perfectION™ Guidebook

perfectION™

Combination Fluoride Electrode

Successful Ion Measurement

METTLER TOLEDO

Contents

Table of Contents

1. 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.

perfectION™ Combination Fluoride Electrode

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The built-in Click & Clear™ reference junction prevents clogging of the diaphragm and provides fast and stable readings.
The perfectION™ Combination Fluoride Electrode is available with a BNC connector (P/N 51344715) and a Lemo connector (P/N 51344815) for METTLER TOLEDO titrators.

2. Required Equipment

1. ISE meter, such as the METTLER TOLEDO SevenMulti™ benchtop meter or the SevenGo pro™ portable meter, or a METTLER TOLEDO titrator, such as the Tx (T50, T70, T90) Excellence or G20 Compact titrators.

   METTLER TOLEDO combined ISEs can be used on any ISE meter with a BNC connection.

2. perfectION™ combined fluoride ion selective electrode
3. Stirrer
4. Volumetric flasks, graduated cylinders, beakers and pipettes. Plastic labware is highly recommended for fluoride analysis.
5. Distilled or deionized water
6. Ion Electrolyte A Reference filling solution (P/N 51344750)
7. Fluoride standard solution 1000 mg/L (P/N 51344775)
8. Total Ionic Strength Adjustment Buffer (TISAB), which provides a constant background ionic strength, decomplexes fluoridet ions and adjusts the solution pH.

Part No.	Description
51344765	TISAB II with CDTA, 3.8 L bottle
51344766	TISAB III with CDTA (concentrated), 475 mL bottle

Note: *TISAB III and TISAB II have the same chemical formula. TISAB III is a more concentrated form of TISAB II, so the reagent to sample or standard ratio is different.*

Low-level TISAB

Low-level TISAB contains no complexing agents and is a lower ionic strength adjuster with fewer components than TISAB II and TISAB III. It will enhance the electrode performance for low-level measurements in samples that do not contain interfering species. Use low-level TISAB when measuring samples that contain less than 0.4 mg/L (2×10^{-5} mol/L) fluoride and do not contain fluoride complexing agents such as iron or aluminum.

To prepare low-level TISAB: Place 500 mL of distilled water in a 1 L 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 mol/L NaOH until the pH is between 5.0 and 5.5. Cool the solution to room temperature. Pour the solution into a 1 L 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.

TISAB IV

TISAB IV will complex more than 100 mg/L of iron or aluminum in the presence of 1 mg/L fluoride. A measurement of 1 mg/L fluoride gives rise to an error of 5% in the presence of 200 mg/L iron or aluminum.

To prepare TISAB IV: Place 500 mL of distilled water in a 1 L volumetric flask. Add 84 mL of concentrated HCl (36 to 38%), 242 g of TRIS (hydroxymethyl) aminomethane and 230 g of sodium tartrate ($Na_2C_4H_4O_6$-$2H_2O$) 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.

3. Electrode and Measurement Setup

Electrode Preparation

Remove the protective shipping cap from the sensing element and save the cap for storage. Fill the electrode with Ion Electrolyte A Reference filling solution.

Electrode Filling Instructions:

1. Install the flip spout cap on the filling solution bottle and lift the flip spout on the bottle to a vertical position.
2. Insert the spout into the fill 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 O-ring and 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, see if the O-ring is moist and repeat steps 2 through 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 2.5 cm above the level of sample in the beaker to ensure a proper flow rate. The fill hole should always be open when taking measurements.*

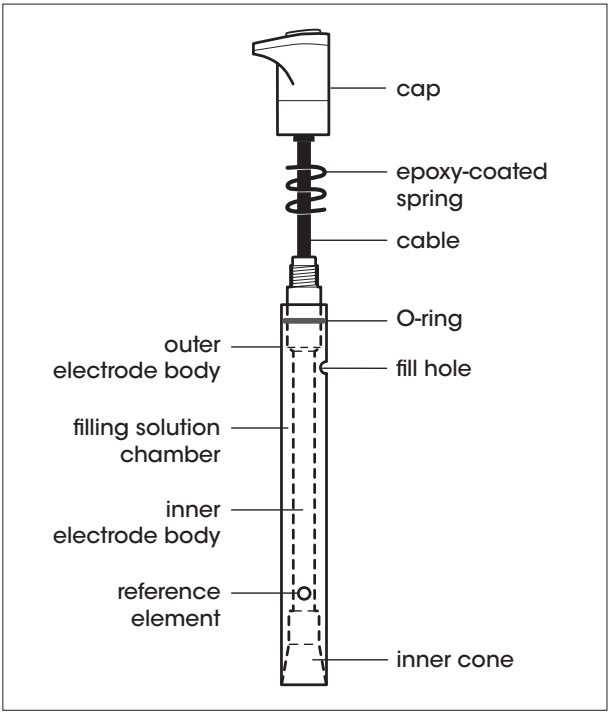


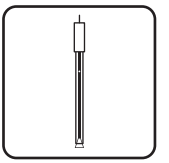
Figure 1 *– perfectION™ Fluoride combination electrode*

Checking Electrode Operation (Slope)

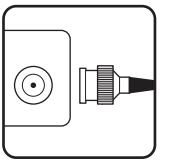
These are general instructions that can be used with most meters to check the electrode operation.

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

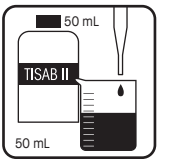
1. If the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.



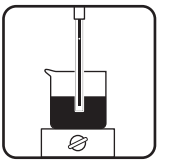
2. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.



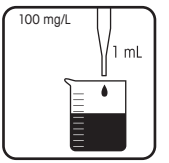
3. Place 50 mL of distilled water and 50 mL of TISAB II into a 150 mL beaker. Stir the solution thoroughly.
   If using TISAB III, place 90 mL of distilled water and 10 mL of TISAB III into a 150 mL beaker. Stir the solution thoroughly.



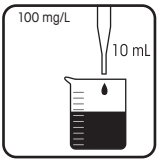
4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.



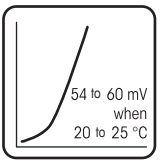
5. Select either a 0.1 mol/L sodium fluoride or 100 mg/L fluoride standard. Pipette 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.



6. Pipette 10 mL of the same standard into the same beaker and stir the solution 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.



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, benzene or acetone.

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

Fluoride concentration can be measured in moles per liter (mol/L), milligramms per liter (mg/L) or any convenient concentration unit.

Table 1 *– Fluoride Concentration Unit Conversion Factors*

mol/L	mg/L Fluoride (F^-)
1.0	19000
10^{-1}	1900
10^{-2}	190
10^{-3}	19
10^{-4}	1.9

- Once TISAB II 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. Add 50 mL of TISAB II to every 50 mL of standard or sample. Add 10 mL of TISAB III to every 90 mL standard or sample.
- 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 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, prepare standards with a background composition similar to the sample.
- Adjust the pH of highly acidic or highly basic solutions to pH 5 - 6 before adding TISAB.
- The fill hole cover must be open during measurements to ensure a uniform flow of reference filling solution.
- If the fluoride 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.
- Start the calibration or measurement with the lowest concentrated standard or sample.

Electrode Storage and Maintenance

Electrode Storage

For storage between measurements and up to one week, store the electrode in a 4 mol/L potassium chloride solution with fluoride. The fluoride concentration of the storage solution should be close to the least concentrated fluoride calibration standard. Do not add TISAB to the storage solution. The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result.

For storage longer than one week, drain the electrode, flush the chamber with distilled water and store the electrode dry with the protective shipping cap covering the sensing element.

Polishing the Sensing Surface of the Fluoride Combination Electrode

The sensing surface of solid state electrodes can wear over time, which causes drift, poor reproducibility and loss of response in low-level samples. The electrode can be restored by polishing the sensing surface with a polishing strip. The polishing strip can also be used if the sensing surface has been etched or chemically poisoned.

1. Cut off about an 2.5 cm of the polishing strip.
2. Hold the electrode with the sensing surface facing up.
3. Place a few drops of distilled water on the sensing surface.
4. With the frosted side of the polishing strip facing down, use light finger pressure to place the polishing strip on top of the sensing surface.
5. Rotate the electrode for about 30 seconds.
6. Rinse the electrode with distilled water and soak the electrode in a 1 mg/L or 10^{-4} mol/L fluoride standard for ten minutes.

Flushing the Fluoride Combination 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 electrode. 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 replenish any lost filling solution.

Disassembling and Reassembling the Fluoride Combination 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 electrode.
2. Unscrew the cap counterclockwise and then slide the cap and spring up the cable.
3. Hold the outer sleeve with one hand and firmly push down on the threaded portion with your thumb and forefinger to separate the inner body from the sleeve.
4. Grasp the inner cone with a clean, lint-free tissue and withdraw the body from the sleeve using a gentle twisting motion. Do not touch the pellet above the cone, as it will damage the pellet. Rinse the outside of the electrode body and the entire sleeve with distilled water. Allow it to air dry.
5. 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.
6. 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.
7. Place the spring onto the electrode body and screw on the cap. Refill the electrode with filling solution.

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 100 mg/L fluoride standard** – Pipette 10 mL of the 1000 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
2. **To prepare a 10 mg/L standard** – Pipette 10 mL of the 100 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
3. **To prepare a 1 mg/L standard** – Pipette 10 mL of the 10 mg/L 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:

$$\mathbf{C_1 * V_1 = C_2 * V_2}$$

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 mg/L fluoride standard from a 100 mg/L fluoride standard:

C_1 = 100 mg/L fluoride
V_1 = unknown
C_2 = 1 mg/L fluoride
V_2 = 100 mL
100 mg/L * V_1 = 1 mg/L * 100 mL
V_1 = (1 mg/L * 100 mL) / 100 mg/L = 1 mL

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

4. 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 a calibration is not required. 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 to 100 times) excess of complexing agents. As in direct calibration, any convenient concentration unit can be used.

- **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. From the change in potential before and after the addition, the original sample concentration is determined.
- **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.

- **Analyte 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 from the change in potential before and after the addition.

- **Analyte 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, with samples for which a stable standard is difficult to prepare and for viscous or very concentrated samples. The method is not suitable 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. A sensing electrode can be used for the 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.

Direct Calibration Technique

Typical Direct Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic paper. 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.

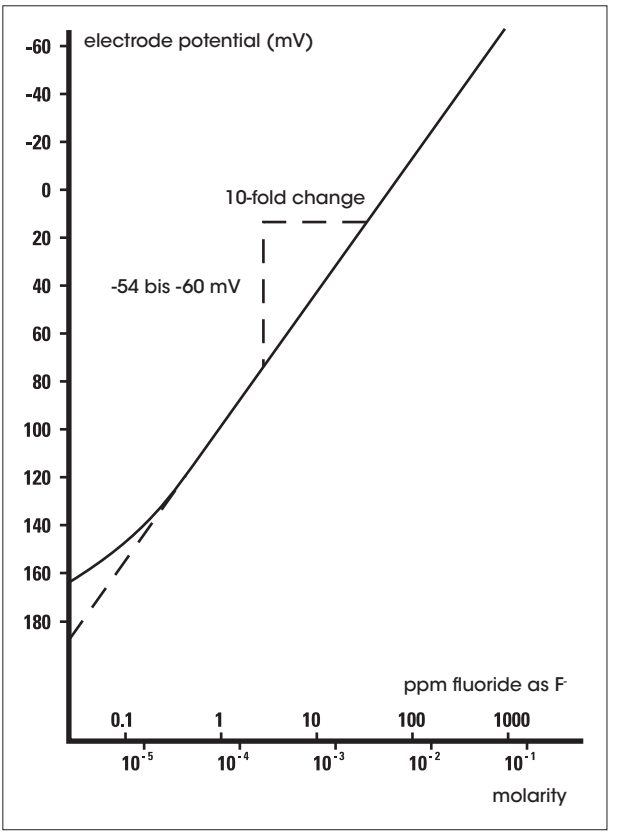


Figure 2 *– Typical Direct Calibration Curve*

Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
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. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

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.

Direct Calibration Procedure Using a Meter with an ISE Mode

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

1. Measure 50 mL of the less concentrated standard and 50 mL of TISAB II and pour both solutions into a 150 mL beaker. Stir the solution thoroughly.
2. Rinse the electrode with deionized water, blot it dry and place it into the beaker with the less concentrated standard. Wait for a stable reading and 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 both solutions into a second 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode with deionized water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and 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 and -60 mV when the standards are between 20 and 25 ˚C.
6. Measure 50 mL of the sample and 50 mL of TISAB II and pour both solutions into a clean 150 mL beaker. Stir the solution thoroughly.
7. Rinse the electrode with deionized water, blot it dry and place it 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 Procedure Using a Meter with a mV Mode

1. Set the meter to the mV mode.
2. Measure 50 mL of the less concentrated standard and 50 mL of TISAB II and pour both solutions into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode with deionized water, blot it dry and place it 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 pour both solutions into a second 150 mL beaker. Stir the solution thoroughly.
5. Rinse the electrode with deionized water, blot it dry and place it into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.
7. Measure 50 mL of the sample and 50 mL of TISAB II and add the sample and pour both solutions into a clean 150 mL beaker. Stir the solution thoroughly.
8. Rinse the electrode with deionized water, blot it dry and place it into the beaker. When a stable reading is displayed, record the mV value.
9. Use the calibration curve prepared in step 6 in order to 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 Calibration Technique

This procedure is for low ionic strength solutions that do not contain fluoride complexing agents and have a fluoride concentration of less than 2 x 10^{-5} mol/L (0.38 mg/L). For solutions low in fluoride but high in total ionic strength, perform the same procedure, but prepare a calibrating solution with a background composition similar to the sample. Accurate measurements requires that the following conditions be met:

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

Low-level Calibration Setup

1. 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. 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 a standard solution. Dilute the 1000 mg/L fluoride standard to 10 mg/L.
5. Add 100 mL of the low-level TISAB and 100 mL of standard to a beaker.

Note: *Low-level TISAB contains no complexing agents and is a lower ionic strength adjuster with fewer components than TISAB II and TISAB III. It will enhance the electrode performance for low-level measurements in samples that do not contain interfering species. Use low-level TISAB when measuring samples that contain less than 0.4 mg/L (2 x 10^{-5} mol/L) fluoride and do not contain fluoride complexing agents such as iron or aluminum.*

Low-level Calibration and Measurement Procedure

1. Measure 50 mL of deionized water and 50 mL of low-level TISAB and add both solutions to a 150 mL beaker.
2. Rinse the electrode with deionized water, blot it dry and place it into the beaker. Stir the solution thoroughly.
3. Add increments of the prepared 10 mg/L or 10^{-3} mol/L fluoride standard with low-level TISAB to the beaker using the steps outlined in **Table 2**. Record the stable millivolt reading after each increment.
4. On semi-logarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis). 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 both solutions to a clean 150 mL beaker. Rinse the electrode with deionized water, blot it dry and place it into the sample.
6. Stir the solution thoroughly. When a stable reading is displayed, record the mV value.
7. 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	mg/L	mol/L
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}

Known Addition Technique

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 measurements require that the following 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.

Known Addition Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. 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*

Known Addition Using a Meter with a Known Addition Mode

1. Set up the meter to measure in the known addition mode. See the meter user guide for more specific information.
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.

Known Addition Using a Meter with a Millivolt Mode

1. Set the meter to the 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 the sample and TISAB to a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode with deionized water, blot it dry and place it into the beaker. When a stable reading is displayed, record the actual mV value.
4. Pipette the appropriate amount of standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the mV value. Subtract the first reading from the second reading to calculate ΔE.
6. Use **Table 4** to find the Q value that corresponds to the change in potential, ΔE. To determine the original sample concentration, use the following formula:

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

$C_{standard}$ = 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.

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

$\Delta E = E_2 - E_1$
S = slope of the electrode
p = volume of standard / volume of sample

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**	**-60.1**
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	02.056	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**	**-60.1**
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	0.0155l
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

Titration Techniques

The electrode makes a highly sensitive endpoint detector for titrations of a fluoride-containing sample using lanthanum nitrate as the titrant. With careful technique, titrations can be performed that are accurate to ± 0.2% of the total fluoride concentration of the sample. The sample should be at least 10^{-3} mol/L total fluoride in concentration for a steep and pronounced inflection in the titration curve.

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

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

1. Prepare a 0.1 mol/L lanthanum nitrate solution by dissolving 43.3 g of reagent-grade $La(NO_3)_3 \bullet 6H_2O$ in a 1 L 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 mol/L 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. Modify a the titration template 'Titer with EQP' available in the Tx Excellence or G20 Compact titrator and perform an equivalence point (EQP) titration. The equivalence point is the point of the greatest slope (inflection point) in the titration curve. See **Figure 3**. The volume at the EQP, VEQ is used for the calculation of the titer of the lanthanum nitrate titrant. 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. Modify a the titration template 'EQP' available in the Tx Excellence or G20 Compact titrator and perform an equivalence point (EQP) titration using the standardized lanthanum nitrate titrant.
   The concentration of the sample solution is calculated using the following equation:

R (mol/L) = Q*C/m

where

Q = VEQ*c*TITER

VEQ = Volume at the EQP

c = nominal concentration of the lanthanum nitrate titrant

TITER = Titer of the lanthanum nitrate titrant

C = 1/z, z=3 (equivalent number of lanthanum nitrate)

m = volume of the sample solution

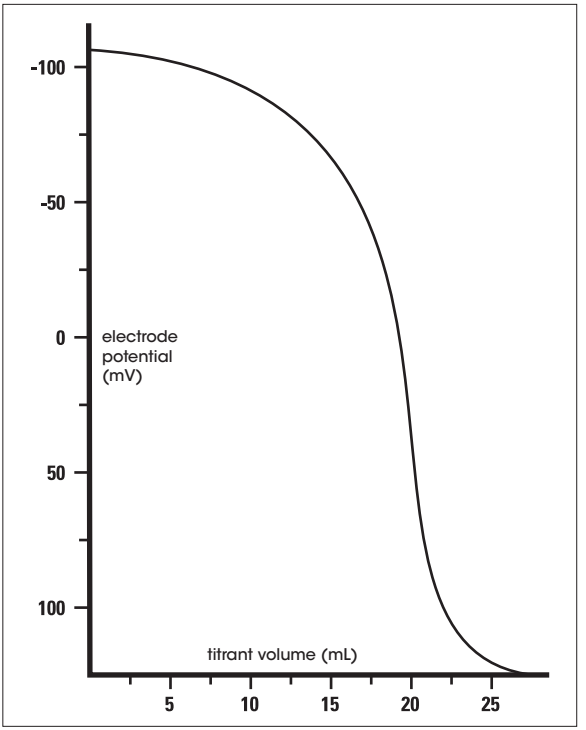


Figure 3 *– Titration of 0.114 mol/L F^- with 0.1 mol/L $La(NO_3)_3$*

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 mg/L 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 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} mol/L 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 mol/L 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 mol/L buffered potassium acetate solution by diluting 2 parts 6.0 mol/L acetic acid (CH_3COOH) with 1 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 mg/L 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 taking measurements (9 parts potassium acetate and 1 part unknown sample).

5. Electrode Characteristics

Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results 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**.

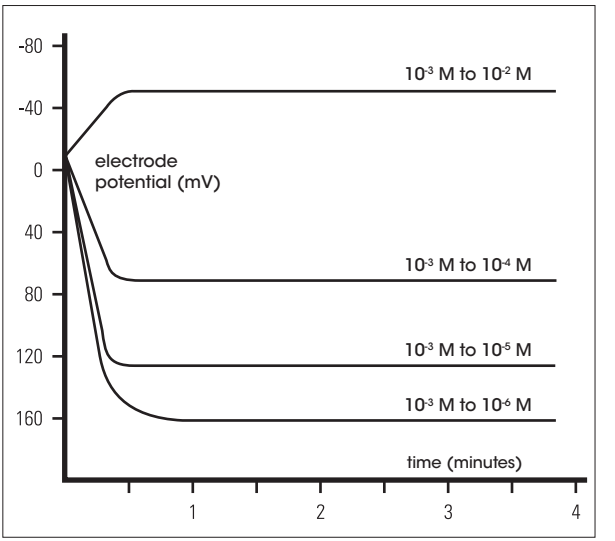


Figure 4 *– Typical Electrode Response To Step Changes in NaF Concentration*

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 ± 2% can be obtained.

Limits of Detection

In neutral solutions, fluoride concentration can be measured down to 10^{-6} mol/L (0.02 mg/L) fluoride. However, care must be taken in making determinations below 10^{-5} mol/L 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 ± 1 °C (± 2 °F) of each other. At the 10^{-3} mol/L fluoride level, a 1 °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.

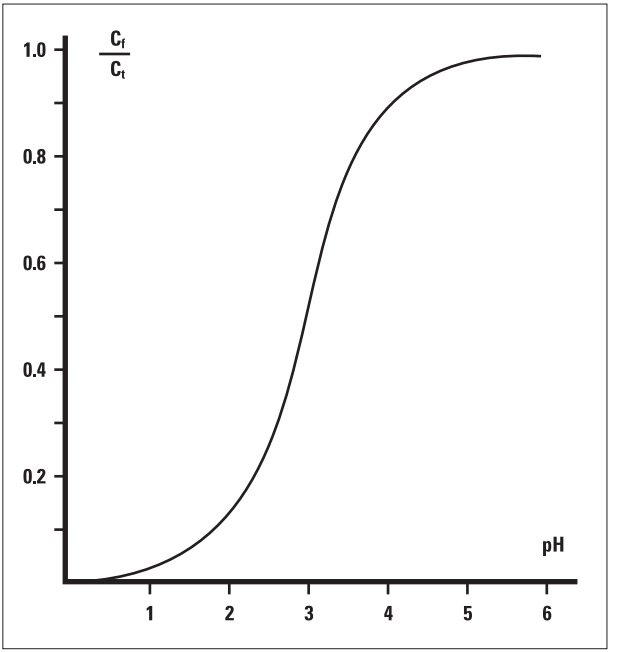


Figure 5 *– Fraction of Free Fluoride as a Function of Solution pH, hydrogen is the only complexing species.*

The electrode can be used at temperatures from 0 to 100 °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 °C.

Table 5 *– Theoretical Slope vs. Temperature Values*

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

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.

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} mol/L or less, there is no hydroxide interference with fluoride measurements. At pH 10, where the hydroxide concentration is 10^{-4} mol/L, there is no error at 10^{-2} mol/L fluoride, about a 10% error at 10^{-4} mol/L fluoride and considerable error at 10^{-5} mol/L 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.

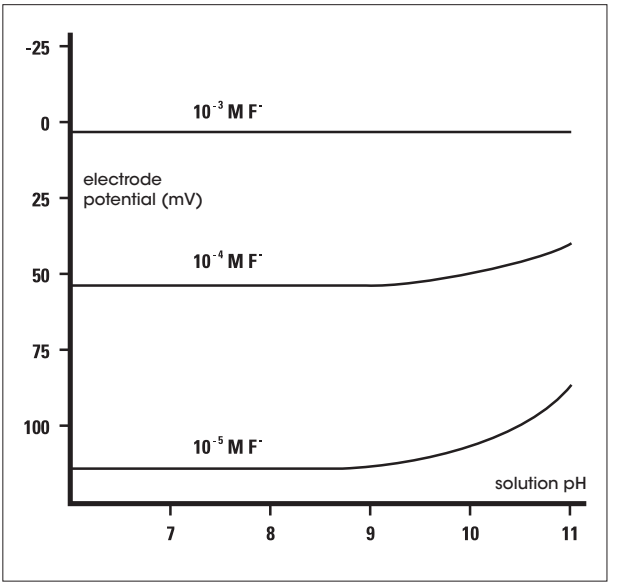


Figure 6 *– Electrode Response in Alkaline Solutions*

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 mg/L fluoride sample, TISAB II or III complexes about 5 mg/L 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.

$$\mathbf{E = E_o + S * \log (A)}$$

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.

$$\mathbf{A = y_i * C_f}$$

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

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

where
C_i = concentration of ion i
Z_i = charge of ion i
$\sum$ symbolizes the sum of all the types of ions in solution

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 the concentration.

Total ionic strength adjustment 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, it is recommended to calibrate in the same pH range as the sample or use a known increment method for ion measurement.

6. 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/Titrator

The meter/titrator is the easiest component to eliminate as a possible cause of error. Consult the meter/titrator 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 passes the procedure, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.
6. 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, analyte addition may solve the problem. If working with low-level samples, follow the procedure in the **Low-level Calibration** section.

Troubleshooting Checklist

- No reference filling solution added – Fill the electrode with filling solution up to the fill hole. Refer to the **Electrode Preparation** section for details.
- Incorrect reference 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.
- 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 **Measurement 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 – Remove air bubble by reimmersing the electrode in solution.
- Electrode not properly connected to meter/titrator – Unplug and reconnect the electrode to the meter/titrator.
- Meter/Titrator or stir plate not properly grounded – Check the meter/titrator and stir plate for proper grounding.
- Static electricity present – Wipe plastic parts on the meter/titrator with a detergent solution.
- Defective meter/titrator – Check the meter/titrator performance. See the meter/titrator user guide.

7. Ordering Information

Parts	Order No.
Combined Fluoride electrode with BNC connector perfectION™ comb F^-:	**51344715**
Combined Fluoride electrode with Lemo connector perfectION™ comb F^- Lemo:	**51344815**
Ion Electrolyte A:	**51344750**
Fluoride Standard Solution 1000 mg/L:	**51344775**
TISAB II with CDTA:	**51344765**
TISAB III concentrate with CDTA:	**51344766**
Removable cone:	**00022986**

8. Electrode Specifications

Membrane type

solid state

Concentration Range

10^{-6} mol/L to saturated
0.02 mg/L to saturated

pH Range

pH 5 to 7 at 10^{-6} mol/L (0.02 mg/L F^-)

Temperature Range

0 to 80 °C continuous use,
80 to 100 °C intermittent use

Electrode Resistance

150 to 200 kΩ

Reproducibility

± 2%

Minimum Sample Size

5 mL in a 50 mL beaker

Size

Body Diameter: 13 mm
Cap Diameter: 16 mm
Cable Length: 1.2 m

* Specifications are subject to change without notice

www.mt.com
For more information

Mettler-Toledo AG
Analytical
Sonnenbergstrasse 74
CH-8603 Schwerzenbach
Switzerland
Phone ++41 (0)44 806 77 11
Fax ++41 (0)44 806 73 50
Internet: www.mt.com

Printed in Switzerland 1001/2.12
ME-51710846