pHOENIX ELECTRODE COMPANY
FLUORIDE ION ELECTRODES
INSTRUCTION MANUAL

GENERAL INSTRUCTIONS

Introduction

The pHoenix Fluoride Ion Electrodes are used to quickly, simply, accurately, and economically measure fluoride ions in aqueous solutions.

Required Equipment

1. A pH/mV meter or an ion meter, either line operated or portable.

2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode.

3. A magnetic stirrer.

4. The pHoenix Fluoride Ion Electrode, Cat. No. F001501 (reference electrode necessary), the pHoenix Fluoride Ion Combination Glass Electrode, Cat. No. F001502, or the pHoenix Fluoride Ion Combination Epoxy Electrode, Cat. No. F001503.

5. The pHoenix Single Junction Reference Electrode, Cat. No. 5731428 (for use with the F001501) with pHoenix Reference Filling Solution, Cat. No. R001011, in the outer chamber.

6. Lab-ware made of plastic, not glass.

7. pHoenix Polishing Paper, Cat. No. 948201, to polish dirty or etched electrode membranes.

Required Solutions

1. Deionized or distilled water for solution and standard preparation.

2. pHoenix Fluoride Standard Solution, 0.1 M NaF, Cat. No. F00AS01. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 4.2 grams of reagent-grade sodium fluoride. Swirl the flask gently to dissolve the solid. Fill the flask to the

mark with distilled water, cap, and upend several times to mix the solution.

3. pHoenix Fluoride Standard, 1000 ppm F^{-1}, Cat. No. F00AS02. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 2.21 grams of reagent-grade sodium fluoride. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.

4. pHoenix Fluoride Standard, 100 ppm F^{-1}, Cat. No. F00AS03. To prepare this solution from you own laboratory stock, half fill a one liter volumetric flask with distilled water and add 0.22 grams of reagent-grade sodium fluoride. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.

5. pHoenix Total Ionic Strength Adjuster Buffer, TISAB 1, Cat. No. F00IS01 (1 Gallon). TISAB 1 is used to adjust the pH of the solution, de-complex fluoride and provide a constant background ionic strength. To prepare this solution from your own laboratory stock, half fill a four liter beaker with distilled water. Place the beaker on a magnetic stirrer, add a large stirring bar, and begin stirring. Slowly add 230 ml of concentrated acetic acid, 232 grams of reagent-grade sodium chloride, and 16 grams of reagent-grade CDTA. After the solids have dissolved, allow the solution to cool to room temperature. Slowly add 150 grams of reagent-grade sodium hydroxide. After the solids have dissolved, allow the solution to cool to room temperature. Calibrate a pH electrode and adjust the pH to 5.25 with small addition of 5 M NaOH. Fill to the mark with distilled water.

6. pHoenix Low Level Total Ionic Strength Adjuster Buffer, TISAB 2, Cat. No. F00IS02 (1 Gallon). Use when measuring in samples containing less than $2X10^{-5}$M (0.4 ppm) fluoride and containing no fluoride complexing agents. To prepare this solution from your own laboratory stock, place about 2000 ml distilled water in a four liter beaker. Add 57 ml glacial acetic acid and 58 grams sodium chloride. Place the beaker on a magnetic stirrer, add a stirring bar and begin stirring. Immerse a calibrated pH electrode into the solution. Slowly add 5 M NaOH until the pH is 5.25. Allow the solution to cool and fill to the mark with distilled water.

7. pHoenix Total Ionic Strength Adjuster Buffer, TISAB 3, Cat. No. F00IS03 (1 Gallon). TISAB 3 will complex more than 100 ppm of aluminum or iron in the presence of 1 ppm fluoride ion. There will be an error of approximately 5% in the measurement of 1 ppm fluoride in the presence of 200 ppm aluminum or iron. To prepare this solution from you own laboratory stock, add about 2000 ml of distilled water to a four liter beaker. Place the beaker on a magnetic stirrer, add a large stirring magnet, and begin stirring. Slowly add 336 ml of concentrated HCl (36-38%), 968 grams of TRIS (hydroxymethylaminomethane) and 920 grams of sodium tartrate ($Na_2C_4H_4O_6\ 2H_2O$). After the solid has dissolved, allow the solution to cool to room temperature. Fill to the mark with distilled water.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber caps covering the electrode tips and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode or the reference electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Connect the electrodes to the proper terminals of the meter as recommended by the meter manufacturer.

Electrode Slope Check (with pH/mV meter)

(check electrodes each day)

1. To a 150 ml plastic beaker, add 50 ml of distilled water and 50 ml of TISAB. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the millivolt mode, lower the electrode tips into the solution.

2. Using a pipet, add 1 ml of 0.1M, 1000 ppm, or 100 ppm fluoride standard to the beaker. When the reading has stabilized, record the mV reading.

3. Using a pipet, add 10 ml of the same fluoride standard used above to the beaker. When the reading has stabilized, record the mV reading.

4. Determine the difference between the two readings. The electrode is operating correctly if the millivolt potential has

changed by 57±2mV, assuming the solution temperature is between 20° and 25°C. See the **TROUBLESHOOTING** section if the potential change is not within this range.

Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

Electrode Slope Check (with ion meter)
(check electrodes each day)

1. Prepare standard fluoride solutions whose concentrations vary by tenfold. Use either the 0.1M, 1000 ppm, or 100 ppm fluoride standard. Use the serial dilution method for this preparation.

2. To a 150 ml beaker, add 50 ml of the lower value standard and 50 ml of TISAB. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. Assure that the meter is in the concentration mode.

3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.

4. Rinse the electrodes with distilled water and blot dry.

5. To another 150 ml beaker, add 50 ml of the higher value standard and 50 ml of TISAB. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.

6. Adjust the meter to the concentration of the standard and fix the value in the memory.

7. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the **TROUBLESHOOTING** section if the slope is not within this range.

MEASUREMENT

Measuring Hints

All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in a 2% measurement error.

Constant, but not violent, stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulating material, such as a styrofoam sheet, between the stirrer and the beaker.

Always rinse the electrodes with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

For samples with high ionic strength, prepare standards whose composition is similar to the sample.

Always check to see that the membrane is free from air bubbles after immersion into standard or sample.

Sample Requirements

All samples must be aqueous and not contain organics which can dissolve the epoxy electrode body and/or the cement bonding the sensing crystal to the electrode body. Inorganic solutions will not affect the electrode. Infrequent measurements in solutions containing methanol, acetone, or dioxane are permitted. Highly polar solvents, such as $CHCl_3$ or DMF, should not be contained in the samples. Please check with pHoenix Electrode Company before using the electrode in other organic solvents.

The addition of TISAB to samples and standards will adjust the pH to 5.0-5.5. Samples must be above pH 5 to avoid forming complexes with hydrogen ions and below pH 7 to avoid interference by hydroxide ions.

The temperature of the standard solutions and of the sample solutions should be the same and below 80°C.

The use of TISAB 1 also preferentially forms complexes with aluminum and with iron, breaking the complexes that fluoride forms with these ions. With 1 ppm fluoride present, up to 3-5 ppm aluminum or iron is complexed. If higher levels of aluminum or iron are present, use TISAB 3.

Units of Measurement

Fluoride concentrations are measured in units of ppm as fluoride, moles per liter, or any other convenient concentration unit. Table

1 indicates some concentration units and conversion factors.

TABLE 1: Concentration Unit Conversion Factors

ppm F^{-1}	moles/liter
190.0	$1.0X10^{-2}M$
19.0	$1.0X10^{-3}M$
1.9	$1.0X10^{-4}M$

MEASUREMENT PROCEDURE

Direct Measurement

Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with TISAB for all fluoride solutions. The temperature of both sample solution and standard solution should be made the same.

Direct Measurement of Fluoride (using a pH/mV meter)

1. By serial dilution, prepare three standard solutions from the 0.1M, 1000 ppm, or the 100 ppm stock standard. The resultant concentrations should be $10^{-2}M$, $10^{-3}M$, and $10^{-4}M$ or 100, 10, and 1 ppm. Add 50 ml of TISAB 1 or TISAB 3 to each 50 ml of standard. When calibrating, assume that the added TISAB has no effect on the standard concentration.

2. Place the most dilute solution on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution. After the reading has stabilized, record the mV reading.

3. Place the mid-range solution on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry, and immerse the electrodes in the solution. When the reading has stabilized, record the mV value.

4. Place the most concentrated solution on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry, and immerse the electrodes in the solution. When the mV reading has stabilized, record the mV value.

5.

Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). Extrapolate the curve down to about 1.0X1^{-5}M. A typical calibration curve can be found in Figure 1.

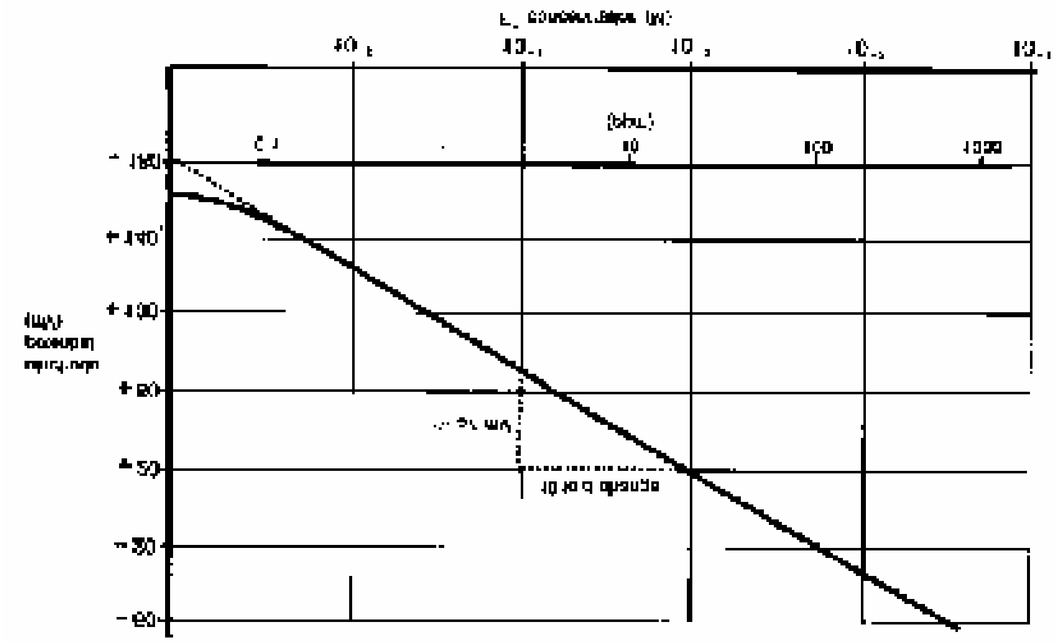


Figure 1
Typical fluoride electrode calibration curve

A calibration curve is constructed on semi-logarithmic paper when using the pH/mV meter in the millivolt mode. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedures.

6.

To a clean, dry, 150 ml plastic beaker, add 50 ml of sample and 50 ml of TISAB 1 or TISAB 3. Place the beaker on the magnetic stirrer and begin stirring. Rinse the electrodes with distilled water, blot dry, and lower the electrode tips into the solution. When the reading has stabilized, record the mV reading. Using the calibration curve, determine the sample concentration.

7. The calibration should be checked every 1-2 hours. Assuming no change in ambient temperature, place the electrode tips in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

Direct Measurement of Fluoride (using an ion meter)

1. By serial dilution of the 0.1M, 1000 ppm, or 100 ppm fluoride standard, prepare two fluoride standards whose concentration is near the expected sample concentration. Add 50 ml of TISAB 1 or TISAB 3, to each 50 ml of standard. When calibrating, assume that the added TISAB has no effect on the standard concentration.

2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.

3. Lower the electrode tips into the solution.

4. Adjust the meter to the concentration of the fluoride standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

5. Rinse the electrodes with distilled water and blot dry.

6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.

7. Lower the electrode tips into the solution.

8. Adjust the meter to the concentration of the fluoride standard and fix the value in the memory according to the manufacturer's instructions after stabilization of the reading.

9. For low level measurements, place the rinsed, dried electrodes into a solution containing equal volumes of distilled water and TISAB 1 or TISAB 3 (or add 10 ml of TISAB-2 to each 100 ml of distilled water). After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.

10. After rinsing the electrodes and blotting dry, place the electrode tips into the sample diluted with an equal volume of TISAB 1 or TISAB 3. After stabilization, read the concentration directly from the meter display.

11. The calibration should be checked every 1-2 hours. Assuming no change in ambient temperature, place the electrode tips in the first fluoride standard. After the reading has stabilized, compare it to the original reading in Step 4 above. A reading differing by more than 0.5 mV or a change in ambient temperature will necessitate repetition of Steps 2-8 (2-9) above. The meter should be re-calibrated daily.

Direct Measurement of Fluoride in Water (ASTM D1179, METHOD B)

The procedure is used to determine total fluoride concentration in water in ppm. TISAB is added to standards and to samples in order to break fluoride complexes of iron and aluminum, adjust the pH, and provide a constant ionic strength. Fluoride sample concentration is determined, using this method, independent of the level or nature of dissolved minerals.

Prepare 2, 1, and 0.5 ppm fluoride standards by serial dilution of the 100 ppm fluoride standard. To each 50 ml of standard, add 50 ml of TISAB 1 or TISAB 3. Calibrate the meter as previously described by using the 2, 1, and 0.5 ppm standards. The calibration curve should be drawn on semi-logarithmic 2-cycle graph paper or use an ion meter.

Direct Measurement of Fluoride in Acid Solutions

Hydrogen ion complexes a portion of the fluoride ion in solutions with a pH below 5, forming HF or HF_2^{-1}, which cannot be detected by the electrodes. Adjustment to weakly acidic/weakly basic range before making the fluoride determination is necessary, but not with strongly basic solutions. The use of sodium acetate buffers the pH above 5 and helps fix the total ionic strength of standards and samples to the same level.

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

2. Prepare a blank solution containing all components of the sample except fluoride. This solution will be used to prepare standards.

3. Add fluoride to the blank solution to prepare standards in the concentration range of the unknown solutions. If using a standard pH/mV meter, prepare three standards and a calibration curve as previously described. If an ion meter is used, only two standards are necessary. Add 9 parts of sodium acetate to each 1 part of standard. Fresh standards should be prepared every two weeks if the standard contains less than 10 ppm fluoride.

4. Calibrate the electrodes as described in the section **Electrode Slope Check.**

5. After diluting each unknown sample 10:1 with sodium acetate (as in 3 above), measure the mV potential and determine the fluoride concentration.

Direct Measurement of Fluoride in Alkaline Solutions

Hydroxide ions interfere with fluoride measurements in basic solutions with a low fluoride content. At a fluoride concentration less than $1.0X10^{-4}M$ and at a pH of 9.5 or above, the electrode potential reading, caused by the concentration of both hydroxide and fluoride ions, is higher than it would be if fluoride alone were present. (See section entitled **pH Effects.**)

Using a 4M buffered potassium acetate solution to adjust the pH to between 5 and 6 eliminates hydroxide ion error and raises the total ionic strength of both standards and samples to the same value. The fluoride ion concentration can be determined in the usual manner after both standards and samples are diluted 10:1 with the buffer solution.

1. To prepare a 4M buffered potassium acetate solution, add one part of distilled water, slowly, to two parts of 6M acetic acid, CH_3COOH, in a large beaker surrounded by a water bath. Slowly add 50% KOH solution to the acetic acid mixture, with constant stirring, until a pH of 5 is reached. Prepare enough buffer to dilute all standards and samples 10:1.

2. Following the directions given in the preceding section (**Determination of Fluoride in Acid Solutions**), prepare standards, calibrate the electrodes and measure the unknown samples.

Low Level Fluoride Measurements (using a pH/mV meter)

Use the following low level fluoride measurement procedure in the non-linear portion of the calibration curve. (See Figure 1.) This procedure is used for fluoride samples containing less than 2X10^{-5}M or 0.4 ppm fluoride and containing no fluoride complexing agents. Use low level TISAB 2 for both samples and standards. A longer response time should be expected for low level fluoride measurements.

1. By serial dilution, prepare a 1.0X10^{-3}M or 10 ppm fluoride standard by diluting the 0.1M, 1000 ppm, or 100 ppm standard solution. Add 50 ml low level TISAB 2 to 50 ml of standard solution.

2. Using a 150 ml beaker, add 50 ml of distilled water and 50 ml of low level TISAB 2. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. Assure that the meter is in the mV mode.

3. Increments of the standard should be added to the beaker according to the steps outlined in Table 2 below. After the reading stabilizes, record the mV reading for each addition.

TABLE 2: Low Level Measurement Calibration Curve

STEP	PIPETTE	ADDED VOLUME (ml)	CONCENTRATION ppm	CONCENTRATION M
1	A	0.1	0.01	1.0X10^{-6}
2	A	0.1	0.02	2.0X10^{-6}
3	A	0.2	0.04	4.0X10^{-6}
4	A	0.2	0.06	6.0X10^{-6}
5	A	0.4	0.10	1.0X10^{-5}
6	B	2.0	0.29	2.9X10^{-5}
7	B	2.0	0.48	4.8X10^{-5}

Pipet A = 1 ml graduated pipet
Pipet B = 2 ml pipet
Solutions: additions of standard/TISAB 2 to 50 ml of distilled water and 50 ml of low level TISAB 2.

4. On semi-logarithmic graph paper, plot the concentration (log axis) against the millivolt reading (linear axis) as in Figure 1. Keep the final solution for checking the electrode calibration.

5. To a 150 ml plastic beaker, add 50 ml of sample and 50 m

l of low level TISAB 2. Place the beaker on a magnetic stirrer and begin stirring. After rinsing the electrodes and blotting dry, place the electrode tips into the solution. After stabilization of the reading, read the mV potential and determine the concentration from the calibration curve. A new low level calibration curve should be prepared daily using fresh standards.

Low Level Fluoride Determination (using an ion meter)

Follow the previous procedure for fluoride measurements with an ion meter, except use low level TISAB 2 instead of TISAB 1 or TISAB 3. Always use the blank correction.

Titration

Titration is a very accurate determination of fluoride. The pHoenix Fluoride Ion Electrodes can be used as highly sensitive endpoint detectors for titrations of a fluoride-containing sample. Though titrations are more time consuming than direct ion measurements, the results are more accurate and reproducible. Titrations accurate to ±0.2% of the total fluoride concentration of the sample can be performed using lanthanum nitrate as the titrant. Total fluoride concentration should be at least $1.0X10^{-3}$M for endpoint detection. Low results are given if aluminum, iron, or trivalent chromium are present at a level of 1% or higher.

Special titration procedures for aluminum, lithium, lanthanum, and thorium also makes use of the fluoride electrode as an endpoint indicator.

Titration Procedure for Fluoride Determination

1. Dissolve 43.3 grams of reagent grade lanthanum nitrate, $La(NO_3)_3 \cdot 6H_2O$, in about 500 ml distilled water in a 1 liter volumetric plastic flask. Fill to the mark with distilled water. This 0.1M lanthanum solution will be used for all titrations.

2. Using the 0.1M fluoride standard, standardize the lanthanum nitrate by titration. To a 150 ml plastic beaker, add approximately 9.0 ml of fluoride standard (accurately measured) and about 50 ml of distilled water. Place the beaker on the magnetic stirrer and begin stirring. Lower the electrode tips into the solution.

3. Using a 10 ml plastic burette, add the $La(NO_3)_3$ titrant in 0.5-1.0 ml increments. Record the mV reading against the volume of titrant added. As the mV potential change increases, add smaller increments, down to 0.1-0.2 ml increments. Continue to add titrant and record the mV potential against the volu

me until little change is noted in the mV reading even when adding 0.5-1.0 ml increments.

4. Using linear graph paper, plot the mV readings (y-axis) against the volume (x-axis). The end-point is determined as the steepest slope on the titration curve. Record the endpoint.

$\overset{o}{V}_t$

5. To a 150 ml plastic beaker, add approximately 9.0 ml of sample solution (accurately measured) and about 50 ml of distilled water. Place the beaker on a magnetic stirrer and begin stirring. Lower the rinsed, dried electrode tips in the solution.

6. Titrate the sample as in step 3 above. The endpoint is denoted as $\overset{x}{V}_t$

Calculate the sample concentration, C_s

$$\overset{x}{C}_s \quad \frac{\overset{x}{V}_t \; \overset{o}{V}_f}{\overset{o}{V}_t \; \overset{x}{V}_f} \; . \; 2\overset{o}{C}_s$$

where:

$\overset{x}{C}_s$ = concentration of sample

$\overset{o}{C}_s$ = fluoride standard concentration (0.1M)

$\overset{x}{V}_t$ = volume of titrant added to achieve the endpoint of unknown sample

$\overset{o}{V}_t$ = volume of titrant added to achieve the endpoint in standardization

$\overset{x}{V}_f$ = volume of sample used in sample titration

$\overset{o}{V}_f$ = volume of standard used in standardization titration.

A typical titration curve is shown in Figure 2.

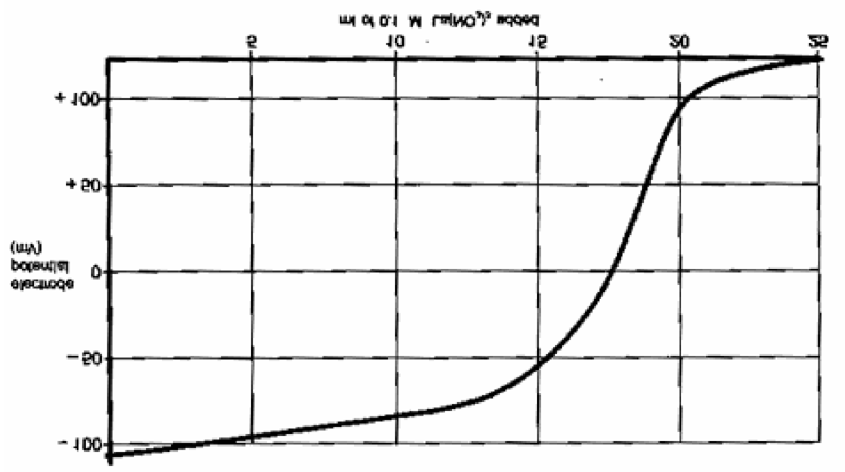


Figure 2
Titration of 25 ml of 0.112 M F- with 0.100 M of La(NO3)3

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to ±2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, noise, and variations in illumination limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

Interferences

The hydroxide ion, OH^{-1}, is an electrode interference. Anions which make the sample more basic, such as CO_3^{-2} or PO_4^{-3} would increase the OH^{-1} interference, but do not interfere with direct electrode operation. Other anions commonly associated with fluoride, such as Cl^{-1}, Br^{-1}, I^{-1}, SO_4^{-2}, HCO_3^{-1}, NO_3^{-1}, and acetate, do not interfere with correct electrode operation. Most cations do not interfere with the response of the fluoride electrode to fluoride ion.

Complexation

Hydrogen ion, as well as some other multivalent cations, aluminum, silicon, iron+3, will form complexes with fluoride. The total ionic strength of the solution, the pH of the solution, the total fluoride concentration, and the concentration of the complexing agent all contribute to the degree of complexation. TISAB 1 and TISAB 2 complex about 5 ppm aluminum or iron in a 1 ppm fluoride solution. TISAB 3 complexes higher levels of iron and aluminum.

Temperature Influences

Samples and standards should be within ±1°C of each other, since electrode potentials are influenced by changes in temperature. Because of solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 3 gives values for the "S" factor in the Nernst equation for the fluoride ion.

TABLE 3: Temperature vs. Values for the Electrode Slope

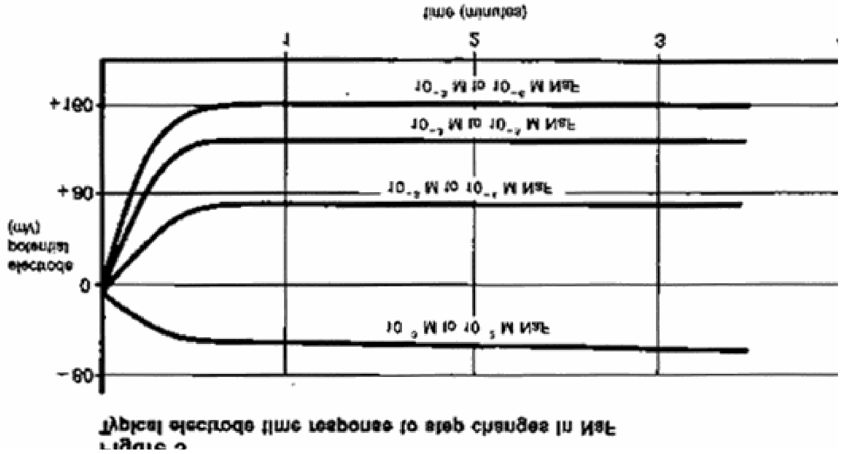
Temp (°C)	"S"
0	54.20
10	56.18
20	58.18
25	59.16
30	60.15
40	62.13
50	64.11

The temperature range for the pHoenix Fluoride Ion Electrodes is 0° - 80°C, provided that temperature equilibrium has occurred. Only intermittent use is recommended at temperatures from 80°-100°C. If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

Electrode Response

Plotting the electrode mV potential against the fluoride concentration on semi-logarithmic paper results in a straight line with a slope of about 57 mV per decade. (Refer to Figure 1.)

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from one minute or less in highly concentrated solutions to several minutes near the detection limit. (Refer to Figure 3.)



Typical electrode time response to step changes in NaF

A drifting potential reading or a decrease in electrode slope may mean that the electrode membrane needs polishing.

To polish the membrane:

1. If using polishing paper, cut off a 1-2" piece and place it face up on the lab bench.
2. Put a few drops of distilled or deionized water in the center of the paper.
3. Holding the paper (cotton) steady with one hand, bring the membrane of the electrode down perpendicular to the paper and, with a slight swirling motion, gently polish the tip of the electrode against the surface of the polishing paper (cotton) for a few seconds.
4. Rinse the electrode surface with distilled or deionized water and soak the electrode tip in standard solution for about five minutes before use.
5. If using jeweller's rouge, place a cotton ball on the table top and flatten it using the bottom of a beaker.
6. Put 1-2 drops of distilled or deionized water in the center of the cotton pad.
7. Add a small amount of jeweller's rouge to the damp cotton.
8. Continue with Steps 3 and 4 above.

Limits of Detection

Fluoride concentration down to $1.0\text{X}10^{-6}$M (0.02 ppm) fluoride can be measured in neutral solutions. Since sample contamination can be a factor in low level fluoride measurements, care must be taken in making determinations below $1.0\text{X}10^{-5}$M. The upper limit of detection is a saturated fluoride solution.

pH Effects

Hydrogen complexes a portion of fluoride in solution, forming the un-dissociated acid HF and the ion HF_2^{-1} in acid solutions with a pH below 5. The proportion of free fluoride ion in acid solutions is shown in Figure 4.

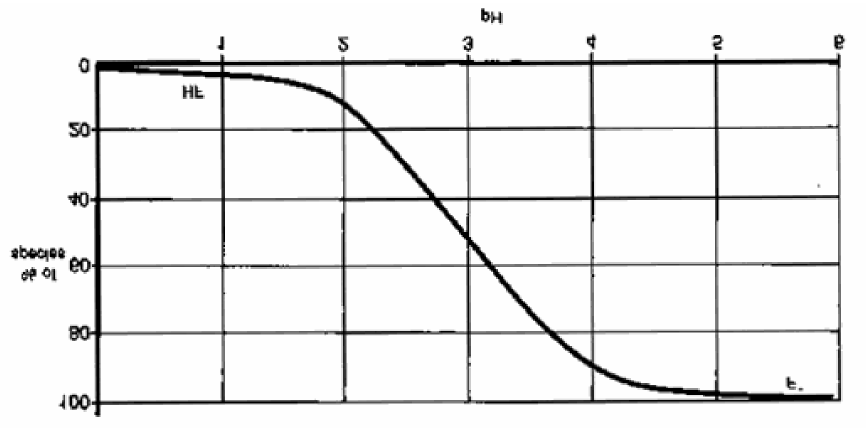


Figure 4
Function of free F- as a function of solution pH, where hydrogen is the only complexing species

When the level of hydroxide is greater than one-tenth the level of fluoride ion present, hydroxide ion interferes with electrode response to fluoride. As an example, no hydroxide interference with fluoride measurements take place at pH 7 when the hydroxide concentration is $1.0X10^{-7}$ or less. As the pH increases, the hydroxide interference becomes appreciable. At pH 10, the hydroxide ion concentration is $1.0X10^{-4}$M and no error is found in measurements of $1.0X10^{-2}$M fluoride. At the same hydroxide ion concentration and a fluoride concentration of $1.0X10^{-4}$M, about a 10% measurement error appears. At a fluoride concentration of $1.0X10^{-5}$M, considerable error exists in a pH 10 solution. Figure 5 illustrates these errors.

The addition of TISAB 1 or TISAB 2 to all fluoride samples and standards buffers the pH between 5.0-5.5 to help avoid hydroxide interferences or the formation of hydrogen complexes of fluoride. TISAB 3 adjusts the pH to about 8.5 and should not be used for very low level measurements.

Electrode Life

The fluoride electrode will last six months in normal laboratory use. On-line measurements might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and electrode replacement is required.

Electrode Storage

The fluoride electrode may be stored for short periods of time in 1.0X10^{-2}M fluoride solution with TISAB added. For longer storage (longer than two weeks), rinse and dry the sensing pellet and cover the membrane tip with any protective cap shipped with the electrode. The reference portion of the combination electrode (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole. The fluoride electrode should never be stored in distilled water.

ELECTRODE THEORY

Electrode Operation

The pHoenix Fluoride Ion Electrodes consist of a single crystal of lanthanum fluoride as the membrane, bonded into a glass or an epoxy body. Only fluoride ions are mobile in the ionic conductor crystal. When the membrane comes in contact with a solution containing fluoride ions, a potential develops across the membrane. This potential is measured against an external (or internal) constant reference potential with a standard pH/mV meter or an ion meter and depends on the level of free fluoride ions in the solution. The Nernst equation describes the level of fluoride ions in the solution corresponding to the measured potential:

$$E = E_o - S \log X$$

where: E = measured electrode potential
E_o = reference potential (a constant)
S = electrode slope (~57 mV/decade)
X = level of fluoride ions in solution

The activity, X, represents the effective concentration of free fluoride ions in the solution. Total fluoride concentration, Ct, may include some bound as well as free fluoride ions. Since the electrode only responds to free ions, the concentration of the free ions, Cf, is found by:

$$Cf = Ct - Cb$$

where Cb represents the concentration of all bound or complexed fluoride ions.

The activity is related to the free ion concentration, Cf, by the activity coefficient, a, by:

$$X = aC_f$$

Activity coefficients vary, depending on total ionic strength, I, defined as:

$$I = 1/2 \, \Sigma \, C_x Z_x^2$$

where: C_x = concentration of ion X
Z_x = charge of ion X
Σ = sum of all of the types of ions in the solution

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient, a, is constant and the activity, X, is directly proportional to the concentration.

All samples and standards containing fluoride ions have TISAB added so that the background ionic strength is high and constant relative to variable concentrations of fluoride. The recommended ISA for the fluoride electrode is TISAB though similar solutions can be used as long as they do not contain ions that would interfere with the electrode's response to fluoride.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the inter-diffusion of ions in the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solution diffuse into the sample should be equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the plastic-ware, the electrodes, the standards & reagents, the sample, and the technique.

Meter

The meter may be checked by following the check-out procedure in the instrument instruction manual.

Plastic-ware

Clean plastic-ware is essential for good measurement. Be sure to wash the plastic-ware well with a mild detergent and rinse very well with distilled or deionized water.

Electrodes

The electrodes may be checked by using the procedure found in the sections entitled **Electrode Slope Check**.

1. Be sure to use distilled or deionized water when following the procedures given in **Electrode Slope Check**.

2. If the electrode fails to respond as expected, see the sections **Measuring Hints** and **Electrode Response**. Repeat the slope check.

3. If the electrodes still fail to respond as expected, substitute another fluoride ion electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.

4. If the problem persists, the reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. (See **Standards & Reagents**, **Sample**, and **Technique** sections below.)

5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:

- Clean and rinse the electrodes thoroughly.
- Prepare the electrodes properly.
- Use the proper filling solution.
- Adjust the pH and the ionic strength of the solution by the use of the proper TISAB.
- Measure correctly and accurately.
- Review **TROUBLESHOOTING HINTS**.

Standards & Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the standard and reagent solutions. If in doubt about the credibility of any of the solutions, prepare them again. Errors may result from contamination of the TISAB, incorrect dilution of standards, poor quality distilled/deionized water, or a simple mathematical miscalculation.

Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode (or the reference electrode) if the electrodes work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. (See **Measuring Hints**, **Sample Requirements**, and **Interferences.**)

Technique

Be sure that the electrode's limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample.

Refer to the instruction manual again. Reread **GENERAL PREPARATION** and **ELECTRODE CHARACTERISTICS**.

If trouble still persists, call pHoenix Electrode Company at 1-800-522-7920 and ask for the Technical Services Department.

TROUBLESHOOTING HINTS

Symptom	**Possible Causes**	**Next Step**
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	electrodes not plugged in properly	unplug electrodes and reseat
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove bubble by re-dipping electrode
	electrodes not in solution	put electrodes in solution
Noisy or Unstable Readings (readings continuously or rapidly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by re-dipping electrode
	TISAB not used	use recommended TISAB
	meter or stirrer not grounded	ground meter or stirrer
	defective electrode	replace electrode
	electrode exposed to interferences	soak electrode in fluoride standard with added TISAB
Drift (reading slowly changing in one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	electrode exposed to complexing agents	check section entitled **Complexation**

	incorrect reference filling solution	use recommended filling solution
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	TISAB not used	use recommended TISAB
	standard used as TISAB	use TISAB
	electrode exposed to complexing agents	check section entitled **Complexation**
	air bubble on membrane	remove bubble by re-dipping probe
"Incorrect Answer" (but calibration curve is good)	incorrect scaling of semi-log paper	plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
	incorrect sign	be sure to note sign of millivolt number correctly
	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: 10^{-3}M = 19 ppm as F^{-1}
	complexing agents in sample	check section entitled **Complexation**

SPECIFICATIONS

Concentration Range: saturated solutions to $1.0\text{X}10^{-6}$M
(saturated solutions to 0.02 ppm)

pH Range: 5 to 7 at $1.0\text{X}10^{-6}$M F^{-1} (0.02 ppm F^{-1})
5 to 11 at $1.0\text{X}10^{-1}$M F^{-1} (1900 ppm F^{-1})

Temperature Range: 0° to 80°C
(80° to 100°C intermittent use)

Resistance: 150-200 kohm

Reproducibility: ±2%

Size: 110 mm length
12 mm diameter
1 m cable length

Storage: in fluoride standard with TISAB added

ORDERING INFORMATION

P/N	DESCRIPTION
FO01501	Fluoride Ion Electrode, mono (reference electrode necessary), epoxy body
FO01502	Fluoride Ion Electrode, combination, glass body
FO01503	Fluoride Ion Electrode, combination, epoxy body
5731428	Reference Electrode, single junction, sleeve, epoxy body, for use with the FO01501
FO0AS01	Fluoride Standard, 0.1M NaF
FO0AS02	Fluoride Standard, 1000 ppm F^{-1}
FO0AS03	Fluoride Standard, 100 ppm F^{-1}
FO0IS01	TISAB 1
FO0IS02	TISAB 2
FO0IS03	Low Level TISAB 3
R001011	Reference Electrode Filling Solution, 4 M KCl/Ag+, for the 5731428, FO01502 inner chamber, and FO01503 outer chamber
R001013	Reference Electrode Filling Solution, 4 M KCl, for the FO01502 outer chamber
948201	Polishing Paper for the Fluoride Electrodes

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