

Clean the probe when:

- Drifting/inaccurate readings occur as a result of contamination on the sensing element or incorrect storage conditions.
- Slow response time occurs as a result of contamination on the sensing element.
- The slope is out of range as a result of contamination on the sensing element.

For general contamination, complete the steps that follow.

1. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
2. If harsh contaminants are attached to the probe, use a small amount of plain fluoride toothpaste on a soft toothbrush or cloth (no teeth whiteners or abrasives) and gently rub it into the crystal with a circular motion. Continue to rub until the toothpaste film is removed. When finished, rinse with deionized water to clean the probe.
3. Soak for 30 minutes in 1 mg/L Fluoride Standard Solution.

### Method performance

The method performance data that follows was derived from laboratory tests during ideal test conditions. Users can get different results under different test conditions.

System	Standard	Precision (95% confidence interval)
HQd meter and ISEF121 ISE probe	1.00 mg/L	$\pm 0.01$ mg/L
sensION+ meter and 9655C/9655 ISE probe	1.00 mg/L	$\pm 0.01$ mg/L

## 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 in the sample. The potential is measured against a constant reference potential with a pH/mV meter or ISE meter.

## Consumables and replacement items

### HQd meters and probes

Description	Unit	Item no.
HQ30d portable single input, multi-parameter meter	each	HQ30D53000000
HQ40d portable dual input, multi-parameter meter	each	HQ40D53000000
HQ430d benchtop single input, multi-parameter meter	each	HQ430D
HQ440d benchtop dual input, multi-parameter meter	each	HQ440D
IntelliCAL™ ISEF121 digital combination fluoride ISE probe, 1 m cable	each	ISEF12101
IntelliCAL™ ISEF121 digital combination fluoride ISE probe, 3 m cable	each	ISEF12103

### sensION+ meters and probes

Description	Unit	Item no.
sensION™+ MM340 lab dual input, pH/mV/ISE meter	each	LPV2200.97.0002
sensION™+ MM374 lab dual input, pH/mV/EC/ISE meter	each	LPV4110.97.0002
sensION™+ MM378 lab dual input, pH/ISE/EC/DO meter	each	LPV4130.97.0002
sensION™+ 9655C combination fluoride ISE probe	each	LZW9655C. 97.002
sensION™+ 9655 fluoride half-cell ISE probe	each	LZW9655.97.0002
sensION™+ 5044 reference electrode	each	LZW5044.97.0002

### Recommended reagents and standards

Description	Unit	Item no.
Fluoride Ionic Strength Adjustor (ISA) Powder Pillows	100/pkg	258999
Fluoride Ionic Strength Adjustor (ISA) Solution	3.78 L	2829017
Fluoride Standard Solution, 0.5-mg/L F <sup>-</sup>	500 mL	40505
Fluoride Standard Solution, 1.0-mg/L F <sup>-</sup>	500 mL	29149
Fluoride Standard Solution, 2.0-mg/L F <sup>-</sup>	500 mL	40520
Fluoride Standard Solution, 5.0-mg/L F <sup>-</sup>	500 mL	2797149
Fluoride Standard Solution, 10-mg/L F <sup>-</sup>	500 mL	35949

### Accessories

Description	Unit	Item no.
Beaker, polypropylene, 50 mL, low form	each	108041
Bottle, wash, 500 mL	each	62011
Graduated cylinder, polypropylene, 25 mL	each	108140
Pipet, TenSette®, 0.1–1.0 mL	each	1970001

**Accessories (continued)**

Description	Unit	Item no.
Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	50/pkg	2185696
Probe clips, color-coded, for IntelliCAL probes	50/pkg	5818400
Probe holder, 3 probes, for sensION+ benchtop meters	each	LZW9321.99
Probe stand, universal	each	8508850
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	each	4531500
Stirrer, electromagnetic, 120 VAC, with electrode stand	each	4530001
Stirrer, electromagnetic, 230 VAC, with electrode stand	each	4530002



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