



sensioTM

Combination Fluoride Electrode

Model 51928

Instruction Manual

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Specifications

Subject to change without notice

Concentration Range

0.01 mg/L F (5×10^{-7} M) to saturated solutions

pH range

pH 5–7 at 5×10^{-7} M (0.01 mg/L) to pH 11 at 10^{-1} M (1900 mg/L)

Slope

-58 ± 3 mV/decade in the linear concentration range

Temperature Range

Operating: 0–80 °C continuous use; 80–100 °C intermittent use

Storage Temperature

–30 to 80 °C (dry)

Reproducibility

$\pm 1\%$

Response Time

95% response in one minute or less in the linear range

Storage

Dry (in air), or in a fluoride standard solution for short-term

Electrode Resistance

150–200 k Ω

Minimum Sample Size

3 mL in a 50-mL beaker

Size

Length: 110 mm (4.4 in.)

Body diameter: 12 mm (0.48 in.)

Cable length: 100 cm (40 in.)

Cap diameter: 16 mm (0.64 in.)

Connector Type

BNC

Safety Precautions

Please read this entire manual before unpacking, setting up, or operating this instrument. Pay particular attention to all danger and caution statements. Failure to do so could result in serious injury to the operator or damage to the equipment.

To ensure the protection provided by this equipment is not impaired, do not use or install this equipment in any manner other than that which is specified in this manual.

Use of Hazard Information

If multiple hazards exist, this manual will use the signal word (Danger, Caution, Note) corresponding to the greatest hazard.

DANGER

Indicates a potentially or imminently hazardous situation which, if not avoided, could result in death or serious injury.

CAUTION

Indicates a potentially hazardous situation that may result in minor or moderate injury.

NOTE

Information that requires special emphasis.

Precautionary Labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed.



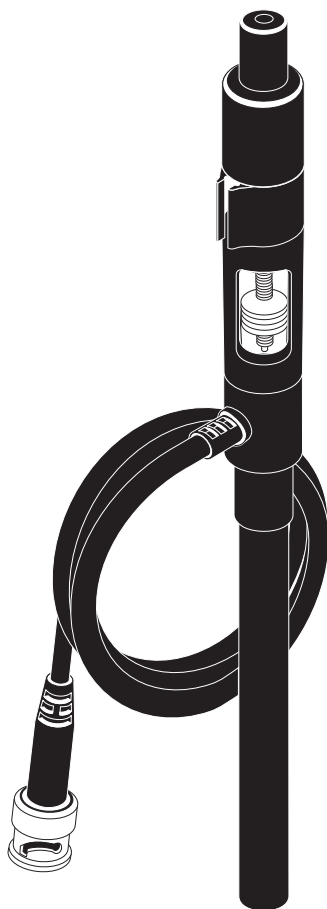
This symbol, if noted on the instrument, references the instruction manual for operational and/or safety information.

Section 1 Introduction

The Hach Combination Fluoride Electrode measures free fluoride ions in aqueous solutions using a sensing element bonded to the electrode body. The electrode (see *Figure 1*) is a complete electrochemical cell consisting of a double-junction reference electrode and a fluoride sensing electrode.

The Fluoride Electrode will measure fluoride in a variety of solutions. Applications include drinking water, acidic solutions, and basic solutions.

Figure 1 **Fluoride Electrode**



1.1 Electrode Description

Platinum Series Fluoride electrodes feature improved reference junction designs and provide fast, stable response with accurate measurements. Conventional combination electrodes use porous frits as the junction between the reference half-cell and the sample. The porous material rapidly clogs with precipitated silver chloride, causing unstable junction potentials. The Platinum Series Fluoride Electrode uses a double junction reference half-cell with a free-flowing outer reference junction. The free-flowing junction provides nearly constant junction potential with greater accuracy and reliability than conventional porous junction electrodes, and is ideal for both routine and demanding applications.

See *Figure 1*.

The Platinum Series Fluoride Electrode has a double-junction reference that contains a silver/silver chloride element in an inner chamber that contacts the electrolyte solution at an inner junction. Electrolyte flows from the free-flowing outer junction at the electrode tip. This design makes it ideal for use with samples containing sulfide or other substances.

1.2 Electrolyte Description

In a conventional electrode, a frit restricts the release of electrolyte into the sample. In the Platinum Series electrodes, medium viscosity electrolyte gel acts as a restriction device. Fresh reference electrolyte is supplied from a replaceable cartridge inside the electrode body by depressing the dispenser button. By refreshing the electrolyte at the reference junction, Hach's free-flowing reference system eliminates junction potential errors caused by clogged frits. The gelling agent is non-ionic and does not interfere with the free flow of ions across the reference junction. Proper use and care will extend the life of the reference half-cell.

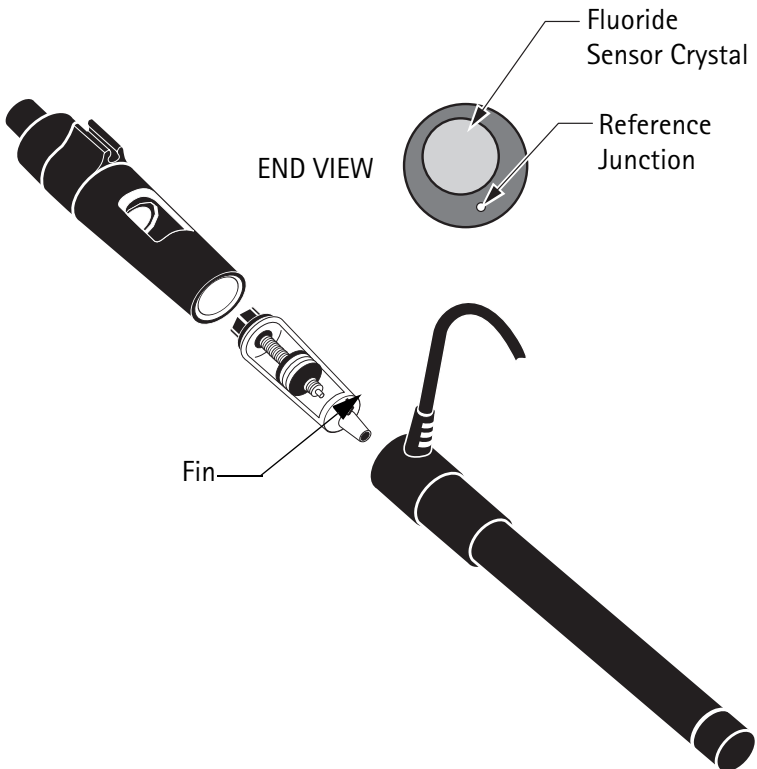
1.3 Preparing the Electrode for Use

1.3.1 Assembling the Electrode

Prepare the electrode as follows:

1. Remove the cap from the electrolyte cartridge. Align the fins on the cartridge with the grooves on the electrode body. Press the cartridge firmly into the inlet tube of the electrode body and rotate the cartridge clockwise until it is seated (*Figure 2*).
2. Place the dispenser unit over the electrolyte cartridge. Screw the dispenser unit onto the electrode body until it stops turning. **Do not over tighten.**

Figure 2 Assembling the Electrode



Introduction, continued

Note: *The electrode will be automatically primed by screwing the dispenser unit onto the electrode body.*

3. If electrolyte gel is not visible at the reference outlet, depress the dispenser button until it clicks; release the button. Repeat this procedure until gel is visible at the reference outlet. Alternatively, fully depress the button and rotate it clockwise until gel is visible at the reference outlet (1 to 3 rotations).
4. Rinse the electrode with deionized water. **Do not scratch the crystal.**
5. To remove an empty cartridge, unscrew the dispenser unit and rotate the cartridge counterclockwise while gently pulling it out of the electrode.
6. If the crystal becomes contaminated by oil, grease, or fingerprints, soak for a few minutes in isopropyl alcohol then rinse with deionized water.

1.4 Before Analysis

1.4.1 Sample Requirements

The epoxy electrode body is resistant to attack by inorganic solutions. The electrode may be used intermittently in solutions containing methanol, benzene, or acetone.

Samples and standards should be at the same temperature, which must be less than 100 °C.

1.4.2 Ionic Strength Adjustors

Use the same ISA for all calibration standards and samples measured using the calibration. Two choices of ISA are available:

1. Fluoride ISA Powder Pillows (Cat. No. 2589-99) – Use in both samples and standards. Do not use powdered ISA with standards that already contain ISA. Use one powder pillow for each 25 mL of sample or standard.

2. Fluoride ISA Solution (Cat. No. 28290-17) – Use in both samples and standards. Do not use with standards that already contain ISA. Use 5.0 mL of concentrated ISA for 25 mL of sample or standard.

1.5 Measuring Hints

- Use ISA for all samples. For convenience, Hach offers Fluoride TISAB powder pillows for 25-mL samples. Swirl or stir to dissolve the powder.
- Liquid ISAs may also be used. These are especially good when measuring low-level fluoride where pipetting improves accuracy.
- Always use the same Fluoride ISA for calibration and samples. Mixing ISAs will cause incorrect results. Do not use powder ISA with standards that already include ISA.
- Stir all sample and standards at a uniform rate during measurement.
- Verify calibration every two hours by placing the electrode in the first standard solution used for calibration. If the value has changed, recalibrate.
- Always use fresh standards for calibration.
- Always rinse the electrode with deionized water between measurements (see *Section 1.3* on page 9).
- Shake after rinsing to prevent solution carryover. Do not wipe or rub the sensing element.
- Allow all standards and samples to come to room temperature for precise measurement.
- After immersion in solution, check the electrode for any air bubbles on the element surface and remove by re-dipping the electrode into solution.
- For high ionic strength samples, prepare standards with composition similar to that of the sample.

Introduction, continued

- Adjust highly acidic or basic solutions to pH 5–6 before adding Fluoride ISA.

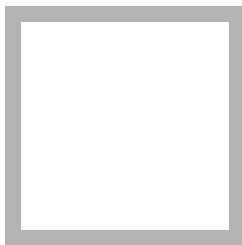
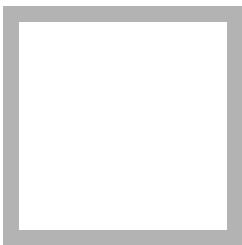
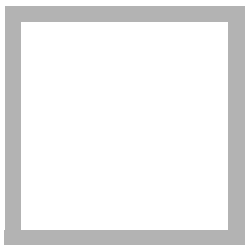
1.6 Units of Measurement

Fluoride concentrations can be measured in moles per liter, equivalents per liter, parts per million, or any convenient concentration unit. *Table 1* shows the equivalent concentrations of moles per liter and ppm.

Table 1 Equivalent Concentrations

Moles/Liter	ppm F⁻
10 ⁻¹	1900
10 ⁻²	190
10 ⁻³	19
10 ⁻⁴	1.9

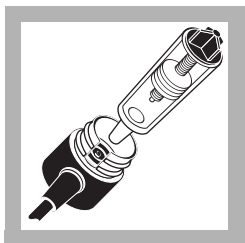
Section 2 Applications



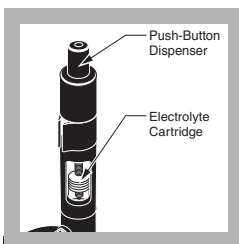
For use with Hach *sens^{ion}*[™] pH or pH/ISE meters

Fluoride in Drinking Water

Fluoride ion concentrations in drinking water, ground water and other clean waters can be determined by direct measurement.



1. Install the electrolyte gel cartridge in the electrode.



2. Prime the electrode by pushing the dispenser button until gel comes out of the reference junction. Rinse excess gel from the tip and the outlet.

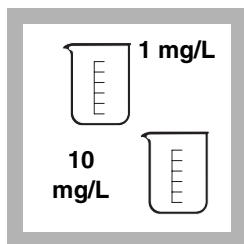


3. Connect the combination fluoride electrode to the meter.

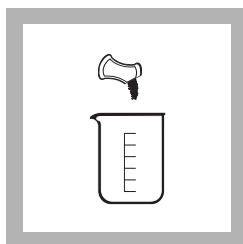
Note: One BNC and one 5-pin connector are on the back of the meter. Choose the BNC for the fluoride electrode.

Disconnect the pH electrode from the 5-pin connector when using the BNC connector.

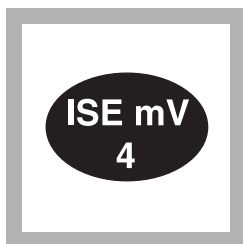
Fluoride in Drinking Water, continued



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



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



6. Turn the meter on by pressing **I/O**.

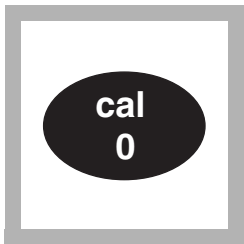
a. Press **SETUP**.

b. Press **ENTER** until **BNC** appears.

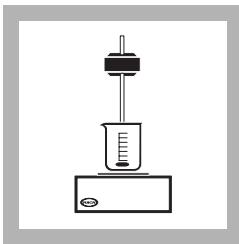
c. Press **EXIT**.

d. Press **ISE/mV** until the display shows **mg/L**.

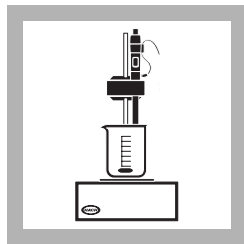
Note: To measure pH with a 5-pin connector, change the setting to 5-pin.



7. Press **CAL**. The display will show **CAL, ?, mg/L** (or other concentration units), and the active keys. The units will be flashing. If necessary, use the arrow keys to select mg/L, then press **ENTER**.

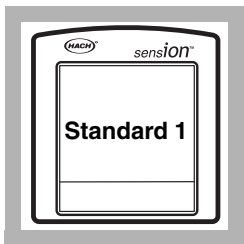


8. Place the beaker with the 1-mg/L standard on a magnetic stirrer. Stir at a moderate rate.



9. Place the electrode into the standard.

Note: *Stirring at a constant moderately fast rate speeds response and improves accuracy. For accurate work, especially at low levels where long stirring times may occur, use the stirrer listed under **REQUIRED APPARATUS**. Using other stirrers requires using a pad to minimize heat transfer to the sample.*



10. The display will show **Standard 1 ?** and **____** or the value of standard 1 from the previous calibration.

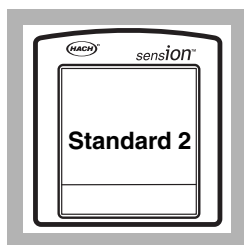


11. Press **ENTER** to accept the numerical value or use the number pad to edit the display to match the concentration of the 1.0 mg/L standard, then press **ENTER**.

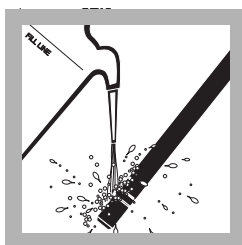


12. The display will show **Stabilizing...** until the reading is stable.

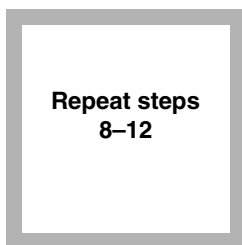
Fluoride in Drinking Water, continued



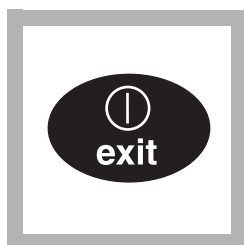
13. The display will show **Standard 2 ?** and **_____** or the value of standard 2 from the previous calibration.



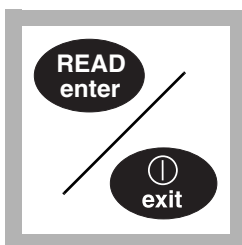
14. Remove the electrode from the standard solution. Rinse it with deionized water and blot dry.



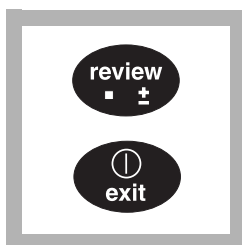
15. Repeat steps 8-12 for the 10-mg/L standard.



16. After the last standard is measured, press **EXIT**.

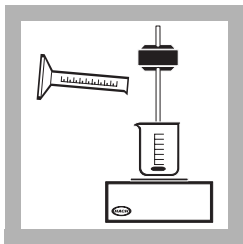


17. The display will show **Store?**. Press **ENTER** to store the calibration or **EXIT** to leave the calibration mode without storing the calibration values.

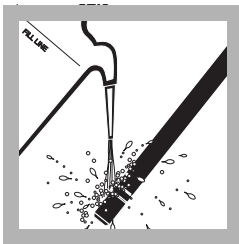


18. Press **REVIEW**. Use the up arrow key to scroll to the last slope value. It should be -58 ± 3 mV/decade. Press **EXIT** to return to the measurement mode.

***Note:** If the slope does not approximate -58 ± 3 mV/decade, recalibration may be necessary. If the slope is still incorrect after recalibration, see Section 6 Troubleshooting.*

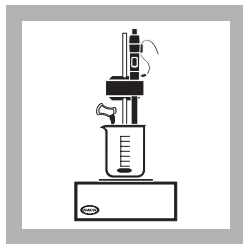


19. Transfer 25 mL of the sample to a 50-mL beaker. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.

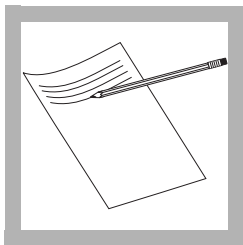


20. Remove the electrode from the standard solution. Rinse it with deionized water and blot dry. Place it into the sample.

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

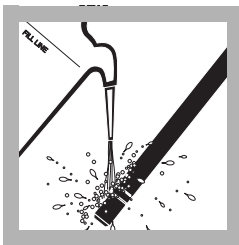


21. Add the contents of one TISAB Powder Pillow or 5.0 mL ISA solution to the sample. Stir to dissolve.



22. The display will show **Stabilizing...** until the reading is stable. Record or store the measurement value.

Repeat steps 19–22 for each sample.



23. 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. To store longer than one month, see Section 5.1 on page 79.

Fluoride in Drinking Water, continued

Sampling and Storage

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

Accuracy and Precision

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- 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 following table and formulas to calculate the percent recovery.

Table 1 Spiking Volumes

Measured sample Concentration n	Volume & Concentration of F ⁻ Standard to Add V C		C x V
0.6–1 mg/L	03 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

Use this formula to calculate the percent recovery (only applicable if sample volume is 25 mL).

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 (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⁻)

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

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

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

Method Performance

Precision

In a single lab using a standard solution of 1.6 mg/L and two electrodes with a single *sensIon2*, a single operator obtained a standard deviation of 0.005 mg/L F⁻. Each electrode was exposed to seven test solutions with no rinsing in between and with a default stability of 0.5 mV/min.

Interferences

Cations and most anions do not interfere with the electrode response to fluoride ions. Anions commonly associated with fluoride (Cl⁻, Br⁻, SO₄²⁻, HCO₃⁻, PO₄³⁻, acetate) do not interfere with electrode operation.

Hydroxyl ions (OH⁻) interfere; see *Section 4.6* on page 75. Some ions, such as CO₃²⁻ or PO₄³⁻, make the sample more basic, which increases OH⁻ interference, but do not directly interfere with the electrode operation.

* Use the volume (V) from *Table 1*.

Fluoride in Drinking Water, continued

REQUIRED REAGENTS

Description	Quantity Required		Cat. No.
	Per Test	Unit	
Choose one ISA:			
Fluoride ISA Buffer Pillows	1	100/pkg	2589-99
Fluoride ISA Solution	5.0 mL	3.78 L ..	28290-17
Fluoride Standard Solutions:			
1.00-mg/L	varies	500 mL	291-49
2.00-mg/L	varies	500 mL	405-20
10.0-mg/L	varies	500 mL	359-49
Description	Quantity Required		Cat. No.
	Per Test	Unit	
Potassium Chloride Reference Electrolyte			
Gel Cartridges.....	varies	2/pkg ..	25469-02
Water, deionized.....	varies	4 L	272-56

REQUIRED APPARATUS

Beaker, 50-mL, polypropylene.....	3	each	1080-41
Bottle, wash, 500-mL.....	1	each	620-11
Cylinder, graduated, 25-mL, poly	3	each	1081-40
Platinum Series Fluoride			
Combination Electrode, BNC.....	1	each ...	51928-00
sens <i>ion</i> TM 2 Portable pH/ISE Meter.....			51725-00
OR			
sens <i>ion</i> TM 4 Laboratory pH/ISE Meter1		each ...	51775-00
Stir Bar, 7/8 X 3/16 in. (22.2 x 4.8 cm)1		each ...	45315-00
Select one based on available voltage:			
Stirrer, electromagnetic, 115 VAC,			
with stand and stir bar.....	1	each ...	45300-01
Stirrer, electromagnetic, 230 VAC,			
with stand and stir bar.....	1	each ..	45300-02

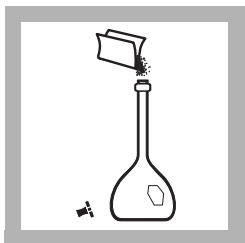
OPTIONAL APPARATUS

Description	Units	Cat. No.
Electrode Washer.....	each ...	27047-00
Pipet, TenSette, 0.1 to 1.0 mL.....	each ...	19700-01
Pipet Tips, for 19700-01 TenSette Pipet.....	50/pkg ...	21856-96

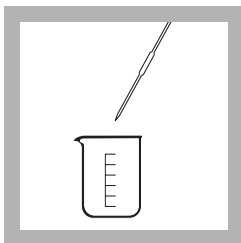
Fluoride in Acid Solutions

In solutions below a pH of 5, hydrogen ion complexes some of the fluoride ions, forming HF or HF_2^- , which the electrode will not detect. To free the complexed fluoride, adjust the pH of the solution so it is weakly acidic to weakly basic before analysis. **Do not use a strong base (such as sodium hydroxide) for adjustment since the amount of base added will vary from sample to sample.** Using a strong base can also change the ionic strength of the sample and alter measurement accuracy.

Dilution of samples and standards with a large excess of sodium acetate will buffer the pH and help adjust the total ionic strength of samples and standards to the same level.

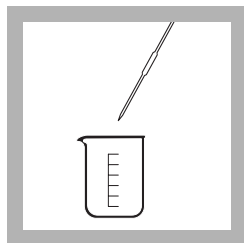


1. Prepare a 15% sodium acetate solution by dissolving 150 g of reagent grade sodium acetate in 1000 mL of deionized water. Prepare enough solution to dilute all the samples and standards.



2. Using deionized water, prepare a background solution containing all the sample matrix components except fluoride. Use this solution to prepare the standards.

Note: If a standard prepared with background solution gives the same reading (after sodium acetate dilution) as standard prepared with pure sodium acetate, it is not necessary to prepare a background solution.

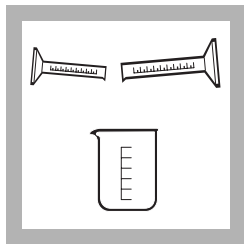


3. For calibration, prepare fluoride standards by adding fluoride to the background solution.

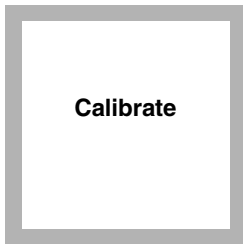
Note: Prepare fresh standards every two weeks if standards are less than 10 mg/L F^- .

Note: If using a direct reading fluoride meter, use two standards. If using a pH/mV meter, use three standards.

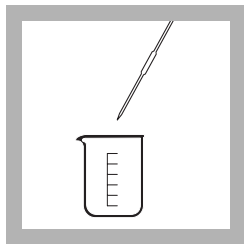
Fluoride in Acid Solutions, continued



4. Dilute each standard 10:1 with sodium acetate solution (9 parts sodium acetate solution:1 part standard).

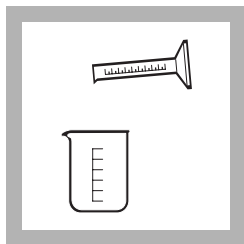


5. Calibrate the electrode following the instructions in steps 5–17 of the Fluoride in Drinking Water procedure on page 16.

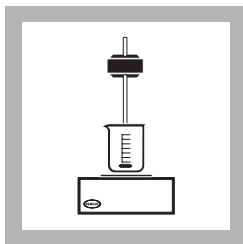


6. Measure the sample into 50-mL beakers.

Note: For example, measure 3 mL of sample and dilute it with 27 mL of sodium acetate.



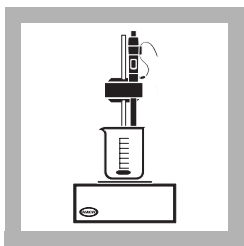
7. Dilute each unknown 10:1 with sodium acetate before measurement.



8. Place a stir bar in the beaker and set the beaker on a magnetic stirrer. Stir at a moderate speed.



9. Rinse the electrode with deionized water and blot dry.



10. Place the electrode into the sample. When the reading is stable, record the value.

Sampling and Storage

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

Accuracy and Precision

To verify measurement accuracy, run a standard addition spike on the sample. This provides more complete information about possible inaccuracies, because the measurement includes any interferences that may be present in the actual sample.

The spike should roughly double the measured concentration without significantly diluting the sample. To run a standard addition sample, use *Table 2* to determine the concentration and volume of standard to spike your sample. It is important that the volume of standard transferred is accurate. Add the amount and concentration of standard specified in *Table 2* to the sample and record the reading when it is stable, then proceed with the calculations. Generally, results from 90–110% recovery are considered acceptable.

Calculate percent recovery as follows:

$$\% \text{ Recovery} = \frac{100(X_s - X_u)}{K}$$

Fluoride in Acid Solutions, continued

Table 2 Spiking volumes

Measured Sample Concentration (mg/L)	Measured Sample Volume (mL)	Standard Concentration (mg/L)	Standard Volume (mL)
0.1–0.6	25	100	0.1
0.6–1.0	25	100	0.2
1.0–1.5	25	100	0.3
1.5–3.0	25	100	0.5
3–6	25	100	1.0
6–10	25	100	2.0
10–15	25	100	3.0
15–25	25	1000	0.5
25–35	25	1000	0.7
35–50	25	1000	1.0
50–100	25	1000	2.0

Where:

X_s = measured value for spiked sample in mg/L

X_u = measured value for unspiked sample adjusted for dilution by the spike, in mg/L

K = known value of the spike in the sample in mg/L

Calculations:

$$1. \quad X_u = \frac{X_i \times V_u}{V_u + V}$$

Where:

X_i = measured value of unspiked sample in mg/L

V_u = volume of separate unspiked portion in mL

V = volume of spike in mL

$$2. \quad K = \frac{C \times V}{V_u + V}$$

Where:

C = concentration of standard used in spike in mg/L

V = volume of spike in mL

V_u = volume of separate portion before spike in mL

3. Final calculation plugging in X_u and K :

$$\% \text{ Recovery} = \frac{100(X_s - X_u)}{K}$$

Example: A sample was analyzed and read 5.0 mg/L F^- . As directed in *Table 2*, a 1.0-mL spike of 100-mg/L F^- standard was added to the 25-mL sample, giving a final reading of 8.75 mg/L.

Calculate the percent recovery as follows:

$$1. \quad X_u = \frac{5.0 \text{ mg/L} \times 25 \text{ mL}}{25 \text{ mL} + 1 \text{ mL}} = 4.81 \text{ mg/L}$$

$$2. \quad K = \frac{100 \text{ mg/L} \times 1 \text{ mL}}{25 \text{ mL} + 1 \text{ mL}} = 3.85 \text{ mg/L}$$

$$3. \quad \% R = \frac{100 \times (X_s - X_u)}{K} = \frac{100 \times (8.75 - 4.81)}{3.85} = 102.3 \% \text{ Recovery}$$

Fluoride in Acid Solutions, continued

REQUIRED REAGENTS

Description	Quantity Required		Cat. No.
	Per Test	Unit	
Fluoride Standard Solutions:			
1.00-mg/L	varies	500 mL	291-49
2.00-mg/L	varies	500 mL	405-20
10.0-mg/L	varies	500 mL	359-49
Potassium Chloride Reference Electrolyte			
Gel Cartridges.....	varies	2/pkg ..	25469-02
Sodium Acetate, ACS.....	varies	454 g ...	178-01H
Water, deionized.....	varies	4 L	272-56

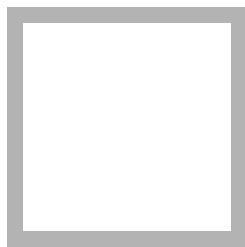
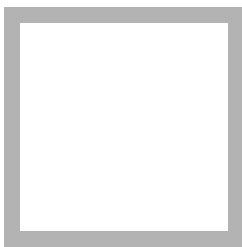
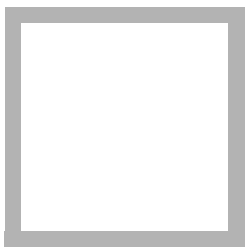
REQUIRED APPARATUS

Beaker, 50-mL, polypropylene.....	3	each	1080-41
Bottle, wash, 500-mL.....	1	each	620-11
Cylinder, graduated, 25-mL, poly	3	each	1081-40
Fluoride Combination Electrode, BNC, w/ filling solution.....	1	each ...	51928-00
sens ^{ion} ™2 Portable pH/ISE Meter....	1	each ...	51725-00
OR			
sens ^{ion} ™4 Laboratory pH/ISE Meter1		each ...	51775-00
Stir Bar, 7/8 X 3/16 in. (22.2 x 4.8 cm)1		each ...	45315-00
Select one based on available voltage:			
Stirrer, electromagnetic, 115 VAC, with stand and stir bar.....	1	each ...	45300-01
Stirrer, electromagnetic, 230 VAC, with stand and stir bar.....	1	each ..	45300-02

OPTIONAL APPARATUS

Electrode Washer.....		each ...	27047-00
Pipet, TenSette, 0.1 to 1.0 mL		each ...	19700-01
Pipet Tips, for 19700-01 TenSette Pipet.....	50/pkg		21856-96

Section 3 Analytical Methods (mV meters)



Direct Measurement Method

(With Graph Paper)

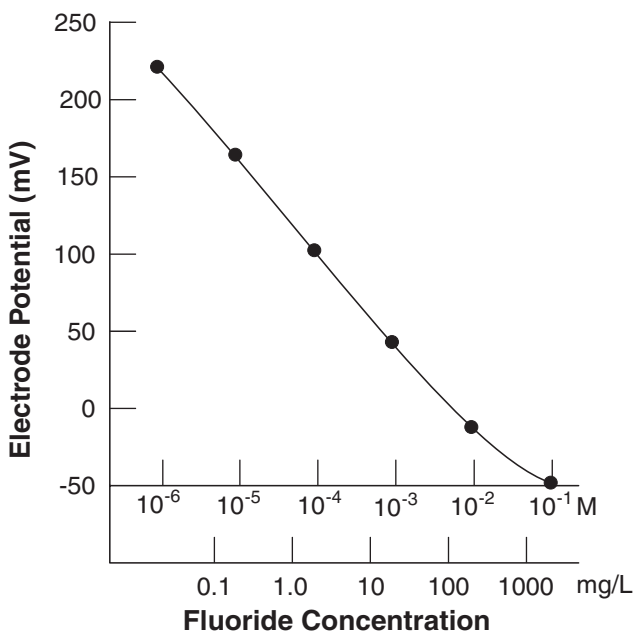
Most modern pH/ISE/mV meter, including the Hach *sensⁱonTM2* and *sensⁱonTM4* meters, allow the user to perform calibrations for the species and concentration range of interest. Once calibrated, the meter will give a direct reading of the concentration for that species. Unlike many meters, which are limited to linear calibrations, the *sensⁱon2* and *sensⁱon4* meters can cover a larger concentration range that has both linear and non-linear electrode response regions. These meters will accurately calculate the concentration from the electrode potential and display the concentration directly in user-selected units including ppm, mg/L, or M.

When the user only has access to a pH/mV meter, the user can still obtain results by using semilogarithmic graph paper, plotting the concentration on the Y (log) axis and the potential (mV) on the X axis (see *Figure 3* and *Figure 4*). A best-fit line is drawn through the points on the graph. Then a straight line is drawn from the sample potential value to the best-fit line. From that point on the best-fit line, another straight line is drawn to the fluoride concentration on the other axis.

This direct method has some advantages:

1. It is fast—only one measurement per sample is necessary. The known addition method requires two measurements per sample and volumetric measurements of standards.
2. It covers a wide range of fluoride levels (see *Figure 3*), including concentration in the non-linear regions. Most portable direct reading meters and the known addition method require the sample to be in the linear response range. This makes analysis at low levels possible with the Hach *sensⁱon2* and *sensⁱon4* pH/ISE meters.

Figure 3 Typical Calibration Curve



3.1 Preparing Standards for a Calibration Curve

The concentration and number of standards depends on the expected sample concentration(s). If the samples have similar fluoride concentrations and are in the linear response region (10^{-6} M or 0.02 mg/L to saturated), use a short method with two standards that bracket the expected fluoride level.

Standards used for linear ISE calibration curves are usually one to two powers of ten (or decades) apart in concentration. To cover a wider range of concentrations, or measure low levels, use several standards. Standards may be purchased or made by diluting a concentrated fluoride solution. Hach sells many fluoride standards that range from 0.2 mg/L to 100 mg/L. See *REQUIRED REAGENTS* on page 39.

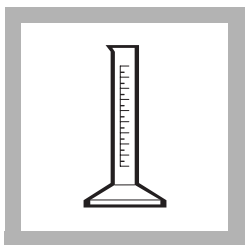
Standards preparation:

1. Use a Class A 100-mL volumetric pipet to measure 100 mL of a concentrated standard (e.g., 19 mg/L F^- [10^{-3} M]) into a 1000-mL volumetric flask.
2. Fill the flask to the mark with deionized water. Mix well. This is a ten-fold dilution of the original standard (e.g., 1.9 mg/L [10^{-4} M]).
3. Pour the solution into a 1-liter plastic container for storage. Label the container and keep capped at all times.
4. Repeat the dilution as with the 1.9-mg/L solution. This is another 10-fold dilution (e.g., 0.19 mg/L).

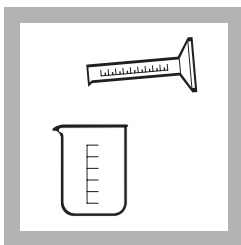
Note: Fluoride is absorbed by glass, so store these standards in plastic containers. The solutions should be stable for at least three months.

The serial dilutions also could be done from a 100-mg/L standard, producing 10, 1 and 0.1 mg/L fluoride solutions. A 100-mg/L fluoride solution can be prepared by adding 0.2210 g anhydrous sodium fluoride (analytical reagent grade, oven dried at 120 °C) to a 1000-mL volumetric flask and diluting to the mark with deionized water.

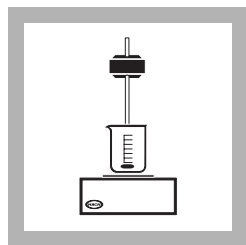
3.2 Analysis Using a Manually Plotted Calibration Curve



1. Select standards that cover the concentration range of the samples. Measure 25 mL of a standard solution in a graduated cylinder.

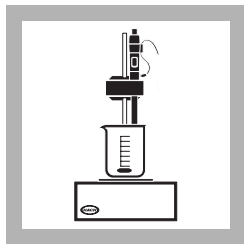


2. Pour the least concentrated standard into a 50-mL plastic beaker.

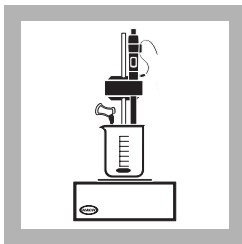


3. Add a clean magnetic stir bar. Place the beaker on a magnetic stirrer and stir at a moderate rate.

Direct Measurement Method, continued

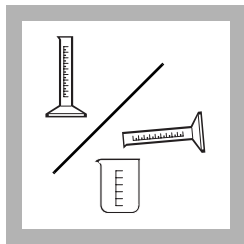


4. Rinse the electrode with deionized water. Place the electrode in the standard.



5. Add the contents of one Fluoride ISA Powder Pillow. Record the mV potential when it is stable.

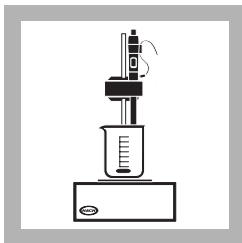
Note: Alternatively, add 5.0 mL of Fluoride ISA Solution.



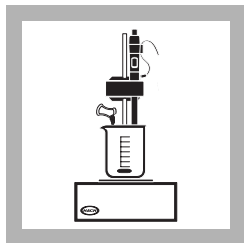
6. Prepare the next standard as in steps 1–3.



7. Remove the electrode from the previous standard. Rinse with distilled water and blot dry with a paper towel.



8. Immerse the electrode in the next standard.

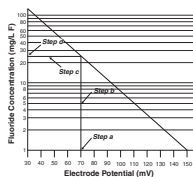
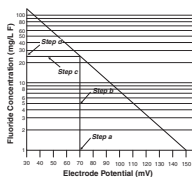


9. Add the contents of one Fluoride ISA Powder Pillow. Record the mV potential when it is stable.

Note: Alternatively, add 5.0 mL of Fluoride ISA Solution.

Direct Measurement Method, continued

Repeat for each standard used

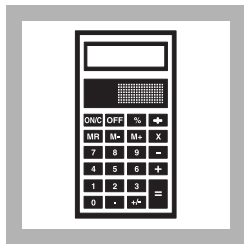


10. Repeat steps 6–9 for any other standards used in making the calibration curve.

11. On a sheet of semilogarithmic graph paper (2–7 cycles), plot the fluoride concentration values vs. the potentials. Plot concentrations on the logarithmic (horizontal) axis. Each cycle is equal to a 10-fold change in concentration. Plot the mV potential on the linear (vertical) axis. See *Figure 4* on page 38.

12. Draw a best-fit line through the points. A straight line should connect the concentrations above 0.2 mg/L F⁻ (10^{-6} M).

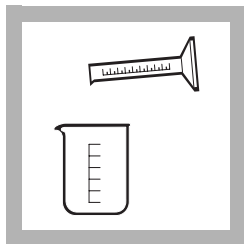
Direct Measurement Method, continued



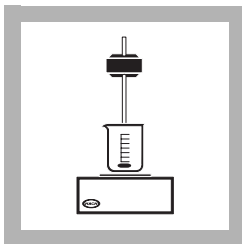
13. Approximate the slope:

- Select two points on the straight portion of the curve that are one decade apart (e.g., 1 and 10 mg/L).
- Subtract the potential of the 1 mg/L standard from the potential of the 10 mg/L standard.
- The difference should be -58 ± 3 mV/decade (at 20–25 °C).

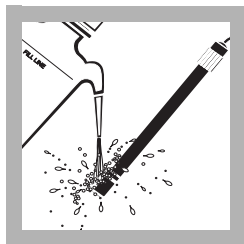
Measuring Samples



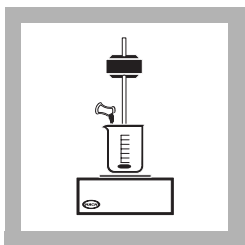
14. Measure 25 mL of sample with a graduated cylinder. Pour it into a 50-mL plastic beaker.



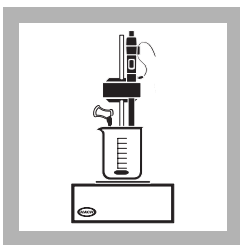
15. Add a magnetic stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.



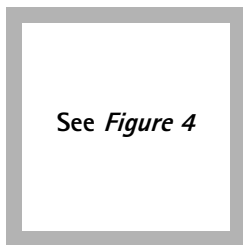
16. Rinse with deionized water or a portion of the next sample. Blot dry with a paper towel (do not rub).



17. Add the contents of one Fluoride ISA Powder Pillow to the beaker.



18. Immerse the electrode in the sample. Record the potential when the reading is stable.



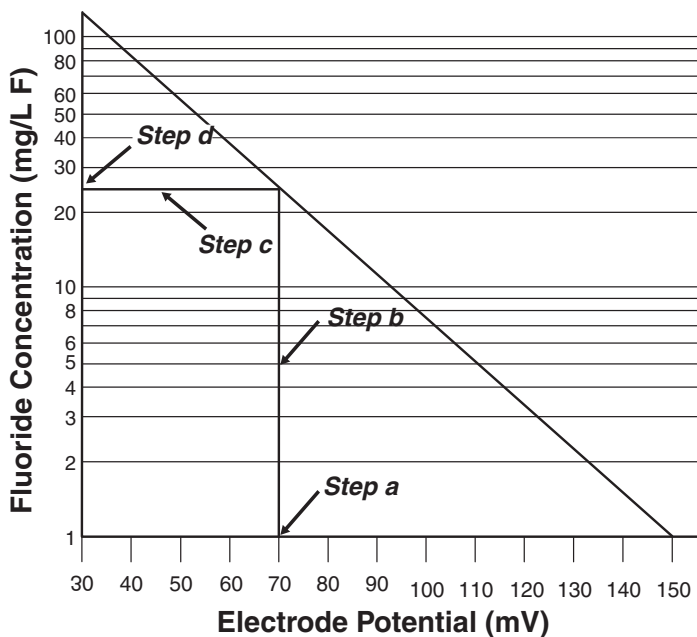
19. Using the calibration curve (see *Figure 4*) and the example below determine the sample fluoride concentration.

Using the Calibration Curve

1. Refer to *Figure 4* on page 38. On the linear (horizontal) axis, locate the potential value recorded (*Step a* in the figure).
2. Draw a straight vertical line from the potential value up to the calibration curve line (*Step b* in the figure).
3. From that point on the curve, draw a straight horizontal line across to the concentration (*Step c* in the figure).
4. Read the point on the concentration line as the sample concentration (*Step d* in the figure).

Direct Measurement Method, continued

Figure 4 Determining Sample Concentration using a Calibration Curve



Example

A water sample, measured using the above procedure, had a potential of 70 mV. What is the fluoride concentration of the sample?

Figure 4 is an example of a calibration curve. To find the fluoride concentration of the sample:

- Locate the 70 mV value on the horizontal (linear) axis.
- Draw a vertical line from 70 mV up to the calibration curve line.
- Then draw a line across to the concentration scale on the vertical (log) axis.
- The sample concentration is 25 mg/L F^- .

Direct Measurement Method, continued

REQUIRED REAGENTS

Description	Quantity Required		
	Per Test	Unit	Cat. No.
Fluoride ISA Buffer Pillows	1	100/pkg.....	2589-99
Fluoride ISA Solution	5.0 mL	3.78 L...	28290-17
Fluoride Standard Solutions (choose appropriate standards):			
0.2-mg/L.....	varies	500 mL.....	405-02
0.5-mg/L.....	varies	500 mL.....	405-05
0.8-mg/L.....	varies	500 mL.....	405-08
1.00-mg/L	varies	500 mL.....	291-49
1.2-mg/L.....	varies	500 mL.....	405-12
1.5-mg/L.....	varies	500 mL.....	405-15
2.00-mg/L	varies	500 mL.....	405-20
10.0-mg/L.....	varies	500 mL.....	359-49
19.0-mg/L	varies	500 mL...	21262-49
100-mg/L.....	varies	500 mL.....	232-49
Potassium Chloride Reference Electrolyte			
Gel Cartridges.....	varies	2/pkg...	25469-02
Water, deionized	varies	4 L.....	272-56

REQUIRED APPARATUS

Description	Quantity Required		
	Per Test	Unit	Cat. No.
Beaker, 50-mL, polypropylene.....	1	each.....	1080-41
Bottle, wash, 500-mL.....	1	each.....	620-11
Semilogarithmic Graph Paper, 4-cycle	1	100/pkg...	23062-01
sens <i>ion</i> TM 1 Portable pH/mV Meter...	1	each....	51700-10
OR			
sens <i>ion</i> TM 3 Laboratory pH/mV Meter	1	each....	51750-10
Stir Bar, 7/8 X 3/16 in. (22.2 x 4.8 cm)	1	each...	45315-00
Select one based on available voltage:			
Stirrer, electromagnetic,			
115 VAC, with stand and stir bar ...	1	each...	45300-01
Stirrer, electromagnetic,			
230 VAC, with stand and stir bar...	1	each...	45300-02

Measuring Low Levels of Fluoride

A new Platinum Series Fluoride electrode has a linear response to 0.1 ppm (mg/L). The lower limit of linear response may rise as the electrode ages. To assure highest accuracy when measuring samples with low fluoride concentration, repetitive addition of small volumes of standards (standard “spikes”) to a known volume of deionized water and ISA solution is recommended.

Table 3, Preparing a Low Level Calibration Curve covers the range 0.01 to 0.50 mg/L in seven steps. Bracket the sample concentration when calibrating the instrument.

Steps above and below the sample concentration can be omitted. The spike volumes for the skipped steps must be added to reach the total spike volume corresponding to the sample concentration.

For example, if the sample concentration is known to be within the range 0.05 to 0.20 mg/L, start with step 3 and end with step 6. The spike volume for step 3 must include the spike volumes of the skipped steps (steps 1–2) to total 0.4 mL, so that the resulting standard concentration at step 3 equals 0.04 mg/L

Table 3 Preparing a Low Level Calibration Curve

Step Number	Initial Volume (mL)	Spike Volume (mL)	Resulting Volume (mL)	Spike Conc. (mg/L)	Resulting Conc (mg/L)	Resulting Conc (Molarity)
1	100	0.1	100.1	10	0.01	5.3×10^{-7}
2	100.1	0.1	100.2	10	0.02	1.1×10^{-6}
3	100.2	0.2	100.4	10	0.04	2.1×10^{-6}
4	100.4	0.2	100.6	10	0.06	3.1×10^{-6}
5	100.6	0.5	101.1	10	0.10	5.2×10^{-6}
6	101.1	2.2	103.3	10	0.30	1.6×10^{-5}
7	103.1	2.4	105.7	10	0.50	2.6×10^{-5}

Measuring Low Levels of Fluoride, continued

For *sensioN2* or *sensioN4*, input the concentration values from Table 3 for each step of the calibration described in the following procedure. The *sensioN2* meter will store a 5-point calibration, while the *sensioN4* meter will store a 7-point calibration.

A three-point calibration spanning the range that brackets the sample concentration is the recommended minimum.

The *sensioN4* has adjustable stabilization criteria. For low-range measurements, set the stabilization criteria at 0.150 mV/minute drift for best results. The default stabilization for the *sensioN2* is 0.5 mV/minute for ISE measurements and cannot be changed.

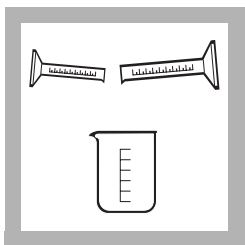
Note: *To override the default 0.5 mV/minute stabilization acceptance for the sensioN2, switch to mV mode during the calibration and note the changing mV reading. Use a stopwatch to measure drift. When the drift is less than 0.2 mV/minute, press **ENTER** to store the calibration point.*

Use the following procedure steps to measure samples that contain less than 0.2 mg/L (2×10^{-5} M) fluoride and have no fluoride complexing agents. For solutions low in fluoride but high in total ionic strength, perform the same procedure using a calibration solution with a composition similar to the sample.

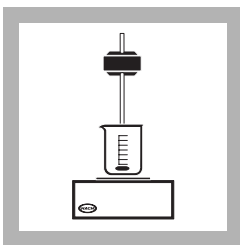
For accurate measurements:

- Allow enough time for electrode stabilization. Response time will increase with decreasing concentration.
- Stir all standards and samples at a uniform rate.

Measuring Low Levels of Fluoride, continued



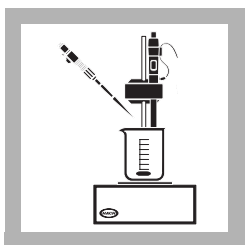
1. Measure 90 mL of deionized water and 10 mL of Fluoride ISA Solution into a 150-mL beaker.



2. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.

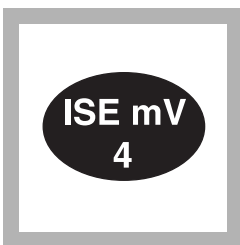


3. Rinse the electrode with deionized water and place it into the beaker.



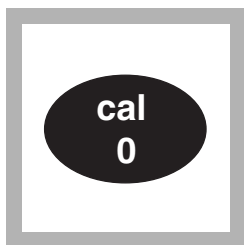
4. Add a 10-mg/L spike from *Table 3*.

Note: The *TenSette Pipet* is useful for the repetitive additions used in this method.



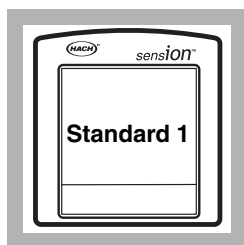
5. Turn the meter on by pressing **I/O**.

- Press **SETUP**.
- Press **ENTER** until **BNC** appears.
- Press **EXIT**.
- Press **ISE/mV** until the display shows **mg/L**.



6. Press **CAL**. The display will show **CAL, ?, mg/L** (or other concentration units), and the active keys. The units will be flashing. If necessary, use the arrow keys to select **mg/L**, then press **ENTER**.

Measuring Low Levels of Fluoride, continued



7. The display will show **Standard 1** and **_____** or the value of standard 1 from the previous calibration.

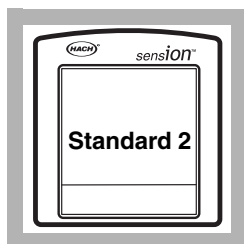


8. Press **ENTER** to accept the numerical value or use the number pad to edit the display to match the concentration corresponding to the step number from *Table 3*, then press **ENTER**.



9. The display will show **Stabilizing...** until the reading is stable.

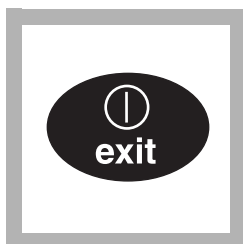
Note: For the *sensION2* in mV mode, press **ENTER** when the reading is stable.



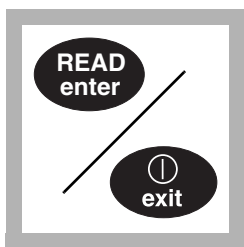
10. The display will show **Standard 2 ?** and **_____** or the value of standard 2 from the previous calibration.



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

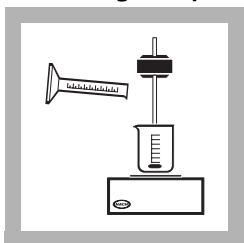


12. After the last standard is measured, press **EXIT**.



13. The display will show Store?. Press **ENTER** to store the calibration or **EXIT** to leave the calibration mode without storing the calibration values.

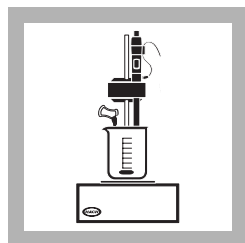
Measuring Samples



1. Transfer 90 mL of the sample to a 150-mL beaker. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.

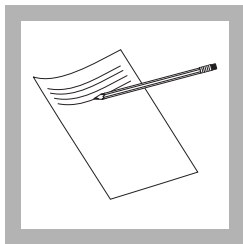


2. Remove the electrode from the standard solution. Rinse it with deionized water and blot dry. Place it into the sample.



3. Add 10 mL of ISA solution to the sample.

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



4. The display will show **Stabilizing...** until the reading is stable. Record or store the measurement value.

Measuring Low Levels of Fluoride, continued

REQUIRED REAGENTS

Description	Quantity Required		
	Per Test	UnitS	Cat. No.
Fluoride ISA Solution	50 mL.....	3.78 L...	28290-17
Fluoride Standard, 10.0-mg/L.....	5 mL.....	500 mL.....	359-49
Potassium Chloride Reference Electrolyte Gel Cartridges.....	varies	2/pkg...	25469-02
Water, deionized.....	varies	4 L.....	272-56

REQUIRED APPARATUS

Beaker, 50-mL, polypropylene.....	3	each.....	1080-41
Bottle, wash, 500-mL.....	1	each.....	620-11
Cylinder, graduated, 25-mL, poly	3	each.....	1081-40
Fluoride Combination Electrode, BNC, w/ filling solution	1	each...	51928-00
sens <i>ion</i> TM 2 Portable pH/ISE Meter.....			51725-00
OR sens <i>ion</i> TM 4 Laboratory pH/ISE Meter	1	each...	51775-00
Stir Bar, $\frac{7}{8}$ X $\frac{3}{16}$ in. (22.2 x 4.8 cm)	1	each...	45315-00
Select one based on available voltage:			
Stirrer, electromagnetic, 115 VAC, with stand and stir bar ...	1	each...	45300-01
Stirrer, electromagnetic, 230 VAC, with stand and stir bar...	1	each...	45300-02
Pipet, TenSette, 0.1 to 1.0 mL.....	1	each....	19700-01
Pipet Tips, for 19700-01 TenSette Pipet.....	varies	50/pkg...	21856-96

OPTIONAL APPARATUS

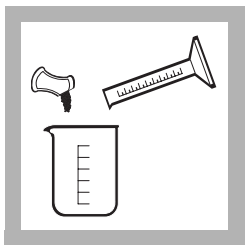
Electrode Washer.....		each...	27047-00
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Analysis with pH/mV Meter and Calculator

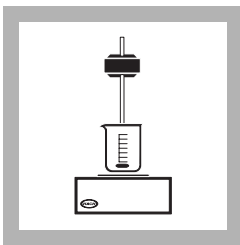
Also known as a linear calibration using two standards that bracket the sample, this method is often used to calibrate for direct measurements. The two-point calibration can be repeated quickly and easily during each series of measurements. *Figure 3* on page 32 is an example of a linear calibration curve.

Note: Use the two-point calibration only in the linear region.

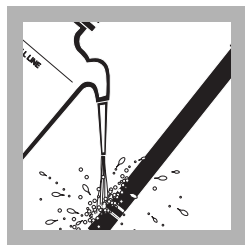
The two standards chosen should be close to the expected concentration range of the samples. The standards often differ by only one decade.



1. Measure 25 mL of Standard 1.
Pour it into a beaker.
Add one powder pillow or 1.5 g of Fluoride TISAB powder or 5 mL of ISA solution.

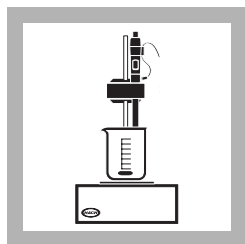


2. Add a clean magnetic stir bar.
Place the beaker on a magnetic stirrer and stir at a moderate rate.

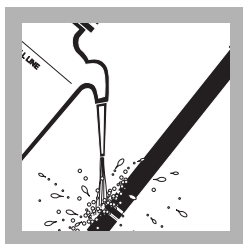


3. Rinse with deionized water and blot dry.

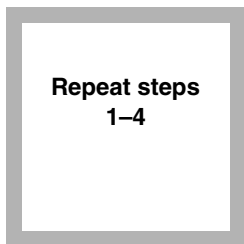
Analysis with pH/mV Meter and Calculator, continued



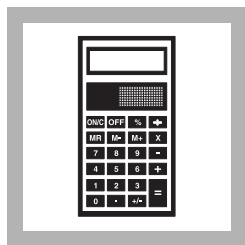
4. Place the electrode into the standard solution. Record the potential when it is stable.



5. Remove the electrode from the standard, rinse with deionized water. Blot dry with a paper towel (do not rub).



6. Repeat steps 1-4 with the second standard.



7. Calculate the slope:

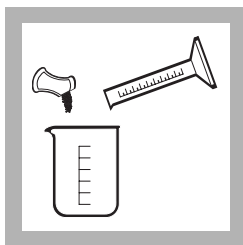
$$s = \frac{E_1 - E_2}{\text{Log } C_1 - \text{Log } C_2}$$

Where:

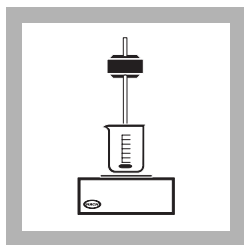
s = slope (mV/decade)

E_1 and E_2 = potentials of standards 1 and 2.

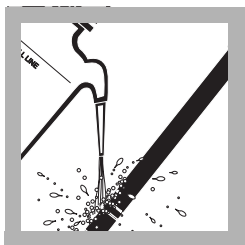
C_1 and C_2 = the F-concentrations of standards 1 and 2.



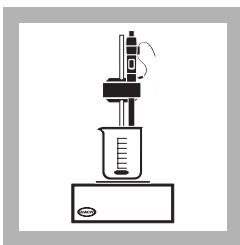
8. Measure 25 mL of sample into a beaker. Add one powder pillow or 1.5 g of Fluoride TISAB powder or 5.0 mL ISA solution. Stir well to dissolve.



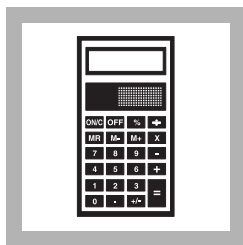
9. Add a clean magnetic stir bar. Place the beaker on a magnetic stirrer and stir at a moderate rate.



10. Rinse the electrode with deionized water and blot dry.



11. Place the electrode into the sample (stirring increases accuracy and response time). Record the mV value when the display is stable.



12. Calculate the sample fluoride concentration using the equations following this step.

Calculating the Fluoride in Samples

$$\Delta E = E_x - E_1$$

Where:

E_x = sample potential

E_1 = standard potential (either standard)

$$C_x = C_1 \times 10^{\Delta E/S}$$

Where:

C_x = sample concentration

C_1 = standard concentration (corresponding to E_1)

S = the electrode slope

Example:

Standard 1 (C_1) = 1.0 mg/L

E_1 = 138 mV (potential of standard 1)

Slope (s) = -58.9 mV/decade

The sample (E_x) reads 146.5 mV/decade

$$\Delta E = 146.5 - 138.0 = 8.5 \text{ mV/decade}$$

$$C_x = 1.0 \text{ mg/L} \times 10^{8.5/-58.9} = 0.72 \text{ mg/L}$$

Analysis with pH/mV Meter and Calculator, continued

Measure the potentials of the standards periodically and compare these values with the calibration values. If the potential of the standard has changed, the offset potential has changed, and a new calibration should be done.

The two-standard calibration in effect determines both the electrode slope and the electrode's standard potential and should be performed at least daily. The slope is more stable than the standard potential, so within a series of samples, a one-standard calibration check can be made to verify calibration accuracy. The potential of one of the standards is re-measured periodically and compared to the calibration value.

If sample temperature and electrode slope are determined to be stable, the one-standard calibration may be used more often. Where the temperature is varying, the two standard calibration is required.

REQUIRED REAGENTS

Description	Quantity Required		
	Per Test	Unit	Cat. No.
Fluoride ISA Buffer Pillows	1	100/pkg	2589-99
Fluoride ISA Solution	5.0 mL	3.78 L ..	28290-17
Fluoride Standard Solutions (choose appropriate standards):			
0.2-mg/L	varies	500 mL	405-02
0.5-mg/L	varies	500 mL	405-05
0.8-mg/L	varies	500 mL	405-08
1.00-mg/L	varies	500 mL	291-49
1.2-mg/L	varies	500 mL	405-12
1.5-mg/L	varies	500 mL	405-15
2.00-mg/L	varies	500 mL	405-20
10.0-mg/L	varies	500 mL	359-49
19.0-mg/L	varies	500 mL ...	21262-49
100-mg/L	varies	500 mL	232-49
Potassium Chloride Reference Electrolyte			
Gel Cartridges.....	varies	2/pkg ..	25469-02
Water, deionized.....	varies	4 L	272-56

Analysis with pH/mV Meter and Calculator, continued

REQUIRED APPARATUS

Beaker, 50-mL, polypropylene.....	1each.....	1080-41
Bottle, wash, 500-mL.....	1each.....	620-11
Calculator	1each buy locally	
sens <i>ion</i> TM 1 Portable pH/mV Meter...1each....		51700-10
OR			
sens <i>ion</i> TM 3 Laboratory pH/mV Meter1each....		51750-10
Stir Bar, 22.2 x 4.76 mm	1each...	45315-00
Water, deionized	varies	4 L.....	272-56

Select one based on available voltage:

Stirrer, electromagnetic,

115 VAC, with stand and stir bar ...1each... 45300-01

Stirrer, electromagnetic,

230 VAC, with stand and stir bar...1each... 45300-02

Known Addition Method with pH/mV Meter

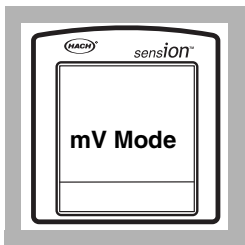
The *sensioN*TM4 meter has a standard addition program that automatically calculates the fluoride concentration. This method

is only necessary if a pH/mv meter is used. In the known or standard addition method, the analyst adds a known amount of fluoride ion to the sample, then calculates the original fluoride level from the change in potential. This technique requires the electrode slope to be known and the measurements to be in the linear region. A calibration curve shows the linear region of the probe and also the slope.

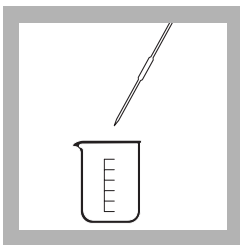
This method may be used when only a few samples need analysis. This method does not require a calibration curve and is a quick way to obtain results on a few samples.

Requirements for accurate measurements:

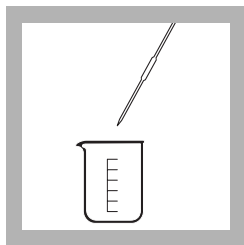
- Concentration should be approximately doubled by the standard addition. This requires knowing the approximate fluoride concentration in the sample, within a factor of three.
- The ratio of uncomplexed ion to complexed ion must not be changed by adding the standard.
- Samples and standards should be at the same temperature.



1. Set the meter to read millivolts.

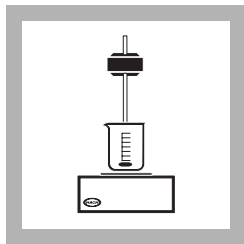


2. Using a volumetric pipet, measure 50 mL of sample into a 150-mL beaker.

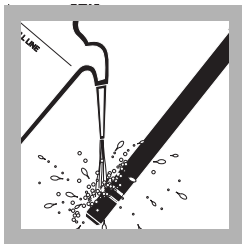


3. Add 10 mL of Fluoride ISA Solution.

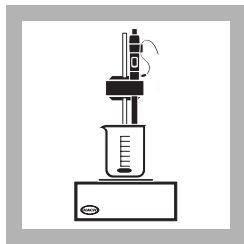
Known Addition Method with pH/mV Meter, continued



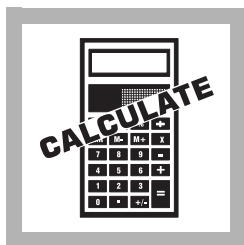
4. Add a stir bar and place the beaker on a magnetic stirrer. Stir moderately.



5. Rinse the electrode with deionized water and blot dry.



6. Place the electrode in the standard. When the reading is stable, set the millivolt reading to 0.0 or record the mV reading.



7. Calculate the volume of fluoride standard to be added to roughly double the fluoride concentration:

$$V_{\text{std}} = \frac{C_s \times V_s}{C_{\text{std}}}$$

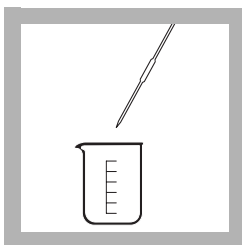
Where:

V_s = sample volume

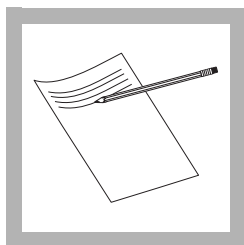
C_s = sample concentration

C_{std} = standard concentration

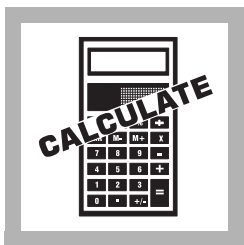
V_{std} = standard volume



8. Add the desired volume of standard to the sample. Stir thoroughly.



9. Record the potential when it is stable. If the meter could not be zeroed in *step 6*, subtract the first mV reading (E_1) from this mV reading (E_2) to find the slope (ΔE).



10. From *Table 4* find the value Q , that corresponds to the change in potential. To determine the original concentration, multiply Q by the concentration of the added standard. See the equations following *Table 4* for more information.

Table 4 may only be used if the volume of standard added was 10% of the sample volume. If this ratio is different, use the second equation following the table.

Table 4 Calculated Q Values

ΔE	Slope (mV/decade)			
	57.2	58.2	59.2	60.1
5.0	0.2940	0.2933	0.2972	0.3110
5.2	0.2806	0.2844	0.2833	0.2921
5.4	0.2722	0.2759	0.2798	0.2835
5.6	0.2642	0.2680	0.2717	0.2754
5.8	0.2567	0.2604	0.2540	0.2677
6.0	0.2495	0.2531	0.2567	0.2603
6.2	0.2426	0.2462	0.2498	0.2533
6.4	0.2361	0.2396	0.2431	0.2566
6.6	0.2298	0.2333	0.2368	0.2402

Known Addition Method with pH/mV Meter, continued

Table 4 Calculated Q Values (Continued)

ΔE	Slope (mV/decade)			
	57.2	58.2	59.2	60.1
6.8	0.2239	0.2273	0.2307	0.2341
7.0	0.2181	0.2215	0.2249	0.2282
7.2	0.2127	0.2160	0.2193	0.2226
7.4	0.2974	0.2107	0.2140	0.2172
7.6	0.2024	0.2056	0.2088	0.2120
7.8	0.1975	0.2007	0.2039	0.2071
8.0	0.1929	0.1961	0.1992	0.2023
8.2	0.1884	0.1915	0.1946	0.1977
8.4	0.1841	0.1872	0.1902	0.1933
8.6	0.1800	0.1830	0.1860	0.1890
8.8	0.1760	0.1790	0.1820	0.1849
9.0	0.1722	0.1751	0.1780	0.1809
9.2	0.1685	0.1714	0.1742	0.1771
9.4	0.1649	0.1677	0.1706	0.1734
9.6	0.1614	0.1642	0.1671	0.1698
9.8	0.1581	0.1609	0.1636	0.1664
10.0	0.1548	0.1576	0.1603	0.1631
10.2	0.1517	0.1544	0.1571	0.1598
10.4	0.1487	0.1514	0.1540	0.1567
10.6	0.1458	0.1484	0.1510	0.1537
10.8	0.1429	0.1455	0.1481	0.1507
11.0	0.1402	0.1427	0.1453	0.1479
11.2	0.1375	0.1400	0.1426	0.1451
11.4	0.1349	0.1374	0.1399	0.1424
11.6	0.1324	0.1349	0.1373	0.1398
11.8	0.1299	0.1324	0.1348	0.1373
12.0	0.1276	0.1300	0.1324	0.1348
12.2	0.1243	0.1277	0.1301	0.1324
12.2	0.1253	0.1277	0.1301	0.1324
12.4	0.1230	0.1254	0.1278	0.1301
12.6	0.1208	0.1232	0.1255	0.1278

Known Addition Method with pH/mV Meter, continued

Table 4 Calculated Q Values (Continued)

ΔE	Slope (mV/decade)			
	57.2	58.2	59.2	60.1
12.8	0.1187	0.1210	0.1233	0.1256
13.0	0.1167	0.1189	0.1212	0.1235
13.2	0.1146	0.1169	0.1192	0.1214
13.4	0.1127	0.1149	0.1172	0.1194
13.6	0.2208	0.1130	0.1152	0.1174
13.8	0.1089	0.1111	0.1133	0.1155
14.0	0.1071	0.1093	0.1114	0.1136
14.2	0.1053	0.1075	0.1096	0.1118
14.4	0.1036	0.1057	0.1079	0.1100
14.6	0.1019	0.1040	0.1061	0.1082
14.8	0.1003	0.1024	0.1045	0.1065
15.0	0.0987	0.1008	0.1028	0.1048
15.5	0.0949	0.0969	0.0989	0.1009
16.0	0.0913	0.0932	0.0951	0.0971
16.5	0.0878	0.0897	0.0916	0.0935
17.0	0.0846	0.0865	0.0883	0.0901
17.5	0.0815	0.0833	0.0852	0.0870
18.0	0.0786	0.0804	0.0822	0.0839
18.5	0.0759	0.0776	0.0793	0.0810
19.0	0.0733	0.0749	0.0766	0.0783
19.5	0.0708	0.0724	0.0749	0.0757
20.0	0.0684	0.0700	0.0716	0.0732
20.5	0.0661	0.0677	0.0693	0.0708
21.0	0.0640	0.0655	0.0670	0.0686
21.5	0.0619	0.0634	0.0649	0.0664
22.0	0.0599	0.0614	0.0629	0.0643
22.5	0.0580	0.0595	0.0609	0.0624
23.0	0.0562	0.0576	0.0590	0.0605
23.5	0.0545	0.0559	0.0573	0.0586
24.0	0.0528	0.0542	0.0555	0.0569
24.5	0.0512	0.0526	0.0539	0.0552

Known Addition Method with pH/mV Meter, continued

Table 4 Calculated Q Values (Continued)

ΔE	Slope (mV/decade)			
	57.2	58.2	59.2	60.1
25.0	0.0497	0.0510	0.0523	0.0536
25.5	0.0482	0.0495	0.0508	0.0521
26.0	0.0468	0.0481	0.0493	0.0506
26.5	0.0455	0.0467	0.0479	0.0491
27.0	0.0442	0.0454	0.0466	0.0478
27.5	0.0429	0.0441	0.0453	0.0464
28.0	0.0417	0.0428	0.0440	0.0452
28.5	0.0405	0.0417	0.0428	0.0439
29.0	0.0394	0.0405	0.0416	0.0427
29.5	0.0383	0.0394	0.0405	0.0416
30.0	0.0373	0.0383	0.0394	0.0405
31.0	0.0353	0.0363	0.0354	0.0364
32.0	0.0334	0.0344	0.0354	0.0364
33.0	0.0317	0.0326	0.0336	0.0346
34.0	0.0300	0.0310	0.0319	0.0328
35.0	0.0285	0.0294	0.0303	0.0312
36.0	0.0271	0.0280	0.0288	0.0297
37.0	0.0257	0.0266	0.0274	0.0283
38.0	0.0245	0.0253	0.0261	0.0269
39.0	0.0233	0.0241	0.0249	0.0257
40.0	0.0222	0.0229	0.0237	0.0245
41.0	0.0211	0.0218	0.0226	0.0233
42.0	0.0201	0.0208	0.0215	0.0223
43.0	0.0192	0.0199	0.0205	0.0212
44.0	0.0183	0.0189	0.0196	0.0203
45.0	0.0174	0.0181	0.0187	0.0194
46.0	0.0166	0.0172	0.0179	0.0185
47.0	0.0159	0.0165	0.0171	0.0177
48.0	0.0151	0.0157	0.0163	0.0169
49.0	0.0145	0.0150	0.0156	0.0162
50.0	0.0138	0.0144	0.0149	0.0155

Known Addition Method with pH/mV Meter, continued

Table 4 Calculated Q Values (Continued)

ΔE	Slope (mV/decade)			
	57.2	58.2	59.2	60.1
51.0	0.0132	0.0137	0.0143	0.0148
52.0	0.0126	0.0131	0.0136	0.0142
53.0	0.0120	0.0125	0.0131	0.0136
54.0	0.0115	0.0120	0.0125	0.0130
55.0	0.0110	0.0115	0.0120	0.0124
56.0	0.0105	0.0110	0.0115	0.0119
57.0	0.0101	0.0105	0.0110	0.0114
58.0	0.0096	0.0101	0.0105	0.0109
59.0	0.0092	0.0096	0.0101	0.0105
60.0	0.0088	0.0092	0.0096	0.0101

Determining original sample fluoride concentration

$$C_{\text{sam}} = Q \times C_{\text{std}}$$

Where:

C_{std} = standard concentration

C_{sam} = sample concentration

Q = reading from the known addition table

The table of Q values is calculated for a 10% volume change for electrodes with slope in the -57.2 to -60.1 mV range.

Calculations if values are not listed in *Table 4*:

The equation for calculating Q for slopes and volume changes not listed in *Table 4* is:

$$Q = \frac{p}{(1 + p) \times (10^{\Delta E/s} - 1)}$$

Where:

Q = reading from the known addition table

s = slope of the electrode

p = volume of standard ÷ volume of sample

$\Delta E = E_2 - E_1$

Known Addition Method with pH/mV Meter, continued

REQUIRED REAGENTS

Description	Quantity Required		
	Per Test	Unit	Cat. No.
Fluoride ISA Solution	varies	3.78 L ..	28290-17
Fluoride Standard Solutions (choose appropriate standard):			
0.2-mg/L	varies	500 mL	405-02
0.5-mg/L	varies	500 mL	405-05
0.8-mg/L	varies	500 mL	405-08
1.00-mg/L	varies	500 mL	291-49
1.2-mg/L	varies	500 mL	405-12
1.5-mg/L	varies	500 mL	405-15
2.00-mg/L	varies	500 mL	405-20
10.0-mg/L	varies	500 mL	359-49
19.0-mg/L	varies	500 mL	21262-49
100-mg/L	varies	500 mL	232-49
Water, deionized	varies	4 L	272-56

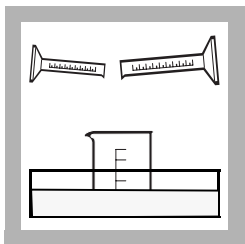
REQUIRED APPARATUS

Beaker, 50-mL, polypropylene.....	1	each	1080-41
Bottle, wash, 500-mL.....	1	each	620-11
sens <i>ion</i> TM 1 Portable pH/mV Meter ..	1	each ...	51700-10
OR			
sens <i>ion</i> TM 3 Laboratory pH/mV Meter1.....	each ...	51750-10	
Stir Bar, 7/8 X 3/16 in. (22.2 x 4.8 cm)1	each ...	45315-00	
Water, deionized.....	varies	4 L	272-56
Select one based on available voltage:			
Stirrer, electromagnetic,			
115 VAC, with stand and stir bar... 1	each ...	45300-01	
Stirrer, electromagnetic,			
230 VAC, with stand and stir bar .. 1	each ..	45300-02	

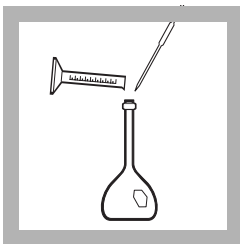
Fluoride in Alkaline Solutions

In basic solutions with a low fluoride content (less than 10^{-4} M at pH 9.5 or above), the electrode responds to hydroxide and fluoride ions. The potential reading caused by the concentration of both F^- and OH^- ions is lower than it would be if only fluoride was present.

This interference is eliminated by adjusting the pH to 5–6 with 4 M buffered potassium acetate. This also raises the total ionic strength of the standards and samples to the same value. Add 9 parts of buffer to 1 part of sample or standard, then determine the fluoride concentration.

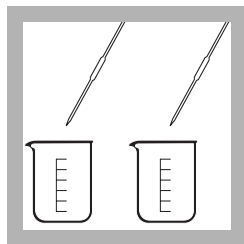


1. Prepare a 4 M buffered potassium acetate solution by diluting 2 parts of 6 M acetic acid with one part of deionized water in a 25 °C water bath. Slowly add 12 N KOH solution to the acetic acid, stirring constantly, until the pH is 5.



2. Prepare a background solution containing all the sample matrix components except fluoride. Use this solution to prepare the standards.

Note: If a standard prepared with background solution gives the same reading (after potassium acetate dilution) as standard prepared with pure potassium acetate, it is not necessary to prepare a background solution.

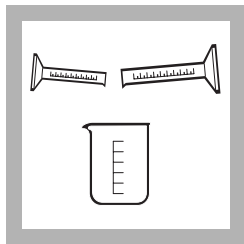


3. For calibration, prepare fluoride standards by adding fluoride to the background solution.

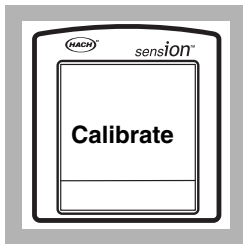
Note: Prepare fresh standards every two weeks if standards are less than 10 mg/L F^- .

Note: If using a direct reading fluoride meter, use two standards. If using a pH/mV meter, use three standards.

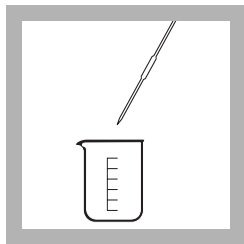
Fluoride in Alkaline Solutions, continued



4. Dilute each standard 10:1 with the buffered potassium acetate solution (9 parts potassium acetate to 1 part standard).

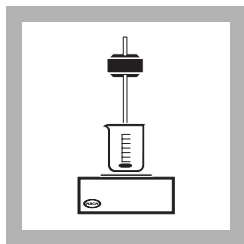


5. Calibrate the electrode following the instructions starting on page 15 (steps 1–17).

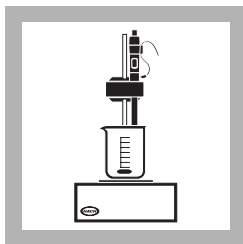


6. Measure the sample into 50-mL beakers. Dilute each unknown 10:1 with buffered potassium acetate before measurement

Note: For example, measure 3 mL of sample and dilute it with 27 mL of buffered potassium acetate.



7. Place a stir bar in the beaker and set the beaker on a magnetic stirrer. Stir at a moderate speed.



8. Rinse the electrode with deionized water and blot dry. Place the electrode into the sample. When the reading is stable, record the value.

Fluoride in Alkaline Solutions, continued

REQUIRED REAGENTS

Description	Quantity Required			Cat. No.
	Per Test	Unit		
Fluoride Standard Solutions:				
1.00-mg/L	varies ...	500 mL.....	291-49	
2.00-mg/L	varies ...	500 mL.....	405-20	
10.0-mg/L.....	varies ...	500 mL.....	359-49	
Potassium Hydroxide, 12 N.....	varies ...	500 mL.....	230-49H	
Water, deionized	varies	4 L.....	272-56	

REQUIRED APPARATUS

Beaker, 50-mL, polypropylene.....	3	each.....	1080-41
Bottle, wash, 500-mL.....	1	each.....	620-11
Cylinder, graduated, 25-mL, poly	3	each.....	1081-40
Platinum Series Fluoride Combination Electrode,			
BNC	1	each... 51928-00	
sens <i>ion</i> TM 2 Portable pH/ISE Meter	1	each... 51725-00	
OR			
sens <i>ion</i> TM 4 Laboratory pH/ISE Meter	1	each... 51775-00	
Stir Bar, 7/8 X 3/16 in. (22.2 x 4.8 cm)	1	each... 45315-00	
Select one based on available voltage:			
Stirrer, electromagnetic,			
115 VAC, with stand and stir bar ...	1	each... 45300-01	
Stirrer, electromagnetic,			
230 VAC, with stand and stir bar... 1	1	each... 45300-02	

OPTIONAL APPARATUS

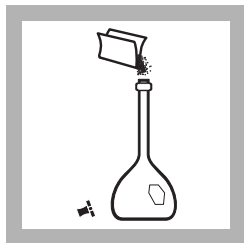
Electrode Washer	each... 27047-00
Pipet, TenSette, 0.1 to 1.0 mL.....	each... 19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg... 21856-96

Titration With Lanthanum Nitrate

Titration is a quantitative analytical technique that measures a species by incremental addition of a reagent (titrant) that reacts with the measured species. Sensing electrodes are useful as endpoint detectors because they are not affected by sample color or turbidity. The fluoride electrode is a sensitive endpoint detector for samples containing fluoride when used with a lanthanum nitrate titrant.

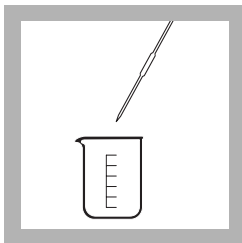
Titration is about 10 times more precise than direct calibration, but takes more time. With careful work, titration accurate to 0.2% of the total fluoride concentration can be performed. The sample should contain at least 10^{-3} M total fluoride for a good endpoint break. This titration gives low results if more than 1% of aluminum, iron, or trivalent chromium is present.

Titration With Lanthanum Nitrate, continued

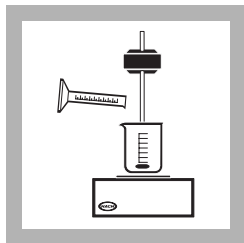


1. Prepare a 0.1 M lanthanum nitrate solution by dissolving 43.3 g of reagent grade lanthanum nitrate hexahydrate [$\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$] in a one-liter volumetric flask containing 700 mL of deionized water. When the solid dissolves, fill to the mark with deionized water.

Note: While the lanthanum nitrate dissolves, create a graph with mL of titrant added on the x-axis and the mV potential on the y-axis.

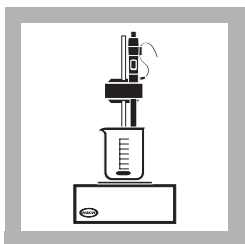


2. To standardize the lanthanum nitrate, titrate against a 0.1 M Fluoride Standard. With a Class A pipet, add exactly 25 mL of fluoride standard to a 250-mL plastic beaker.



3. Add about 50 ml of deionized water to the beaker. Add a stir bar and place the beaker on a magnetic stirrer.

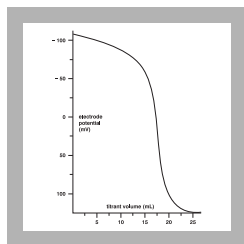
Titration With Lanthanum Nitrate, continued



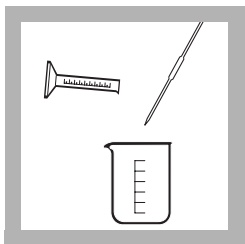
4. Rinse the electrode with deionized water. Place the electrode in the beaker. Stir at a moderately fast rate.



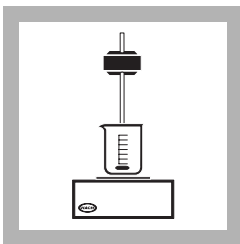
5. Set the meter in mV mode. Use a 10-mL buret to add small increments of lanthanum fluoride.



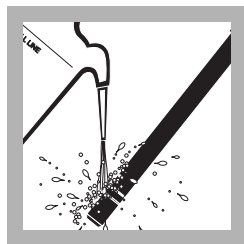
6. Plot the electrode potential against the mL of lanthanum nitrate added. The endpoint is the point of greatest slope. Record the endpoint (V_{t0}).



7. Pipet exactly 25 mL of sample into a 250-mL beaker. Add about 50 mL of deionized water.

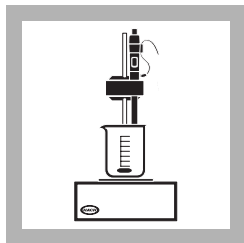


8. Add a stir bar to the beaker and place the beaker on a magnetic stirrer. Stir at a moderately fast rate.

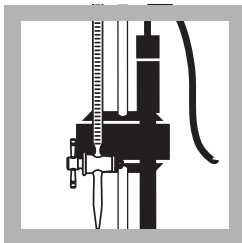


9. Rinse the electrode with deionized water and blot dry.

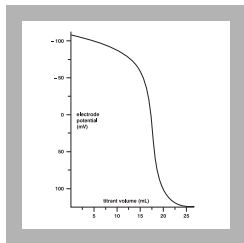
Titration With Lanthanum Nitrate, continued



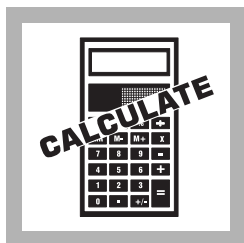
10. Place the electrode in the beaker.



11. Use a 10-mL buret to add small increments of lanthanum fluoride.



12. Plot the electrode potential against the mL of lanthanum nitrate added. The endpoint is the point of greatest slope. Record the endpoint (V_{tX}).



13. Calculate the sample fluoride concentration using the following formula.

Calculating Sample Fluoride Concentration

$$C_{sX} = \left[\frac{V_{tX} \times V_{f0}}{V_{t0} \times V_{fX}} \right] \times C_{s0}$$

Where:

C_{sX} = sample concentration

C_{s0} = fluoride standard concentration (0.1 M)

V_{tX} = volume of titrant added to unknown sample at the endpoint

V_{t0} = volume of titrant added in standardization at the endpoint

V_{fX} = volume of sample used in the titration (25 mL)

V_{f0} = volume of standard used in standardization (25 mL)

Titration With Lanthanum Nitrate, continued

REQUIRED REAGENTS

Description	Quantity Required		
	Per Test	Unit	Cat. No.
Lanthanum Nitrate, reagent grade	43.3 g.....	*	
Water, deionized	varies	4 L.....	272-56

REQUIRED APPARATUS

Beaker, 250-mL, polypropylene.....	3	each.....	1080-46
Bottle, wash, 500-mL.....	1	each.....	620-11
Buret, Class A, 10-mL, Teflon [®] stopcock.....	1	each... 26365-38	
Platinum Series Fluoride Combination Electrode, BNC	1	each... 51928-00	
Pipet, volumetric, Class A, 25.0-mL .2	each... 14515-40		
sens ⁱ on™ 2 Portable pH/ISE Meter....	1	each... 51725-00	
OR sens ⁱ on™ 4 Laboratory pH/ISE Meter	1	each... 51775-00	
Stir Bar, 7/8 X 3/16 in. (22.2 x 4.8 cm)	1	each... 45315-00	
Select one based on available voltage:			
Stirrer, electromagnetic, 115 VAC, with stand and stir bar ...	1	each... 45300-01	
Stirrer, electromagnetic, 230 VAC, with stand and stir bar... 1	each... 45300-02		

OPTIONAL REAGENTS

Fluoride Standard Solutions:

1.00-mg/L	varies ... 500 mL.....	291-49
2.00-mg/L	varies ... 500 mL.....	405-20
10.0-mg/L.....	varies ... 500 mL.....	359-49

OPTIONAL APPARATUS

Electrode Washer	each... 27047-00	
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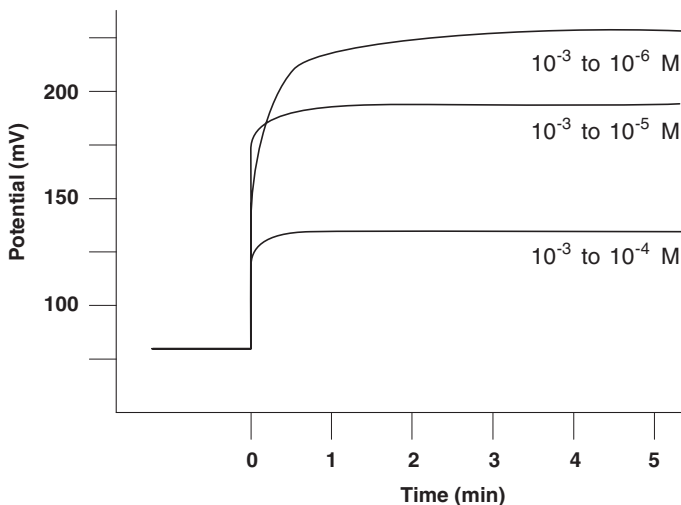
* Not sold by Hach

Section 4 Electrode Characteristics

4.1 Electrode Response

The electrode potential (mV) plotted against concentration on semilogarithmic graph paper results in a straight line with a slope of -54 to -60 mV per decade.

Figure 5 Response Time vs. F^- Level



The time required to reach 99% of the stable potential reading varies from several seconds in concentrated solutions to several minutes near the limit of detection. See *Figure 5*.

4.2 Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the electrodes operating range, reproducibility is independent of concentration. Direct electrode measurements reproducible to $\pm 1\%$ can be obtained with calibration every hour.

4.3 Limits of Detection

In neutral solutions, fluoride concentration can be measured down to 5×10^{-7} M (0.01 ppm fluoride). However, care must be taken to avoid sample contamination when measuring concentrations below 10^{-5} M.

The upper limit of detection is a saturated fluoride solution.

4.4 Temperature Effects

Since electrode performance is affected by changes in temperature, samples and standards should be within 1 °C (2 °F) of each other. At 10^{-3} M, a 1 °C temperature difference results in a 2% error.

The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope also varies with temperature, as indicated by the factor “S” in the Nernst equation. Values of the Nernst factor for the fluoride ion are listed in *Table 5*.

If temperature changes occur, recalibrate the meter/electrode.

The electrode can be used at temperatures from 0 to 100 °C; providing temperature equilibrium has occurred. For temperatures that are significantly different than room temperature, wait one hour for equilibrium to occur. In solutions above 80 °C, only use the electrode intermittently.

Table 5 Theoretical Slope vs. Temperature

Temperature °C	Slope (mV/decade)
0	-54.2
10	-56.2
20	-58.2
25	-59.2
30	-60.1
40	-62.1
50	-64.1

4.5 Interferences

Cations and most anions do not interfere with the electrode response to fluoride ions. Anions commonly associated with fluoride (Cl^- , Br^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} , acetate) do not interfere with electrode operation.

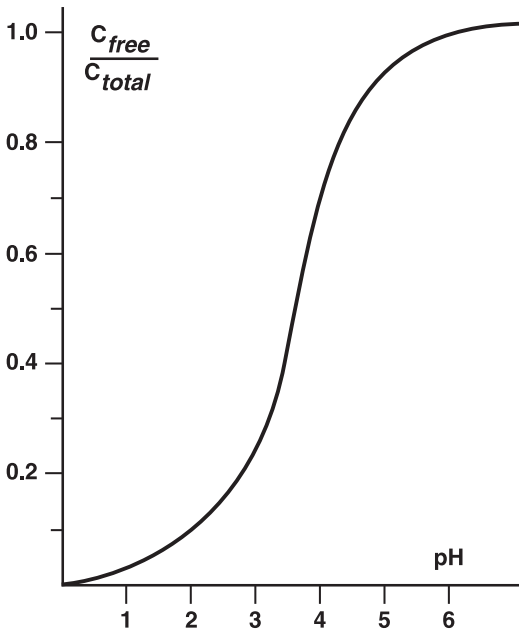
Hydroxyl ions (OH^-) interfere; see *Section 4.6*.

Some ions, such as CO_3^{2-} or PO_4^{3-} , make the sample more basic, which increases OH^- interference, but do not directly interfere with the electrode operation.

4.6 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 6* shows the proportion of free fluoride ion in acid solutions.

Figure 6 **Ratio of Free F^- in Acid Solutions**



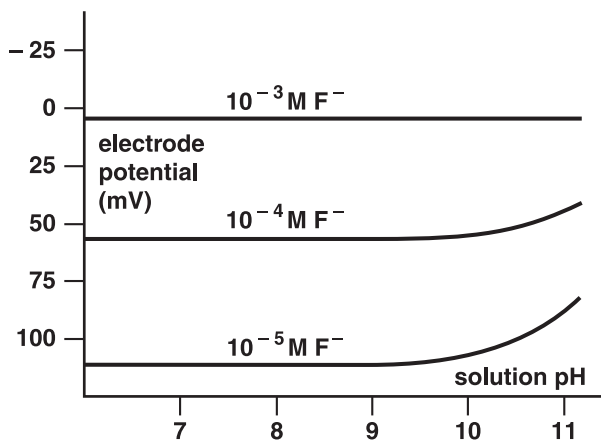
Electrode Characteristics, continued

Hydroxide (OH^-) ion interferes with the electrode response to fluoride when the level of hydroxide is greater than 10% of the level of fluoride present. At pH 7 or less there is no hydroxide ion to interfere. The error increases with increasing pH and decreasing fluoride levels; see *Table 6* and *Figure 7*.

Table 6 Hydroxide Error

F ⁻ Concentration	Percent Error at pH 10
10^{-2} M	0
10^{-4} M	10%
10^{-5} M	20%

Figure 7 Electrode Response in Alkaline Solutions



Adding Fluoride Ionic Strength Adjustor to fluoride standards and samples buffers the pH between 5.0–5.5 and prevents hydroxyl ion interference and the formation of hydrogen complexes of fluoride.

4.7 Complexation

Fluoride complexes with aluminum, silicon, iron (+3), and other polyvalent cations as well as hydrogen. The extent of complexation depends on the concentration of the complexing species, the total fluoride concentration, the pH of the solution, and the total ionic strength of the solution. The Fluoride ISA

solutions contain CDTA, which preferentially complexes aluminum or iron in the sample.

4.8 Theory of Operation

The fluoride electrode consists of a sensing LaF 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. The measured potential corresponding to the level of fluoride ion in solution is described by the Nernst equation:

$$E = E_o - S \log (A)$$

Where:

E = measured cell potential in millivolts

E_o = reference cell potential

A = activity of fluoride ions

S = electrode slope (-57 ± 3 mV/decade)

The level of fluoride ion, A , is the activity or “effective concentration” of free fluoride ion in solution. The fluoride ion activity is related to free fluoride ion concentration, C_f , by the activity coefficient (γ_y).

$$A = \gamma_y C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ionic strength is defined as:

$$\text{Ionic strength} = \frac{1}{2} \sum C_i Z_i^2$$

Where:

C_i = concentration of ion i

Z_i = charge of ion i

Σ = the sum of all the types of ions in 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.

4.9 Electrode Life

With proper care, the combination fluoride electrode should last about six months. In time, the electrode slope will decrease and reading will start to drift, indicating the electrode should be replaced. Before replacement, refer to *Table 7* on page 83 to verify the symptoms are caused by the electrode and cannot be fixed.

Section 5 Electrode Maintenance

5.1 Storing the Electrode

Proper electrode storage requires different approaches based on how long the electrode will be stored, how quickly the electrode needs to be used, and the type of sample being measured. Storage affects the reference electrolyte gel, the Ag/AgCl reference element, and the fluoride sensing crystal.

Intermittent storage: Between uses, store the electrode in solutions of similar ionic strength and pH to the samples of interest. Before measuring a new sample, refresh the reference electrolyte gel by clicking the dispenser until fresh gel emerges. Carefully rinse the electrode to prevent sample contamination.

Overnight storage: Fill the electrode tip protector with a few milliliters of a prepared fluoride standard. Place this cap snugly over the electrode tip. The KCl will not leach excessively from the electrolyte gel overnight. Prior to use, click the electrolyte gel dispenser. A dilute gel/storage solution will initially be ejected from the reference junction tube. The reference gel of thicker viscosity will follow. Eliminating the dilute gel/storage solution will guarantee continuity of the reference junction with the sample. Blot the reference junction with a tissue to clearly see that the electrolyte gel, not gel diluted with storage solution, is emerging.

Longer-term storage: To store electrodes for longer periods, follow the *Overnight Storage* procedure (above) and re-establish gel at the reference junction on a daily basis to keep the electrode ready for use. If the electrode soaks for longer periods without purging the diluted electrolyte, the entire reference electrolyte gel cartridge can become diluted through diffusion. Typically this will not harm the Ag/AgCl reference element, but the electrolyte cartridge itself will be ruined. This storage method keeps the electrode ready to use, but requires purging the gel every day.

Shelf storage: For very long-term storage, store the electrode dry. To empty the reference half-cell of electrolyte gel, remove

and discard the electrolyte cartridge. Use a syringe with a male Luer fitting and no needle to inject deionized water through the reference cell to flush out the reference electrolyte gel. Expel the water injected into the reference cell with an air-filled syringe. Place the storage cap over the electrode. This procedure allows for the longest term storage, but takes more time to store and set up.

5.2 Cleaning 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. 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. Reassemble the electrode according to *Section Section 1.3.1*.

Section 6 Troubleshooting

6.1 General Troubleshooting

The most important principle in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are meter, electrodes, standards, samples, and technique.

6.1.1 Meter

The meter is the easiest component to eliminate as a possible cause of error. Each meter has an instrument checkout procedure in the instruction manual and a shorting strap for convenience in troubleshooting. Consult the manual for complete instructions and verify the instrument operates as indicated and is stable in all steps.

6.1.2 Electrodes

1. Rinse the electrodes thoroughly with deionized water.
2. Check electrode operation (slope); see *step 1* through *step 18*, beginning on page *15*.
3. Clean the reference electrode as described in *Section 5.2* on page *80*.
4. Repeat *step 2*.
5. If the stability and slope check out properly, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error. See the *Standards*, *Sample* and *Technique* sections.
6. Before replacing a “faulty” electrode, or if another electrode is not available for test purposes, review the instruction manual and be sure to:
 - Clean the electrode thoroughly
 - Prepare the electrode properly
 - Use proper reference electrolyte gel cartridge, ISA, and standards
 - Measure correctly
 - Review *Table 7* on page *83*.

6.1.3 Standards

The quality of the results depends greatly upon the quality of the standards. *ALWAYS* prepare fresh standards when problems arise— it could save hours of frustrating troubleshooting! Error may result from contamination of prepared standards, quality of dilution, deionized water, or a numerical error in calculating the concentrations.

The best method for preparation of standards is serial dilution. An initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared. An alternative to dilution is to use the variety of fluoride standards that Hach has available.

If using Fluoride standards containing ISA, do not add powdered ISA.

6.1.4 Sample

If the electrodes work properly in standards but not in the sample, look for possible interferences, complexing agents, or substances which could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See *Section 4.5* on page 75, and *Section 4.6* on page 75.

6.1.5 Technique

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If a large amount of complexing agents are present, known addition may be best. If the sample is viscous, analyte addition may solve the problem. If working at low levels, follow the low level measurement technique.

Be sure that the expected fluoride concentration is within the electrode's limits of detection.

If problems persist, review operational procedures and instruction manuals to be sure that proper technique has been followed. Review *Section 1.4* on page 10.

Table 7 Troubleshooting Checklist

Symptom	Possible Cause	Remedy
Overrange Reading	Defective meter	Perform meter check out procedure (see meter manual).
	Electrode not properly connected	Disconnect electrodes and reconnect.
	Dry reference junction	Click button to dispense fresh gel. Rinse. Replace cartridge if necessary.
	Air bubble on sensing element	Remove bubble by redipping electrode in solution.
	Electrode not in solution	Ensure electrode is immersed in the solution.
	Static electricity	Wipe the plastic parts of the meter with detergent solution.
Noisy or unstable readings	Defective meter	Perform meter check out procedure (see meter manual).
	Meter or stirrer is improperly grounded	Check meter and stirrer for grounding.
	Air bubble on sensing element	Remove bubble by redipping electrode in solution.
	Fluoride ISA not used	Use recommended ISA.
	pH electrode connected to 5-pin connector	Disconnect pH electrode.

Troubleshooting, continued

Table 7 Troubleshooting Checklist (Continued)

Symptom	Possible Cause	Remedy
Drift (readings change slowly in one direction)	Samples and standards are at different temperatures	Allow solutions to come to equal temperature before measuring.
	Dirty sensing element	Remove organic deposits.
	Incorrect reference electrolyte gel cartridge	Use Cat. No. 25469-02.
Low slope or no slope	Standards are contaminated or incorrectly made	Prepare fresh standards.
	Fluoride ISA not used	Use recommended Fluoride ISA.
	Standard used as fluoride ISA	Be sure to use Fluoride ISA.
	Defective meter	Refer to <i>Section 6.1.1</i> on page 81.
	Glass labware used	Use plastic labware.
	pH electrode connected to 5-pin connector	Disconnect pH electrode.

Table 7 Troubleshooting Checklist (Continued)

Symptom	Possible Cause	Remedy
Incorrect answer, but calibration is OK	Incorrect scaling of semilogarithmic paper	Plot mV on the linear (horizontal) axis. On the log axis, be sure the numbers within each decade are increasing with increasing concentration.
	Incorrect sign (+ or -)	Note sign of millivolt value correctly.
	Incorrect standards	Prepare fresh standards.
	Wrong units used	Apply correct conversion factor: $10^{-3} = 19 \text{ ppm F}^{-}$
	Complexing agents in sample	Use known addition method, titration or decomplex the compounds in the sample.
	pH electrode connected to 5-pin connector	Disconnect pH electrode.



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International Customers

Hach maintains a worldwide network of dealers and distributors. To locate the representative nearest you, send E-mail to intl@hach.com or contact:

In Canada, Latin America, Africa, Asia, Pacific Rim:

Telephone: (970) 669-3050; FAX: (970) 669-2932

In Europe, the Middle East, or Mediterranean Africa:

HACH Company, c/o Dr. Bruno Lange GmbH

Willstätterstr. 11

D-40549 Düsseldorf, Germany

Telephone: +49/[0]211.52.88.0

Fax: +49/[0]211.52.88.231

Repair Service

Authorization must be obtained from Hach Company before sending any items for repair. Please contact the HACH Service Center serving your location.

In the United States:

Hach Company
100 Dayton Avenue
Ames, Iowa 50010
(800) 227-4224 (U.S.A. only)
Telephone: (515) 232-2533
FAX: (515) 232-1276

In Canada:

Hach Sales & Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba
R3H 0X4
(800) 665-7635 (Canada only)
Telephone: (204) 632-5598
FAX: (204) 694-5134
E-mail: canada@hach.com

In Latin America, the Caribbean, the Far East, the Indian Subcontinent, Africa, Europe, or the Middle East:

Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado, 80539-0389
U.S.A.
Telephone: (970) 669-3050
FAX: (970) 669-2932
E-mail: intl@hach.com

Warranty

Hach warrants most products against defective materials or workmanship for at least one year from the date of shipment; longer warranties may apply to some items.

HACH WARRANTS TO THE ORIGINAL BUYER THAT HACH PRODUCTS WILL CONFORM TO ANY EXPRESS WRITTEN WARRANTY GIVEN BY HACH TO THE BUYER. EXCEPT AS EXPRESSLY SET FORTH IN THE PRECEDING SENTENCE, HACH MAKES NO WARRANTY OF ANY KIND WHATSOEVER WITH RESPECT TO ANY PRODUCTS. HACH EXPRESSLY DISCLAIMS ANY WARRANTIES IMPLIED BY LAW, INCLUDING BUT NOT BINDING TO ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

LIMITATION OF REMEDIES: Hach shall, at its option, replace or repair nonconforming products or refund all amounts paid by the buyer. **THIS IS THE EXCLUSIVE REMEDY FOR ANY BREACH OF WARRANTY.**

LIMITATION OF DAMAGES: IN NO EVENT SHALL HACH BE LIABLE FOR ANY INCIDENTAL OR CONSEQUENTIAL DAMAGES OF ANY KIND FOR BREACH OF ANY WARRANTY, NEGLIGENCE, ON THE BASIS OF STRICT LIABILITY, OR OTHERWISE.

This warranty applies only to Hach products purchased and delivered in the United States.

Catalog descriptions, pictures and specification, although accurate to the best of our knowledge, are not a guarantee or warranty.

For a complete description of Hach Company's warranty policy, request a copy of our Terms and Conditions of Sale for U.S. Sales from our Customer Service Department.



HACH COMPANY
WORLD HEADQUARTERS
P.O. Box 389
Loveland, Colorado 80539-0389
Telephone: (970) 669-3050
FAX: (970) 669-2932

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:

In the U.S.A. - **Call toll-free 800-227-4224**

Outside the U.S.A. - **Contact the HACH office or distributor serving you.**

On the Worldwide Web - **www.hach.com; E-mail - techhelp@hach.com**
