

Direct ISE Method

Method 8323
0.1 to 100.0 mg/L F⁻
Fluoride ISE

Scope and application: For industrial waters (solutions below a pH of 5).



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.

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.

Adjust the sample pH to 5–8 to release the complexed fluoride (HF or HF₂⁻) in the sample. Do not use a strong base (e.g., Sodium Hydroxide) to adjust the pH. A strong base can change the ionic strength of the sample and decrease the measurement accuracy.

Dilution of samples and standards with a large quantity of sodium acetate adjusts the pH and helps adjust the total ionic strength of samples and standards to the same level.

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

Make sure that the calibration solutions and the samples are at the same temperature (± 2 °C (± 3.6 °F)) for best results.

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 pillows or solution (1 pillow or 5.0 mL per 25 mL solution)	varies
Fluoride Standard Solutions, 100 and 1000 mg/L	varies
Sodium Acetate, ACS	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 7 for order information.

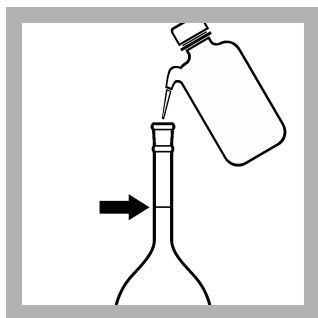
Sample collection

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

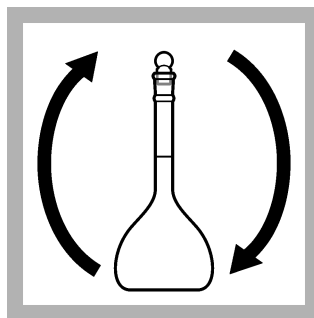
Test procedure



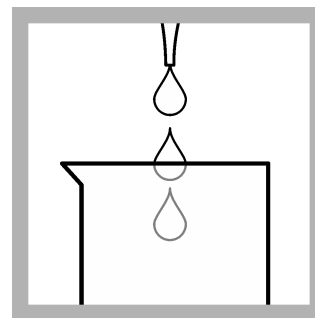
1. Prepare a 15% Sodium Acetate Solution: Add 150 g of Sodium Acetate to a 1000-mL volumetric flask.



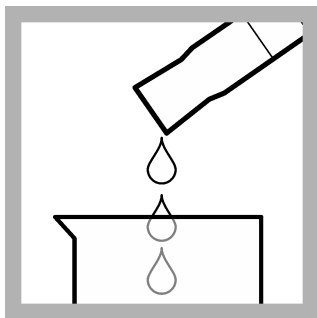
2. Dilute to the mark with deionized water.



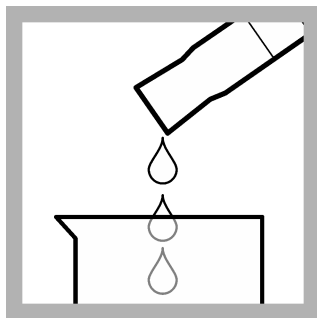
3. Put in the stopper. Invert the flask to mix well.



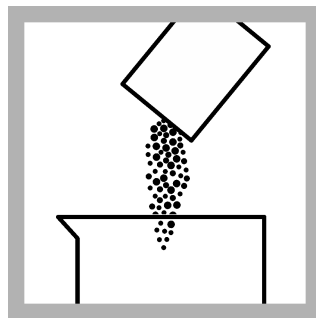
4. Prepare the sample: Add 3 mL of sample to a 50-mL beaker.



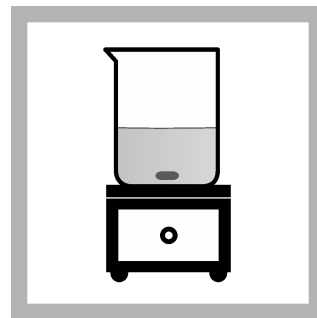
5. Add 27 mL of sodium acetate solution to the beaker.



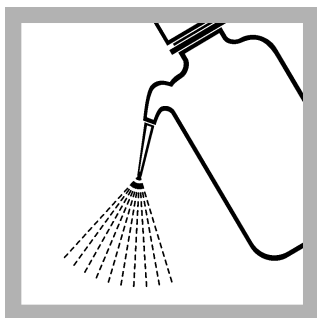
6. Add 25 mL of the prepared sample to a second 50-mL beaker.



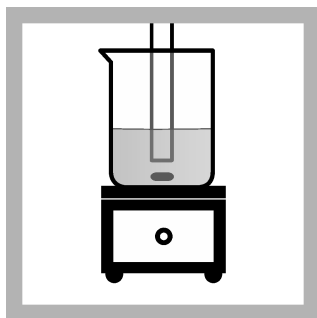
7. Add the contents of one Fluoride ISA Powder Pillow. **Note:** As an alternative, add 5 mL of Fluoride ISA Solution.



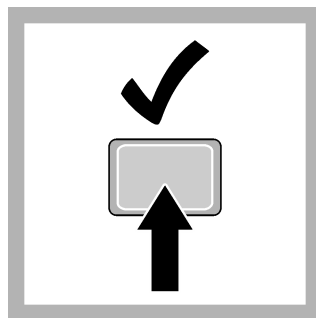
8. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



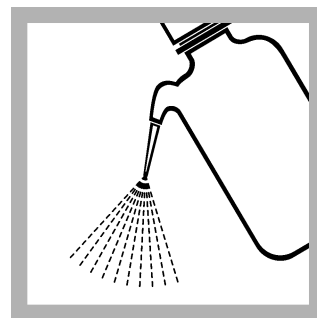
9. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



10. 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.



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

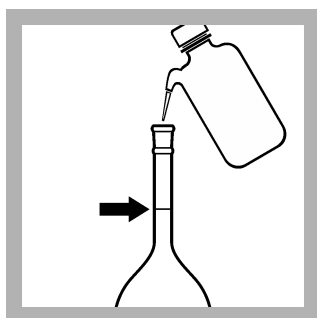


12. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

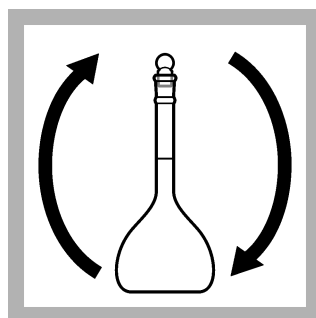
Calibration procedure



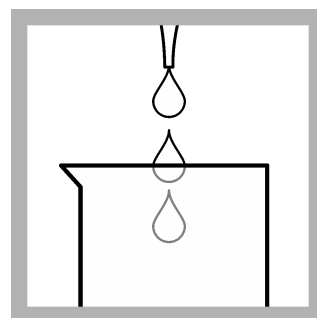
1. **Prepare a 15% Sodium Acetate Solution:** Add 150 g of Sodium Acetate to a 1000-mL volumetric flask.



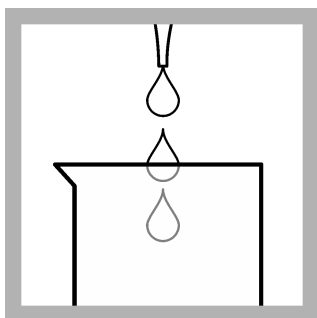
2. Dilute to the mark with deionized water.



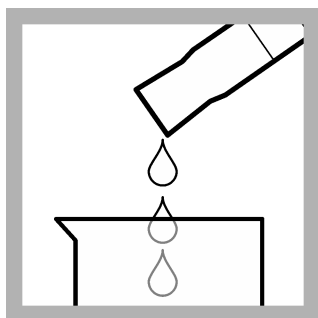
3. Put in the stopper. Invert the flask to mix well.



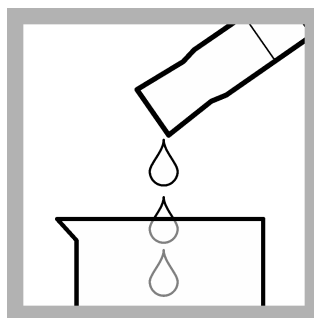
4. **Prepare the standards:** Prepare 1-mg/L and 10-mg/L Fluoride Standard Solutions. Refer to [Determine the diluent for standards](#) on page 5. Use standards that are less than 10 mg/L within 2 weeks.



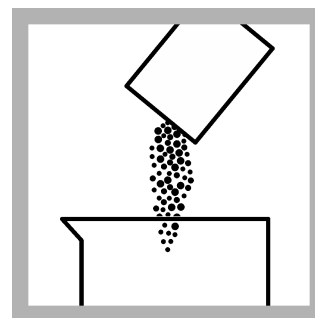
5. Add 3 mL of the lowest concentration standard solution to a 50-mL beaker.



6. Add 27 mL of the Sodium Acetate Solution to the beaker.



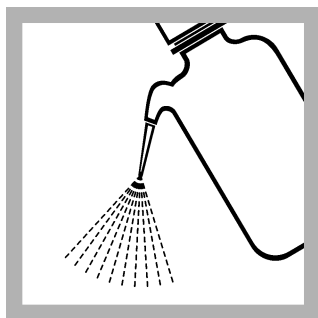
7. Add 25 mL of the prepared standard to a second 50-mL beaker.



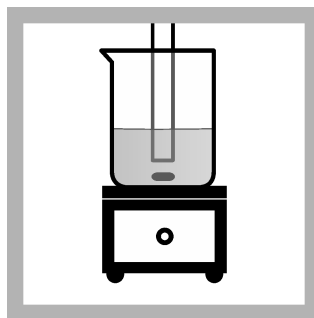
8. Add the contents of one Fluoride ISA Powder Pillow.
Note: As an alternative, add 5 mL of Fluoride ISA Solution.



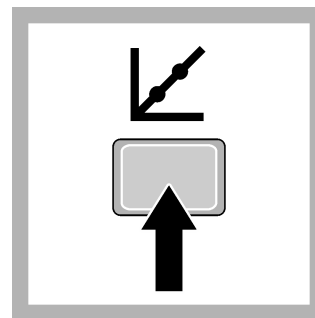
9. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



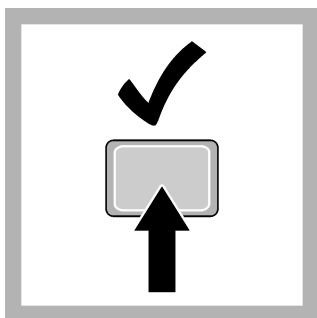
10. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



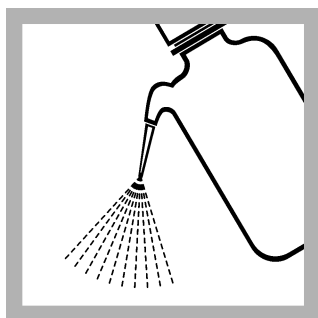
11. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.



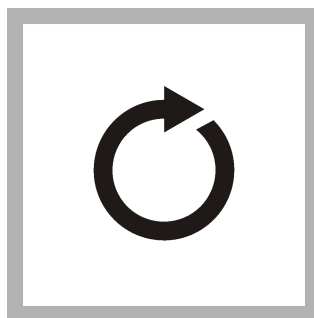
12. Push **Calibrate**. The standard solution value is shown.



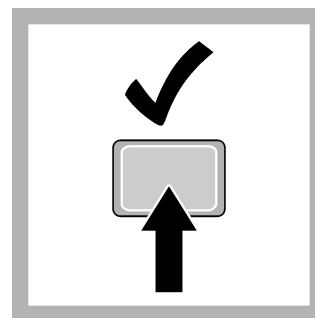
13. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



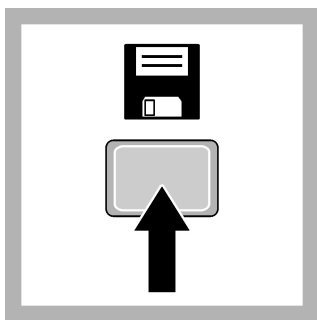
14. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



15. Measure the remaining standard solutions.



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



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

Determine the diluent for standards

Determine if a prepared background solution or deionized water is used to prepare the standard solutions.

1. Use deionized water to prepare a background solution that contains all the matrix components of a typical sample—but not fluoride.
2. Use the background solution to prepare a 10-mg/L Fluoride Standard Solution.
3. Use the test procedure to measure the concentration of the standard solution.
4. Use deionized water to prepare a 10-mg/L Fluoride Standard Solution.
5. Use the test procedure to measure the concentration of the standard solution.
6. If the results of the standard solution measurements are the same, use the background solution or deionized water to prepare the standard solutions.
7. If the results of the measurements are different, use the background solution to prepare the standard solutions.

Interferences

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 when the sample pH is 8 or more. The ISA adjusts the sample pH to 5.0–5.5.
CO ₃ ²⁻ or PO ₄ ³⁻	Do not interfere but can increase the OH ⁻ 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⁻.

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 ($\pm 2\text{ }^{\circ}\text{C}$ ($\pm 3.6\text{ }^{\circ}\text{F}$)) 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	± 0.01 mg/L
sensION+ meter and 9655C/9655 ISE probe	1.00 mg/L	± 0.01 mg/L

Summary of method

The fluoride electrode has a sensing Lanthanum Fluoride element bonded into an epoxy body. When the sensing element touches 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, 10-mg/L F ⁻	500 mL	35949
Fluoride Standard Solution, 100-mg/L F ⁻	500 mL	23249
Sodium Acetate, ACS ¹	—	—

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
Pipet tips for TenSette 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

¹ Sodium acetate is not available from Hach.

Accessories (continued)

Description	Unit	Item no.
Stirrer, electromagnetic, 120 VAC, with electrode stand	each	4530001
Stirrer, electromagnetic, 230 VAC, with electrode stand	each	4530002



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