

Thermo Scientific Orion
Fluoride Ion Selective
Electrode

254792-001 • Revision B • September 2016

Table of Contents

Introduction	1
Required Equipment	3
Electrode Setup	5
Electrode Preparation	5
Checking Electrode Operation (Slope)	5
Sample Requirements	7
Electrode Storage	8
Analytical Techniques	11
Direct Calibration	13
Low-Level Measurements	17
Single Known Addition	19
Titrations	24
Fluoride in Alkaline Solutions	27
Electrode Characteristics	29
Electrode Response	29
Reproducibility	29
Limits of Detection	29
Temperature Effects	30
Complexation	31
Theory of Operation	32
Troubleshooting	34
Assistance	35
Warranty	35
Ordering Information	37
Specifications	38

Introduction

This user guide contains information on the preparation, operation and maintenance for the fluoride ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Fluoride electrodes measure free fluoride ions in aqueous solutions quickly, simply, accurately and economically.

The measurement of fluoride in drinking water and wastewater using an ion selective electrode is an EPA approved test procedure. EPA-approved ISE test procedures for fluoride in drinking water and waste water are ASTM D1179(B) and Standard Methods 4500-F⁻C. EPA-approved ISE test procedures for fluoride in wastewater are ASTM D1179-93, 99 (B) and Standard Methods 4500-F- C-97 (online) or 4500-F- B (18, 19, 20th editions). Approved test method lists are updated periodically. Check with your regulatory agency for latest approve method revisions.

Technical Support Chemists can be consulted for assistance and troubleshooting advice. Within the United States and Canada, call 1.800.225.1480 or 978.232.6000 or email wai.techservbev@thermofisher.com. For countries outside of North America, contact your local authorized dealer. For the most current contact information, visit www.thermofisher.com/water.

Fluoride ionplus® Sure-Flow® Combination ISE

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The Sure-Flow reference junction prevents electrode clogging and provides fast and stable readings. The fluoride ionplus combination ISE is available with a waterproof BNC connector, Cat. No. 9609BNWP. Electrodes with a waterproof BNC connector can be used on any ISE meter with a BNC connection.

Fluoride Half-Cell ISE

The fluoride half-cell electrode must be used with the single junction reference electrode, Cat. No. 900100. The fluoride half-cell is available with a BNC connector, Cat. No. 9409BN; and a screw cap connector, Cat. No. 9409SC. Electrodes with a screw cap connector require a separate cable.

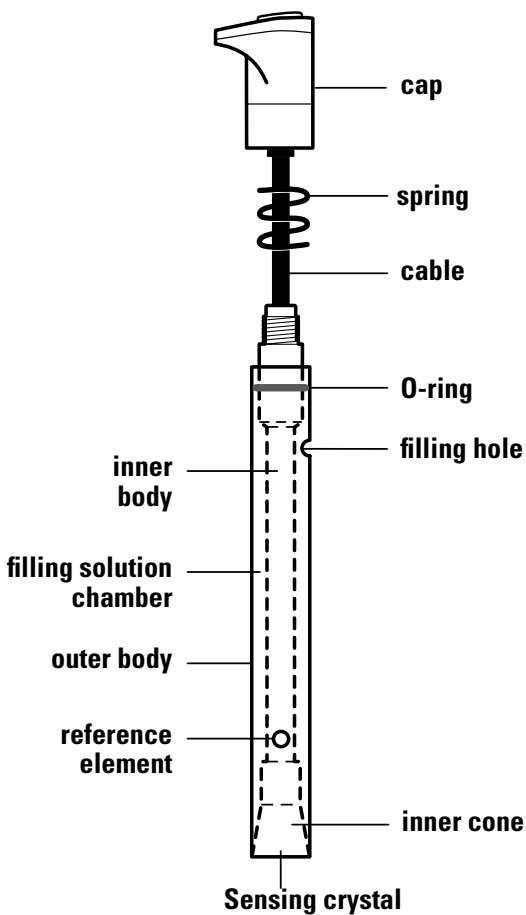


Figure 1 9609BNWP Fluoride Combination Electrode

Required Equipment

1. Thermo Scientific Orion ISE meter, such as the Orion Star A214 pH/ISE meter, Orion Dual Star two channel pH/ISE meter or Orion Versa Star Pro pH/ISE meter. The fluoride electrode can also be used on a variety of ISE meters with a BNC connection, please reference the meter manual for additional information.
2. Thermo Scientific Orion fluoride ion selective electrode. The 9609BNWP fluoride electrode is a combination electrode. The 9409BN and 9409SC fluoride half-cell electrodes require a separate reference electrode, Cat. No. 900100.
3. Magnetic stirrer or Orion stirrer probe, Cat. No. 096019. The Orion stirrer probe can be used with Orion Star A214 pH/ISE meter, Orion Dual Star two channel pH/ISE meter or Orion Versa Star Pro pH/ISE meter.
4. Volumetric flasks, graduated cylinders and beakers. **Plastic labware is highly recommended for fluoride analysis.**
5. Distilled or deionized water.
6. Fluoride electrode filling solution.

Use Optimum Results A filling solution, Cat. No. 900061, for the 9609BNWP fluoride electrodes.

Use single junction reference electrode filling solution, Cat. No. 900001, for the reference electrode used with the 9409BN and 9409SC fluoride electrodes.

7. Fluoride calibration standards.

Cat. No.	Description
940906	0.1 M NaF, 475 mL bottle
940907	100 ppm F ⁻ , 475 mL bottle
040908	10 ppm F ⁻ with TISAB II, 475 mL bottle
F40905	5 ppm F ⁻ with TISAB II, 475 mL bottle
040907	2 ppm F ⁻ with TISAB II, 475 mL bottle
040903	1 ppm F ⁻ with TISAB II, 475 mL bottle
F40904	0.5 ppm F ⁻ with TISAB II, 475 mL bottle

8. Total Ionic Strength Adjustment Buffer (TISAB), which provides a constant background ionic strength, decomplexes fluoride ions and adjusts the solution pH.

Cat. No.	Description
940909	TISAB II, 3.8 L bottle
940999	TISAB II, 4 x 3.8 L bottle
940911	TISAB III concentrate, 475 mL bottle

9. User-Prepared TISAB for special applications.

Low-Level TISAB

For use when measuring in samples containing less than 0.4 ppm (2×10^{-5} M) fluoride and no fluoride complexing agents such as iron or aluminum are present.

To prepare low level TISAB: Place 500 mL of distilled water in a 1 liter beaker. Add 57 mL of glacial acetic acid and 58 g of reagent grade sodium chloride to the beaker. Place the beaker in a water bath for cooling. Immerse a calibrated pH electrode into the solution and slowly add 5 M NaOH until the pH is between 5.0 and 5.5. Cool the solution to room temperature. Pour the solution into a 1 liter volumetric flask and dilute to the flask mark with distilled water. All reagents must be as pure as possible to keep the fluoride level low in the buffer.

Use as directed for TISAB II; combine equal volumes of low level TISAB and sample or standard before taking any measurements.

TISAB IV

TISAB IV will complex more than 100 ppm of iron or aluminum in the presence of 1 ppm fluoride. A measurement of 1 ppm fluoride will be in error by 5% in the presence of 200 ppm iron or aluminum. TISAB IV adjusts the pH to about 8.5, and should only be used for fluoride levels above 1 mg/L.

To prepare TISAB IV: Place 500 mL of distilled water in a 1 liter volumetric flask. Add 84 mL of concentrated HCl (36 to 38 %), 242 g TRIS (hydroxymethyl) aminomethane and 230 g sodium tartrate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$) to the flask. Stir to dissolve the solids and cool the solution to room temperature. Dilute to the flask mark with distilled water.

Use as directed for TISAB II; combine equal volumes of TISAB IV and sample or standard before measurements.

Electrode Setup

Electrode Preparation

9409BN and 9409SC Fluoride Half-Cell Electrode– Remove the protective shipping cap from the sensing element and save the cap for storage.

900100 Single Junction Reference Electrode– Prepare the reference electrode according to the reference electrode user guide. Fill the reference electrode with single junction reference filling solution, Cat. No. 900001.

9609BNWP Fluoride Combination Electrode– Remove the protective shipping cap from the sensing element and save the cap for storage. Fill the electrode with Optimum Results A filling solution, Cat. No. 900061.

Note: *Optimum Results A filling solution minimizes junction potential issues and fluoride contamination in the sample. The use of any other filling solution will void the electrode warranty.*

Electrode Filling Instructions

1. Lift the flip spout on the filling solution bottle to a vertical position.
2. Insert the spout into the filling hole on the outer body of the electrode and add a small amount of filling solution to the reference chamber. Invert the electrode to moisten the top O-ring and then return the electrode to the upright position.
3. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
4. Release the electrode cap. If the sleeve does not return to its original position, check if the O-ring is moist and repeat steps 2-4 until the sleeve returns to the original position.
5. Add filling solution to the electrode up to the filling hole.

Note: *Add filling solution each day before using the electrode. The filling solution level should be at least one inch above the level of sample in the beaker to ensure a proper flow rate. The fill hole should always be open when taking measurements.*

Checking Electrode Operation (Slope)

These are general instructions that can be used with most meters to check the electrode operation. Refer to the meter user guide for more specific information.

This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every tenfold change in concentration. Obtaining the slope value provides the best means for checking electrode operation.

1. If the electrode has been stored dry, prepare the electrode as described in the **“Electrode Preparation”** section.
2. Connect the electrode to the meter. Set the meter to the mV mode.
3. Place 50 mL of distilled water and 50 mL of TISAB II (Low-level TISAB or TISAB IV) into a 150 mL beaker. Stir the solution thoroughly.

If using TISAB III, place 90 mL of distilled water and 10 mL of TISAB III into a 150 mL beaker. Stir the solution thoroughly.

4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.
5. Select either a 0.1 M sodium fluoride or 100 ppm fluoride standard. Pipette 1 mL of the standard into the beaker and stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
6. Pipette 10 mL of the same standard into the same beaker and stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. There should be a 54 to 60 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C. If the millivolt potential is not within this range, refer to the **“Troubleshooting”** section.

Measurement Units

Fluoride concentration can be measured in moles per liter (M), parts per million (ppm) or any convenient concentration unit.

Table 1 Concentration Unit Conversion Factors

Moles/Liter (M)	ppm
1.0	19000
10^{-1}	1900
10^{-2}	190
10^{-3}	19
10^{-4}	1.9

Sample Requirements

The epoxy body of the fluoride electrode is resistant to damage by inorganic solutions. The electrode may be used intermittently in solutions that contain methanol or acetone. Contact Technical Support for information on using the electrode for specific applications.

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

In all analytical procedures, TISAB must be added to all samples and standards before measurements are taken.

Measuring Hints

- Add 50 mL of TISAB II (Low-level TISAB or TISAB IV) to every 50 mL of standard or sample. Add 10 mL of TISAB III to every 90 mL standard or sample. Once TISAB II (Low-level TISAB or TISAB IV) or TISAB III is selected, it should be added to all samples and standards so the dilution ratio of TISAB to solution remains the same.
- Stir all standards and samples at a uniform rate.
- Always use fresh standards for calibration.
- Always rinse the electrode with deionized water between measurements and shake the electrode to remove the water and prevent sample carryover. Do not wipe or rub the electrode sensing element.
- Allow all standards and samples to come to the same temperature for precise measurements.
- Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stirrer and beaker to prevent measurement errors from the transfer of heat to the sample.
- Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. If using more than 2 standards, use a mid-level standard. If the value has changed by more than 2%, recalibrate the electrode.
- After immersing the electrode in a solution, check the electrode sensing surface for air bubbles and remove air bubbles by reimmersing the electrode in the solution.
- For high ionic strength samples (e.g., more concentrated than 0.1 M), prepare standards with a background composition similar to the sample or use manual known addition procedure or a Dual Star meter.

- For acidic samples (pH < 5) or alkaline samples (pH >9.5), use the Fluoride in Acid Solutions or Fluoride in Alkaline Solutions Procedures found in this User Guide.
- Remove the filling hole cover during measurements to ensure a uniform flow of filling solution.
- If the electrode is used in dirty or viscous samples or the electrode response becomes sluggish, empty the electrode completely, hold the junction open and flush the junction with deionized water. Empty any water from the electrode and refill it with fresh filling solution. Press down on the electrode cap to let a few drops of the filling solution flow out of the electrode and then replenish any lost solution. If this procedure does not resolve the issue, refer to the “Electrode Maintenance” section for further cleaning.

Electrode Storage

9409BN and 9409SC Fluoride Half-Cell Electrode

The fluoride half-cell electrodes should be rinsed thoroughly with distilled water and stored dry in the air at all times. When storing the electrode for long periods of time, cover the sensing element with the protective shipping cap.

900100 Single Junction Reference Electrode

The single junction reference electrode may be stored in the single junction electrode filling solution, Cat. No. 900001, between sample measurements and up to one week. The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result. For storage longer than one week, drain the reference electrode, flush the inside with distilled water and store the electrode dry.

9609BNWP Fluoride Combination Electrode

For storage between measurements and up to one week, store the electrode in electrode filling solution, Cat. No. 900061, with fluoride added to 1 – 10 ppm level. The fluoride concentration of the storage solution should be close to least concentrated fluoride calibration standard. Do not add TISAB to the storage solution. The filling solution should not be allowed to evaporate, as crystallization will result. If filling solution is unavailable, store in ~0.7 M potassium chloride with 1 – 10 ppm fluoride added.

For storage longer than one week, drain the electrode. Flush the chamber with distilled water. Disassemble the electrode as described in the electrode maintenance section. Rinse the inner sleeve with distilled water and blot dry with a Kimwipe. Do not touch the reference element other than to blot dry. Let air dry and then reassemble for storage. Use the protective shipping cap to cover the sensing element.

Electrode Maintenance

Polishing the Sensing Surface of the Fluoride Combination Electrodes and Fluoride Half-Cell Electrodes

The sensing surface of the fluoride electrode might need restoration over time as deposits coat the sensing surface. The sensing crystal can be restored using the following procedure. Toothpaste that contains fluoride will be needed for this procedure.

1. Dispense a small amount of toothpaste on a kimwipe. Add a few drops of deionized water. A soft toothbrush can also be used in place of a kimwipe.
2. Rub the toothpaste on the sensing element on the bottom of the electrode in a circular motion for around one minute.
3. Rinse the electrode thoroughly with DI water, flush the electrode fill solution out (if using a combination fluoride electrode) by pressing on the cap of the electrode) then refill with fresh fill solution.
4. Soak the electrode in 100 ppm fluoride standard for 2 hours.

Flushing the 9609BNWP and 900100 Single Junction Reference Electrode

If the area between the electrode sleeve and inner cone becomes clogged with sample or precipitate, flush the area with filling solution or distilled water.

1. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the chamber. Push down on the cap until all the filling solution is drained from the chamber.
2. Fill the electrode with distilled water and then push down on the cap until all the water is drained from the chamber.
3. Fill the electrode with fresh filling solution up to the fill hole. Push down on the cap to allow a few drops of filling solution to drain out of the electrode and then refill any lost filling solution.

Disassembling the Fluoride Combination Electrodes and Single Junction Reference Electrode

Note: *Disassembly is usually not required and should not be done unless a thorough cleaning is required.*

1. Tip the electrode so the filling solution moistens the O-ring on the electrode body. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the chamber.

2. Unscrew the cap counter clock-wise and then slide the cap and the spring up the cable.
3. Hold the outer sleeve with one hand and firmly push down on the threaded portion with the thumb and forefinger to separate the inner body from the sleeve.
4. Grasp the cone with a clean, lint-free tissue and withdraw the body from the sleeve using a gentle twisting motion. Do not touch the reference electrode element (coiled wire in combination electrode, pellet in single junction reference) above the cone, it will damage to the reference element. Rinse the outside of the electrode body and the entire sleeve with distilled water. Blot dry with a Kimwipe and allow to air dry if needed.

Reassembling the Fluoride Combination Electrodes and Single Junction Reference Electrode

1. Moisten the O-ring on the electrode body with a drop of filling solution. Insert the screw-thread end of the electrode body into the tapered, ground end of the sleeve.
2. Push the body into the sleeve using a gentle twisting motion until the bottom surface of the inner cone is flush with the tapered end of the sleeve.
3. Place the spring onto the electrode body and screw on the cap. Refill the electrode with filling solution.

Analytical Techniques

A variety of analytical techniques are available to the analyst. The following is a description of these techniques.

Direct Calibration is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed using a series of standards. The concentration of the samples is determined by comparison to the standards. TISAB is added to all solutions to ensure that samples and standards have similar ionic strength.

Incremental Techniques provide a useful method for measuring samples, since calibration is not required. As in direct calibration, any convenient concentration unit can be used. The different incremental techniques are described below. They can be used to measure the total concentration of a specific ion in the presence of a large (50-100 times) excess of complexing agents.

- **Known Addition** is useful for measuring dilute samples, checking the results of direct calibration (when no complexing agents are present), or measuring the total concentration of an ion in the presence of an excess complexing agent. The electrode is immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample when performing single known addition. From the change in potential before and after the addition, the original sample concentration is determined. Double known addition is recommended for complex sample matrices.
- **Known Subtraction** is useful as a quick version of a titration, or for measuring species for which stable standards do not exist. It is necessary to know the stoichiometric ratio between standard and sample. For known subtraction, an electrode sensing the sample species is used. Stable standards of a species reacting completely with the sample in a reaction of known stoichiometry are necessary.
- **Analate Addition** is often used to measure soluble solid samples, viscous samples, small or very concentrated samples, to diminish the effects of complex sample matrices, or to diminish the effects of varying sample temperatures. This method is not suitable for dilute or low concentration samples. Total concentration is measured even in the presence of complexing agents. The electrode is immersed in a standard solution containing the ion to be measured and an aliquot of the sample is added to the standard. The original sample concentration is determined on the change in potential before and after the addition.
- **Analate Subtraction** is used in the measurement of ions for which no ion-selective electrode exists. The electrode is immersed in a reagent solution that contains a species that the electrode senses, and that reacts with the sample. It is useful when sample size is small, or samples for which a

stable standard is difficult to prepare, and for viscous or very concentrated samples. The method is not suited for very dilute samples. It is also necessary to know the stoichiometric ratio between standard and sample.

- **Titrations** are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used for determination of the titration end point. Ion selective electrodes are useful as end point detectors, because they are unaffected by sample color or turbidity. Titrations are approximately 10 times more precise than direct calibration, but are more time-consuming.

Typical Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or in an electronic spreadsheet and graphing the log of the fluoride concentration against the millivolt value readings. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. These direct calibration procedures are given for concentrations in the region of linear electrode response. Low level measurement procedures are given in the next section for measurements in the non-linear region.

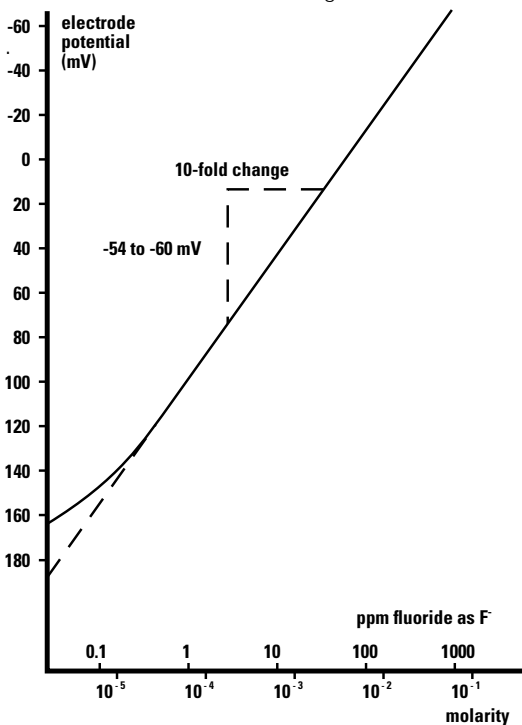


Figure 2 Typical Calibration Curve

Direct Calibration

Setup

1. Prepare the electrode as described in the **“Electrode Preparation”** section. If using the 9409BN or 9409SC half-cell fluoride electrode with the 900100 reference electrode, fill the reference electrode with Cat. No. 900001. If using the 9609BNWP combination fluoride electrode, fill the electrode with Cat. No. 900061.
2. Connect the electrode to the meter.
3. Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. Single Known Addition For details on temperature effects on electrode performance, refer to the **“Temperature Effects”** section.

Orion Fluoride Standards with TISAB II

The following Orion fluoride standard solutions do not require the addition of TISAB II because TISAB II has already been added in a ratio of 1:1 to the standard solution.

- 10 ppm fluoride with TISAB II standard, Cat. No. 040908
- 5 ppm fluoride with TISAB II standard, Cat. No. F40905
- 2 ppm fluoride with TISAB II standard, Cat. No. 040907
- 1 ppm fluoride with TISAB II standard, Cat. No. 040906
- 0.5 ppm fluoride with TISAB II standard, Cat. No. F40904

For sample measurement after calibration, add 50 mL of TISAB II to every 50 mL of sample to keep the dilution ration of TISAB II to solution consistent for the standards and samples.

User-Prepared Standards by Serial Dilutions

Serial dilution is the best method for the preparation of standards. Serial dilution means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second standard is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

1. **To prepare a 10^{-2} M NaF standard (190 ppm fluoride)**– Pipette 10 mL of the 0.1 M NaF standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

2. **To prepare a 10^{-3} M NaF standard (19 ppm fluoride)**– Pipette 10 mL of the 10^{-2} M NaF standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
3. **To prepare a 10^{-4} M NaF standard (1.9 ppm fluoride)**– Pipette 10 mL of the 10^{-3} M NaF standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

To prepare standards with a different concentration use the following formula:

$$C_1 * V_1 = C_2 * V_2$$

where: C_1 = concentration of original standard

V_1 = volume of original standard

C_2 = concentration of standard after dilution

V_2 = volume of standard after dilution

For example, to prepare 100 mL of a 1 ppm fluoride standard from a 100 ppm fluoride standard:

C_1 = 100 ppm fluoride

V_1 = unknown

C_2 = 1 ppm fluoride

V_2 = 100 mL

$100 \text{ ppm} * V_1 = 1 \text{ ppm} * 100 \text{ mL}$

$V_1 = (1 \text{ ppm} * 100 \text{ mL}) / 100 \text{ ppm} = 1 \text{ mL}$

To make the 1 ppm fluoride standard, pipette 1 mL of the 100 ppm fluoride standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

Direct Calibration Using a Meter with an ISE Mode

Note: See the meter user guide for more specific information.

Sample measurement can be performed after a two-point direct calibration. It is recommended that the two standard concentrations used in the calibration bracket the sample concentration. It is also recommended that the two standard concentrations be 10 fold apart for general applications.

Using Orion Standard Solutions Containing TISAB II:

1. Pour an adequate amount (e.g. 100 mL) of the less concentrated standard (e.g., 0.5 ppm fluoride with TISAB II standard, or 1 ppm fluoride with TISAB II standard) into a 150 mL beaker.
2. Rinse the electrode with deionized water, blot dry and place into the beaker containing the less concentrated standard. Stir the solution thoroughly. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.
3. Pour an adequate amount (e.g. 100 mL) of the more concentrated standard (e.g., 5 ppm fluoride with TISAB II standard, or 10 ppm fluoride with TISAB II standard, respectively) into a 150 mL beaker.
4. Rinse the electrode with deionized water, blot dry and place into the beaker with the more concentrated standard. Stir the solution thoroughly. Wait for a stable reading and then adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between -54 to -60 mV when the standards are between 20-25 °C.
6. Measure 50 mL of the sample and 50 mL of TISAB II and pour into a clean 150 mL beaker. Stir the solution thoroughly.
7. Rinse the electrode with deionized water, blot dry and place into the sample. The concentration of the sample will be displayed on the meter.

Using User-Prepared Fluoride Standard Solutions without TISAB:

1. Measure 50 mL of the less concentrated standard and 50 mL of TISAB II and pour into a 150 mL beaker. Stir the solution thoroughly.
2. Rinse the electrode with deionized water, blot dry and place into the beaker with the less concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.
3. Measure 50 mL of the more concentrated standard and 50 mL of TISAB II and pour into a second 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode with deionized water, blot dry and place into the beaker with the more concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the second standard, as described in the meter user guide.

5. Record the resulting slope value. The slope should be between -54 to -60 mV when the standards are between 20-25 °C. When using a Thermo Scientific meter with the Autoblank function enabled, the absolute value of the slope should be greater than 54 mV.
6. Measure 50 mL of the sample and 50 mL of TISAB II (or either low-level TISAB or TISAB IV) and pour into a clean 150 mL beaker. Stir the solution thoroughly.
7. Rinse the electrode with deionized water, blot dry and place into the sample. The concentration of the sample will be displayed on the meter.

Note: *If using TISAB III, add 5 mL of TISAB III to the 50 mL of standard or sample in step 1, step 3 and step 6.*

Direct Calibration Using a Meter with a Millivolt Mode

1. Adjust the meter to measure mV.
2. Measure 50 mL of the less concentrated standard and 50 mL of TISAB II and add the standard and TISAB II to a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode with deionized water, blot dry and place into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Measure 50 mL of the more concentrated standard and 50 mL of TISAB II and add the standard and TISAB II to a second 150 mL beaker. Stir the solution thoroughly.
5. Rinse the electrode with deionized water, blot dry and place into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using a calculator or electronic spreadsheet, prepare a calibration curve by graphing the log of the fluoride concentration against the millivolt value readings.
7. Measure 50 mL of the sample and 50 mL of TISAB II and add the sample and TISAB II to a clean 150 mL beaker. Stir the solution thoroughly.
8. Rinse the electrode with deionized water, blot dry and place into the beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in step 6, determine the unknown concentration of the sample.

Note: If using TISAB III, add 5 mL of TISAB III to the 50 mL of standard or sample in step 2, step 4 and step 7.

Low-Level Measurements

These procedures are for low ionic strength solutions that do not contain fluoride complexing agents and have a fluoride concentration of less than 2×10^{-5} M (0.38 ppm). For solutions low in fluoride but high in total ionic strength, perform the same procedure by preparing a calibrating solution with a composition similar to the sample. Accurate measurement requires that the following conditions be met:

- Adequate time must be allowed for electrode stabilization. Longer response time will be needed at low-level measurements.
- Stir all standards and samples at a uniform rate.
- Low-level TISAB is recommended for samples and standards.

Low-Level Setup

1. Prepare the electrode as described in the **“Electrode Preparation”** section.
2. Connect the electrode to the meter. Set the meter to read mV.
3. Prepare the low-level TISAB. Refer to the **“Required Equipment”** section for instructions. Use low-level TISAB for low-level measurements only.
4. Prepare 100 mL of standard solution. Dilute the 100 ppm fluoride standard, Cat. No. 940907, to 10 ppm or dilute the 0.1 M NaF standard, Cat. No. 940906, to 10^{-3} M.
5. Add 100 mL of the low-level TISAB to the 100 mL of standard.

Low-Level Calibration and Measurement Using a Thermo Scientific Orion ISE Meter with Autoblank Capability

1. When using a Thermo Scientific Orion ISE meter in ISE mode with Autoblank mode enabled, a three point calibration is usually sufficient to prepare an accurate calibration curve at low levels.
2. Choose three calibration points to bracket the concentrations of interest. It is advised to choose points which are not more than a factor 10 between each point, for example, 0.05, 0.5, and 5 mg/L fluoride standards.

3. Prepare the standards as described in the Direct Calibration section of this user guide. Prepare calibration standards for testing by mixing a portion of the standard with an equal portion of low level TISAB in a non-glass beaker. Stir the solution.
4. Ensure that the Autoblank mode is enabled in the meter setup mode.
5. Rinse the electrode with deionized water, blot dry and place into the beaker with the least concentration standard. While stirring the solution, select the meter calibration mode and wait for a stable reading. Adjust the meter to display the value of the standard, as described in the meter user guide.
6. Repeat step 5 for the second and third standards and complete the calibration, as described in the meter user guide.
7. Record the resulting slope value. The absolute value of millivolt difference should be greater than 54 mV.
8. Measure equal amounts of the sample and low level TISAB into a non-glass beaker. Stir the solution.
9. Rinse the electrode with deionized water, blot dry and place into the beaker with the prepared sample. Continue stirring the solution and wait for a stable reading. The concentration of the sample will be displayed on the meter.

Low-Level Calibration and Measurement When Using a Meter with Millivolt Mode

1. Measure 50 mL of deionized water and 50 mL of low-level TISAB and add to a 150 mL beaker.
2. Rinse the electrode with deionized water and place into beaker. Stir the solution thoroughly.
3. Add increments of the 10 ppm or 10^{-3} M fluoride standard mixed with low-level TISAB to the beaker using the steps outlined in **Table 2**. Record the stable millivolt reading after each increment.
4. Using a calculator or electronic spreadsheet, prepare a calibration curve by graphing the log of the fluoride concentration against the millivolt value readings. Prepare a new calibration curve with fresh standards each day.
5. Measure 50 mL of sample and 50 mL of low-level TISAB and add to a clean 150 mL beaker. Rinse the electrode with deionized water, blot dry and place into the sample.
6. Stir the solution thoroughly. When a stable reading is displayed, record the mV value.

- Determine the sample concentration corresponding to the measured potential from the low-level calibration curve.

Table 2 Calibration Curve For Low-Level Measurements

Additions of standard (with low-level TISAB) to 50 mL distilled water and 50 mL low-level TISAB solution.

Step	Pipette Size	Volume Added	Concentration	
			ppm	M
1	1 mL	0.1 mL	0.01	1×10^{-6}
2	1 mL	0.1 mL	0.02	2×10^{-6}
3	1 mL	0.2 mL	0.04	4×10^{-6}
4	1 mL	0.2 mL	0.06	6×10^{-6}
5	1 mL	0.4 mL	0.10	1×10^{-5}
6	2 mL	2.0 mL	0.29	2.9×10^{-5}
7	2 mL	2.0 mL	0.48	4.8×10^{-5}

Single Known Addition

Known addition is a convenient technique for measuring samples because no calibration curve is required. It can be used to verify the results of a direct calibration or to measure the total concentration of an ion in the presence of a large excess of a complexing agent. The sample potential is measured before and after addition of a standard solution. Accurate measurement requires that the following conditions be met:

- Concentration should approximately double as a result of the addition.
- Sample concentration should be known to within a factor of three.
- Either no complexing agent or a large excess of the complexing agent may be present.
- The ratio of the uncomplexed ion to complexed ion must not be changed by addition of the standard.
- All samples and standards should be at the same temperature.

Single Known Addition Setup

- Prepare the electrode as described in the **“Electrode Preparation”** section.
- Connect the electrode to the meter.

3. Prepare a standard solution that will cause the fluoride concentration of the sample to double when added to the sample solution. Refer to **Table 3** for guidelines.
4. Determine the electrode slope by performing the procedure in the **“Checking Electrode Operation (Slope)”** section.
5. Rinse the electrode with deionized water.

Table 3 Guideline For Known Addition

Volume of Addition	Concentration of Standard
1 mL	100 times sample concentration
5 mL	20 times sample concentration
10 mL*	10 times sample concentration

* Most convenient volume to use

Single Known Addition Using a Meter with a Known Addition Mode

Note: See the meter user guide for more specific information.

1. Set up the meter to measure in the known addition mode.
2. Measure 50 mL of the sample and 50 mL of TISAB II or 5 mL of TISAB III and add to a beaker. Rinse the electrode with deionized water and place it into the sample solution. Stir the solution thoroughly.
3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.
4. Pipette the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Single Known Addition Using a Meter with a Millivolt Mode

1. Set the meter to relative millivolt mode. If a relative millivolt mode is not available, use the millivolt mode.
2. Measure 50 mL of sample and 50 mL of TISAB II or 5 mL of TISAB III and add to a 150 mL beaker. Stir the solution thoroughly.

- Rinse the electrode with deionized water, blot dry and place into the beaker. When a stable reading is displayed, set the meter to read 0.0 mV. If the reading cannot be adjusted to 0.0 mV, record the actual mV value.
- Pipette the appropriate amount of standard solution into the beaker. Stir the solution thoroughly.
- When a stable reading is displayed, record the mV value. If the meter could not be set to 0.0 mV in step 3, subtract the first reading from the second reading to calculate ΔE .

Note: Double known addition method is outlined in the Dual Star meter manual.

- Use **Table 4** to find the Q value that corresponds to the change in potential, ΔE . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sample}} = Q * C_{\text{standard}}$$

where:

C_{standard} = standard concentration

C_{sample} = sample concentration

Q = value from **Table 4**

The table of Q values is calculated for a 10% volume change. The equation for the calculation of Q for different slopes and volume changes is given below.

$$Q = (p * r) / \{[(1 + p) * 10^{\Delta E/S}] - 1\}$$

where:

Q = value from **Table 4**

$\Delta E = E_2 - E_1$

S = slope of the electrode

p = volume of standard / volume of sample and ISA

r = volume of sample and ISA / volume of sample

Alternately, calculate the results using an electronic spreadsheet, described in Table 5.

Table 4 Q Values for a 10% Volume Change
Slopes (in column heading) are in units of mV/decade.

ΔE	Q Concentration Ratio			
	Monovalent	57.2	58.2	59.2
5.0	0.2894	0.2933	0.2972	0.3011
5.2	0.2806	0.2844	0.2883	0.2921
5.4	0.2722	0.2760	0.2798	0.2835
5.6	0.2642	0.2680	0.2717	0.2754
5.8	0.2567	0.2604	0.2640	0.2677
6.0	0.2495	0.2531	0.2567	0.2603
6.2	0.2436	0.2462	0.2498	0.2533
6.4	0.2361	0.2396	0.2431	0.2466
6.6	0.2298	0.2333	0.2368	0.2402
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	0.2074	0.2107	0.2140	0.2172
7.6	0.2024	0.2056	0.2088	0.2120
7.8	0.1975	0.2007	0.2039	0.2023
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	0.1253	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
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	0.1108	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

ΔE	Q Concentration Ratio			
	Monovalent	57.2	58.2	59.2
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	0.0740	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	0.055
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	0.0373	0.0384
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
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

Calculating Known Addition for Samples using an Electronic Spreadsheet

If it is more convenient, a simple spreadsheet can be set up to calculate the known addition results, using any ratio of sample to addition. A typical worksheet is shown in Table 5. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 5
Known Addition Calculations using Lotus, Excel, or Quattro Spreadsheets

A	B	C
1		Enter Value
2	Volume of sample and ISA (mL)	102
3	Volume of additon (mL)	10
4	Concentration of addition	10
5	Volume of Sample	100
6	Initial mV reading	45.3
7	Final mV reading	63.7
8	Electrode Scope	-59.2
9		
10		Derived Values
11	Delta E	+C7 -C6
12	Solution volume ratio	+C3/C2
13	Antilog term	+10 [^] (C11/C8)
14	Sample volume ratio	+C2/C5
15	Q term	+C2*C14/ (((1+C12)*C13)-1)
16	Calculated intial concentration in same units as addition	+C15*C4

Note: For Excel, use = instead of + at start of formulas.

Titration

The electrode makes a highly sensitive endpoint detector for titrations of a fluoride-containing sample using lanthanum nitrate as the titrant. Titrations are more time-consuming than direct electrode measurements, but results are more accurate and reproducible. With careful technique, titrations can be performed that are accurate to $\pm 0.2\%$ of the total fluoride concentration of the sample.

The sample should be at least 10^{-3} M total fluoride in concentration for a good endpoint break. 10^{-3} M total fluoride in concentration for a good endpoint break.

Titration for fluoride give low results in the presence of 1% or more (based on total fluoride) aluminum, iron, or trivalent chromium.

The fluoride electrode can also be used to detect titration endpoints of samples containing species that react with fluoride, such as aluminum, lithium, lanthanum, and thorium. Contact Technical Support .

The following procedure is for the titration of a fluoride containing sample with lanthanum nitrate.

1. Prepare a 0.1 M lanthanum nitrate solution by dissolving 43.3 g of reagent-grade $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in a 1 liter volumetric flask that contains approximately 700 mL of distilled water. Once the solids are dissolved, fill the flask to the mark with distilled water.
2. Standardize the lanthanum nitrate solution by titrating against a 0.1 M fluoride standard. Pipette exactly 25 mL of fluoride standard into a 250 mL plastic beaker and add 50 mL of distilled water. Place the electrode in the sample. Stir the solution thoroughly throughout the titration.
3. Using a 10.0 mL burette, add increments of lanthanum nitrate and plot the electrode potential against mL of lanthanum nitrate added. The endpoint is the point of the greatest slope. See **Figure 3**. Alternately, use a first derivative calculation or an on-line titration calculator to determine the end point. Record the endpoint, V_{t0} . Rinse the electrode and blot dry..
4. Titrate the unknown samples. Pipette exactly 25 mL of sample into a 250 mL beaker and add 50 mL of distilled water. Place the electrode in the sample. Stir the solution thoroughly throughout the titration.
5. Using a 10 mL burette, add increments of lanthanum nitrate and plot the electrode potential against mL of lanthanum nitrate added. Determine the endpoint, V_{tx} .
6. Calculate sample concentration, C_{sx} :

$$C_{sx} = [(V_{tx} * V_{t0}) / (V_{tx} V_{t0})] * C_{s0}$$

where: C_{sx} = sample concentration

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

V_{tx} = volume of titrant added in unknown sample titration at endpoint

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

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

V_{i0} = volume of standard used in standardization titration (25 mL)

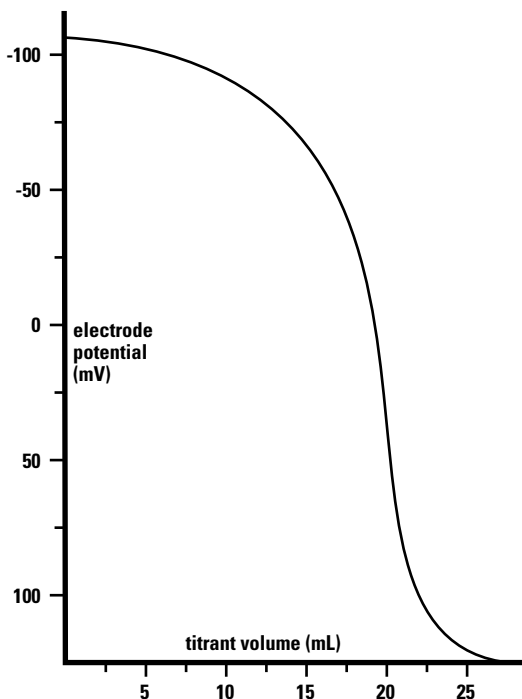


Figure 3 Titration of 0.114 M F^- with 0.1 M $La(NO_3)_3$

Fluoride in Acid Solutions

In solutions with a pH below 5, hydrogen ions complex a portion of the fluoride ions, forming HF or HF_2^- , which cannot be detected by the fluoride electrode. To free the complexed fluoride, the pH of the solution must be adjusted to the weakly acidic to weakly basic region before making measurements. A strong base, such as sodium hydroxide, should not be used for pH adjustment, since the total ionic strength of the adjusted samples and standards will vary according to the original solution pH and the amount of sodium hydroxide added. Variations in total ionic strength affect the accuracy of concentration measurements. Dilution of samples and standards with a large excess of sodium acetate, on the other hand, will buffer the pH to above 5 and help adjust the total ionic strength of samples and standards to the same level.

Procedure

1. Prepare a 15% sodium acetate solution. Dissolve reagent-grade sodium acetate (CH_3COONa) in distilled water. Prepare a large enough quantity of 15% sodium acetate solution to dilute all samples and standards.

2. Prepare a background solution that contains all sample components except fluoride. Use this solution to prepare the standards.
3. Prepare standards in the concentration range of the unknown samples by adding fluoride to the background solution. Dilute each standard 10:1 with the sodium acetate solution (9 parts sodium acetate and 1 part standard). Prepare fresh standards every two weeks if the standard contains less than 10 ppm fluoride. If an ISE (concentration) meter is used, prepare at least two standards. If a meter with a mV mode is used, prepare at least three standards.
4. Calibrate the electrode using the instructions in the **“Checking Electrode Operation (Slope)”** section.
5. Measure the unknown samples: Dilute each unknown sample 10:1 with sodium acetate before performing taking measurements (9 parts sodium acetate and 1 part unknown sample).

Note: *In many cases, standards do not need to be prepared using background solutions. If a standard prepared from the background solution gives the same reading (after dilution with sodium acetate) as a standard prepared from pure sodium fluoride, then the background solution is unnecessary.*

Fluoride in Alkaline Solutions

In basic solutions containing low fluoride content (less than 10^{-4} M at a pH of 9.5 or above), the electrode responds to hydroxide ion as well as to fluoride ion. The potential reading, caused by the concentration of both hydroxide and fluoride ion, is lower than it would be if fluoride alone were present. Refer to the **“Interferences”** section.

Adjusting the pH to between 5 and 6 with a 4.0 M buffered potassium acetate solution eliminates any hydroxide error and raises the total ionic strength of both samples and standards to the same value. After both samples and standards are diluted 10:1 with the buffer solution, the fluoride ion concentration can be determined in the usual manner.

Procedure

1. Prepare a 4.0 M buffered potassium acetate solution by diluting 2 parts 6.0 M acetic acid (CH_3COOH) with one part distilled water and surrounding the reaction with a water bath. Add 50% KOH solution to the acetic acid slowly, stirring constantly, until a pH of 5 is reached. Prepare a large enough quantity of the potassium acetate solution to dilute all samples and standards.
2. If required, prepare a background solution that contains all sample components except fluoride. Use this solution to prepare the standards.

3. Prepare standards in the concentration range of the unknown samples by adding fluoride to the background solution. Dilute each standard 10:1 with the potassium acetate solution (9 parts potassium acetate and 1 part standard). Prepare fresh standards every two weeks if the standard contains less than 10 ppm fluoride. If an ISE (concentration) meter is used, prepare at least two standards. If a meter with a mV mode is used, prepare at least three standards.
4. Calibrate the electrode using the instructions in the **“Checking Electrode Operation (Slope)”** section.
5. Measure the unknown samples: Dilute each unknown sample 10:1 with potassium acetate before performing taking measurements (9 parts potassium acetate and 1 part unknown sample).

Electrode Characteristics

Electrode Response

The electrode potentials when using a calibration curve by graphing the log of the fluoride concentration against the millivolt values will result in a straight line with a slope of about 54 to 60 mV per decade change in concentration. See **Figure 2**.

The time response of the electrode, 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 4**.

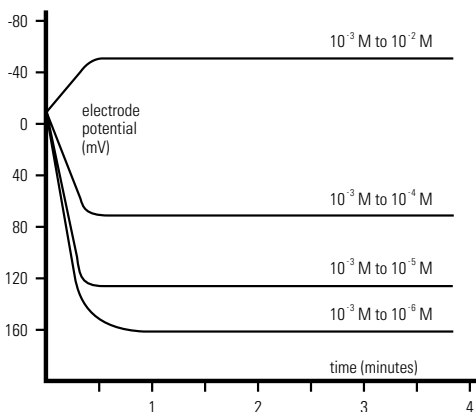


Figure 4 Typical Electrode Response To Step Changes in NaF Concentration

Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With hourly calibrations, direct electrode measurements reproducible to $\pm 2\%$ can be obtained.

Limits of Detection

In neutral solutions, fluoride concentration can be measured down to 10^{-6} M (0.02 ppm) fluoride. However, care must be taken in making determinations below 10^{-5} M to avoid sample contamination. The upper limit of detection is a saturated fluoride solution.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within $\pm 1\text{ }^{\circ}\text{C}$ ($\pm 2\text{ }^{\circ}\text{F}$) of each other. At the 10^{-3} M fluoride level, a $1\text{ }^{\circ}\text{C}$ difference in temperature 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 of the fluoride electrode also varies with temperature, as indicated by the factor S in the Nernst equation. Values of the Nernst equation for the fluoride ion are given in **Table 5**. If the temperature changes, the meter and electrode should be recalibrated.

Table 5 Theoretical Slope vs. Temperature Values

Temperature ($^{\circ}\text{C}$)	Slope (mV)
0	- 54.2
10	- 56.2
20	- 58.2
25	- 59.2
30	- 60.1
40	- 62.1
50	- 64.1

The electrode can be used at temperatures from 0 to $100\text{ }^{\circ}\text{C}$, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, equilibrium times of up to one hour are recommended. The electrode must be used only intermittently at solution temperatures above $80\text{ }^{\circ}\text{C}$.

Interferences

Most cations and anions do not interfere with the response of the fluoride electrode to fluoride. Anions commonly associated with fluoride, such as Cl^{-} , Br^{-} , I^{-} , SO_4^{2-} , HCO_3^{-} , PO_4^{3-} and acetate, do not interfere with electrode operation. The OH^{-} ion is an electrode interference, see the **pH Effects** section. Some anions, such as CO_3^{2-} or PO_4^{3-} , make the sample more basic, which increases the OH^{-} interference, but are not direct electrode interferences. See section on complexation for more details on interferences resulting from polyvalent cations.

pH Effects

In acid solutions with a pH below 5, hydrogen complexes a portion of fluoride in solution, forming the undissociated acid HF and the ion HF_2^{-} . **Figure 5** shows the proportion of free fluoride ion in acid solutions. Hydroxide ion interferes with the electrode response to fluoride when the level of hydroxide is greater than one-tenth the level of fluoride ion present. For example, at pH 7, when the

hydroxide concentration is 10^{-7} M or less, there is no hydroxide interference with fluoride measurements. At pH 10, where the hydroxide concentration is 10^{-4} M, there is no error at 10^{-2} M fluoride, about a 10% error at 10^{-4} M fluoride and considerable error at 10^{-5} M fluoride. See **Figure 6**. Addition of TISAB II or III to fluoride standards and samples will buffer the pH between 5.0 and 5.5 to avoid hydroxide interferences or the formation of hydrogen complexes of fluoride. TISAB IV adjusts the pH to about 8.5, and should not be used for very low-level measurements.

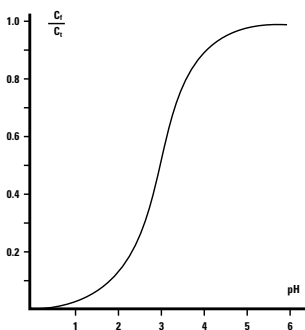


Figure 5 Fraction of Free Fluoride as a Function of Solution pH, hydrogen is the only complexing species

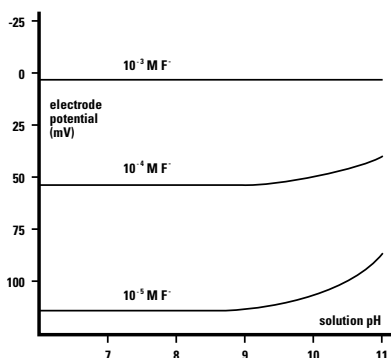


Figure 6 Electrode Response in Alkaline Solutions

Complexation

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

TISAB II and III contain a reagent, CDTA, that preferentially complexes aluminum or iron in the sample. In a 1 ppm fluoride

sample, TISAB II or III complexes about 5 ppm aluminum or iron. Higher levels of aluminum or iron can be complexed by using TISAB IV.

Theory of Operation

The fluoride electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing fluoride ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free fluoride ion in solution, is measured against a constant reference potential with a digital pH/mV meter or ISE (concentration) 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 electrode potential

E_o = reference potential (a constant)

A = fluoride ion activity level in solution

S = electrode slope (about 57 mV per 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, y_i.

$$A = y_i * C_f$$

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

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

where

C_i = concentration of ion i

Z_i = charge of ion i

∑ symbolizes the sum of all the types of ions in solutions

If background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to concentration.

Total ionic strength adjustor buffer (TISAB) is added to all fluoride standards and samples so that the background ionic strength is high, fluoride is decomplexed and the pH of the solution is correct.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time when two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, the electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions.

In making electrode measurements, it is important that this potential is the same when the reference is in the standardizing solution as well as in the same solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable that analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be nearly as equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then no junction potential can result.

However, there are a few samples where no filling solution adequately fulfills the condition stated above. Particularly troublesome are samples containing high levels of strong acids (pH 0-2) or strong bases (pH 12-14). The high mobility of hydrogen and hydroxide ions in samples makes it impossible to “swamp out” their effect on the junction potential with any concentration of an equitransferent salt. For these solutions, use the acid or alkaline (strong base) testing procedures that are described in this user guide.

For more information, contact Technical Support. Within the United States and Canada, call 1.800.225.1480 or 978.232.6000 or email wai.techservbev@thermofisher.com. For countries outside of North America, contact your local authorized dealer. For the most current contact information, visit www.thermofisher.com/water.

Troubleshooting

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the meter user guide for directions.

Electrode

1. Rinse the electrode thoroughly with distilled water.
2. Verify the electrode performance by performing the procedure in the **“Checking Electrode Operation (Slope)”** section.
3. If the electrode fails this procedure, review the **“Measuring Hints”** section. Clean the electrode thoroughly as directed in the **“Electrode Maintenance”** section. Drain and refill the electrode with fresh filling solution.
4. Repeat the procedure in the **“Checking Electrode Operation (Slope)”** section.
5. If the electrode fails this procedure again and the half-cell fluoride electrode is being used, determine whether the fluoride or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the procedure in the **“Checking Electrode Operation (Slope)”** section.
6. If the electrode passes the procedure, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.
7. Before replacing a faulty electrode, review this user guide and be sure to thoroughly clean the electrode; correctly prepare the electrode; use the proper filling solutions, TISAB, and standards; correctly measure the samples and review the **“Troubleshooting Checklist”** section.

Sample/Application

The quality of results depends greatly upon the quality of the standards. Always prepare fresh standards when problems arise, it could save hours of frustrating troubleshooting! Errors may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is serial dilution. Refer to the **Serial Dilution** section. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects. Refer to the **“Sample Requirements”**, **“Temperature Effects”**, **“Interferences”**, and **“pH Effects”** sections.

Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

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 the best method. If the sample is viscous, analate addition may solve the problem. If working with low-level samples, follow the procedure in the **“Low-Level Measurements”** section.

Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States and Canada, call 1.800.225.1480 or 978.232.6000 or email wai.techservbev@thermofisher.com. For countries outside of North America, contact your local authorized dealer. For the most current contact information, visit www.thermofisher.com/water.

Warranty

For the most current warranty information, visit www.thermofisher.com/water.

Troubleshooting Checklist

- No electrode filling solution added.
Fill the electrode with filling solution up to the fill hole.
Refer to the **“Electrode Preparation”** section for details.
- Incorrect electrode filling solution used.
Refer to the **“Electrode Preparation”** section to verify the correct electrode filling solution.
- Electrode junction is dry.
Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
- No reference electrode present.
The 9409BN and 9409SC fluoride half-cell electrodes require a separate reference electrode, Cat. No. 900100.

- Electrode is clogged or dirty.
Refer to the **“Electrode Maintenance”** section for cleaning instructions.
- Standards are contaminated or made incorrectly.
Prepare fresh standards. Refer to the **“Measuring Hints”** and **“Analytical Techniques”** sections.
- TISAB not used or incorrect TISAB used.
TISAB must be added to all standards and samples. Refer to the **“Required Equipment”** section for information on TISAB solutions.
- Samples and standards at different temperatures.
Allow solutions to reach the same temperature.
- Air bubble on sensing element.
Tap the electrode gently to remove the air bubble or remove the electrode from the solution and immerse again.
- Electrode not properly connected to meter.
Unplug and reconnect the electrode to the meter
- Meter or stir plate not properly grounded.
Check the meter and stir plate for proper grounding.
- Static electricity present.
Wipe plastic parts on the meter with a detergent solution.
- Defective meter.
Check the meter performance. See the meter user guide.

Ordering Information

Cat. No.	Description
9609BNWP	Fluoride ionplus Sure-Flow combination electrode, waterproof BNC connector
9409BN	Fluoride half-cell electrode, BNC connector (requires separate reference electrode)
9409SC	Fluoride half-cell electrode, screw cap connector (requires separate reference electrode)
900100	Single junction reference electrode, pin tip connector
900061	Optimum Results A electrode filling solution, 5 x 60 mL bottles
900001	Single junction reference electrode filling solution, 5 x 60 mL bottles
940906	0.1 M NaF, 475 mL bottle
940907	100 ppm F ⁻ , 475 mL bottle
040908	10 ppm F ⁻ with TISAB II, 475 mL bottle
F40905	5 ppm F ⁻ with TISAB II, 475 mL bottle
040907	2 ppm F ⁻ with TISAB II, 475 mL bottle
040906	1 ppm F ⁻ with TISAB II, 475 mL bottle
F40904	0.5 ppm F ⁻ with TISAB II, 475 mL bottle
940909	TISAB II, 3.8 L bottle
940999	TISAB II, 4 x 3.8 L bottle
940911	TISAB III concentrate, 475 mL bottle

Specifications

Concentration Range

10^{-6} M (0.02 ppm) to saturated

pH Range

pH 5-7 at 10^{-6} M (0.02 ppm F⁻)

Temperature Range

0 to 80 °C continuous use

80 to 100 °C intermittent use

Electrode Resistance

150 to 200 kilohms

Reproducibility

± 2%

Minimum Sample Size

5 mL in a 50 mL beaker

Size– 9609BNWP

Body Diameter: 13 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

Size– 9409BN and 9409SC

Body Diameter: 12 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

** Specifications are subject to change without notice.*

Find out more at thermofisher.com/water

© 2016 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries unless otherwise specified.

Water and Lab Products

North America

Toll Free: 1-800-225-1480

Tel: 1-978-232-6000

info.water@thermofisher.com

Germany

Tel: (49) 6184-90-6000

info.water.uk@thermofisher.com

China

Tel: (86) 21-68654588

wai.asia@thermofisher.com

India

Tel: (91) 22-4157-8800

wai.asia@thermofisher.com

Singapore

Tel: (65) 6778-6876

wai.asia@thermofisher.com

Japan

Tel: (81) 045-453-9175

wai.asia@thermofisher.com

Australia

Tel: (613) 9757-4300

In Australia: (1300) 735-295

InfoWaterAU@thermofisher.com