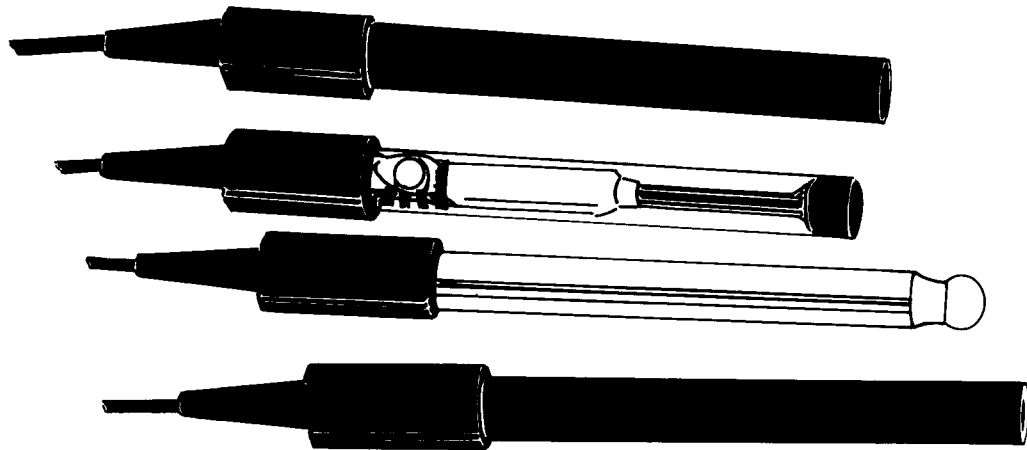


ISE-8790 & ISE-8795

Fluoride Ion Selective Electrodes



Operator's Manual
M0780/0892



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SECTION 1 GENERAL DESCRIPTION

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

SECTION 2 PREPARATION FOR MEASUREMENT

2.1 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 OMEGA Fluoride Ion Electrode, ISE-8790, (reference electrode necessary) or the Fluoride Combination Electrode, ISE-8795.
5. The Reference Electrode, PHE-3217, to be used with ISE-8790.
6. Labware made of plastic (not glass).

2.2 REQUIRED SOLUTIONS

1. Deionized or distilled water for solution and standard preparation.
2. Fluoride Standard Solution, 0.1 M, ISE-8790-SSI, 100 ppm, ISE-8790-SS2.
3. Total Ionic Strength Adjustor Buffer (TISAB-1), ISE-8790-RI, or Ionic Strength Adjustor Buffer (TISAB-2) ISE-8790-R2, is used to adjust the pH of the solution, decomplex fluoride and provide a constant background ionic strength. To each 50 mL of sample or standard, add some of the TISAB-1 or TISAB-2.
4. Low level TISAB to use when measuring in samples containing less than 2×10^{-5} M (0.4ppm) fluoride and containing no fluoride complexing agents.

To prepare TISAB -2 (low level) from your own laboratory stock, fill a 1 liter volumetric flask about half full of distilled water. While gently swirling the flask, slowly add 57mL of glacial acetic acid. Add 58 grams of sodium chloride to the flask. Put the flask into a water bath and slowly add 5M NaOH, swirling the solution gently after each incremental addition and replacing in the water bath. When the meter to which the pH electrode is connected reads 5.0-5.5 pH, stop adding the NaOH and allow the flask to cool to room temperature. Dilute to the mark with distilled water, taking care to rinse down the neck of the flask well during the addition. Use analytical grade reagents for all solution preparations.

5. TISAB-1 will complex more than 100ppm of aluminum or iron in the presence of 1ppm 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 TISAB-1 from your own laboratory stock, add about 500 mL of distilled water to a liter beaker. Place the beaker on a magnetic stirrer, add a large stirring bar, and begin stirring. Slowly add 84 mL of concentrated HCl (36-38%, 242 grams of TRIS (hydroxymethyl) amino methane, and 230 grams of sodium titate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$). After the solid has dissolved, allow the solution to cool to room temperature. Quantitatively transfer the solution to a 1 liter volumetric flask and fill to the mark with distilled water. Combine equal volumes of TISAB-1 and standard or sample before measurements.

2.3 ELECTRODE PREPARATION

Remove the rubber cap covering the electrode tip and the rubber band covering the filling hole of the reference electrode.

Connect the electrode to the proper terminals as recommended by the meter manufacturer.

NOTE

Do not be alarmed if white crystals form at end of electrode. This is normal with pH electrodes. These crystals are potassium chloride. Remove the shipping cap and rinse with distilled water to dissolve the crystals.

2.3.1 Electrode Slope Check

Check the electrode on a daily basis. To a 150mL plastic beaker, add 50 mL of distilled water and 50 mL of TISAB-1 or 90 mL of distilled water and 10 mL of TISAB-2. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution.

Using a pipet, add 1 mL of 0.1M or 100 ppm standard to the beaker. Adjust the meter to 0mV.

Again using a pipet, add 10 mL of the same standard to the beaker. After the reading has stabilized, record the mV reading. The electrode is operating correctly if the mV potential has changed by 56 ± 2 mV, assuming the solution temperature is between 10° 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 ten.

SECTION 3 MEASUREMENT PROCEDURE

3.1 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 styrofoam sheet or asbestos sheet, between the stirrer and the beaker.

Inorganic solutions will not affect the electrode. Infrequent measurements in solutions containing methanol, acetone, or dioxane are permitted. Highly polar solvents, such as chloroform, or DMF, should not be contained in the samples.

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 hydrogen ions.

The use of TISAB 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 are present, use TISAB-1.

3.2 UNITS OF MEASUREMENT

Fluoride is measured in units of ppm as fluoride, moles per liter, or any other convenient concentration unit. Table 3-1 indicates some concentration units and conversion factors.

TABLE 3-1
CONCENTRATION UNIT CONVERSION FACTORS

<u>ppm(F⁻)</u>	<u>moles/liter</u>
190	1.0 X 10 ⁻²
19	1.0 x 10 ⁻³
1.9	1.0 X 10 ⁻⁴

3.3 MEASUREMENT PROCEDURES

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. The temperature of both sample solutions and standard solutions should be the same.

Titration is a very accurate determination of fluoride. This method makes use of the electrode as an end-point detector, using lanthanum nitrate as the titrant. Special titration procedures for aluminum, lithium, lanthanum, and thorium also makes use of the fluoride electrode as an end-point indicator.

3.3.1 Direct Measurement (using standard pH/mV meter)

1. By serial dilution prepare three standard solutions from the 0.1M or from the 100 ppm stock standard. The resultant concentrations should be 10^{-2} , 10^{-3} , and 10^{-4} or 100, 10, and 1 ppm. To each solution, add 50mL of TISAB-1 or 5mL TISAB-2, to each 50mL of standard. When calibrating, assume that the added TISAB has no effect on the standard concentration.
2. Place the midrange 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. Adjust the meter to zero mV.
3. Rinse the electrode with distilled water, blot dry, and lower the electrode into the most dilute standard solution. After the reading has stabilized, record the mV value.
4. Rinse the electrode with distilled water, blot dry, and lower the electrode into the most concentrated standard solution. After the mV reading has stabilized, record the mV value.
5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against concentration (log axis). A typical calibration curve can be found in Figure 3-1. Extrapolate the calibration curve down to about 2.0×10^{-5} M or 0.4 ppm.
6. To clean, dry, 150 mL plastic beaker, add 50 mL of the sample and 50 mL of TISAB-1, or 5 mL or TISAB-2.
7. Place the beaker on the magnetic stirrer and begin stirring. Rinse the electrode with distilled water, blot dry, and lower the electrode tip into the solution. After the reading has stabilized, record the mV reading. Using the calibration curve, determine the sample concentration.
8. The calibration should be checked every 1-2 hours. Assuming no change in ambient temperature, place the electrode tip in the midrange standard. After the reading has stabilized, compare it to the original reading recorded in Step 2. 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.

3.3.2 Direct Measurement (using an ion meter)

1. By serial dilution of the 0.1M or of the 100 ppm fluoride standards, prepare two standards whose concentration is near the expected sample concentration. Add 50mL of TISAB-1 or 5mL of TISAB-2 to each 50mL 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. Assure that the meter is in the concentration mode.
3. Lower the electrode tip into the solution.
4. Adjust the meter to the fluoride concentration in the standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
5. Rinse the electrode with distilled water and blot dry.
6. Place the most concentrated fluoride standard on the magnetic stirrer and begin stirring at a constant rate.
7. Lower the electrode tip 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 measurement, place the rinsed, dried electrodes into a solution containing equal volumes of distilled water and TISAB-1 or add 10mL of TISAB-2 to each 100mL of distilled water. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.
10. After rinsing the electrode and blotting dry, place the electrode tip into the sample diluted with an equal volume of TISAB-1 or add 5mL of TISAB-2 to 50mL of sample. 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 tip in the first fluoride standard. After the reading has stabilized, compare it to the original reading in Step 4. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-8 (2-9). The meter should be re-calibrated daily.

3.3.3 LOW LEVEL FLUORIDE DETERMINATION

Use the following low level fluoride measurement procedure in the non-linear portion of the calibration curve. Refer to Figure 3-1. This procedure is used for fluoride samples containing less than 2.0×10^{-5} or 0.4 ppm fluoride and containing no fluoride complexing agents.

Use low level TISAB for both samples and standards. A longer response time should be expected for low level fluoride measurements.

For low level determinations using an ion meter, follow the previous procedure for fluoride measurements with an ion meter, except use low level TISAB instead of TISAB-1. Always use the blank correction.

For low level determinations using a standard pH/mV meter:

1. Prepare low level TISAB as described in Section 2.2.
2. By serial dilution, prepare a 10^{-3} or 10ppm fluoride standard by diluting the 0/.1M or the 100 ppm standard solution. Add 50mL low level TISAB to 50mL of standard solution.
3. Using a 150mL plastic beaker, add 50mL of distilled water and 50mL of low level TISAB. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution. Assure that the meter is in the mV mode.
4. Increments of the standard should be added to the beaker according to the steps outlined in Table 3-2 below. After the reading stabilizes, record the mV reading for each addition.
5. Plot the concentration (log axis) against the concentration (linear axis) as in Figure 3-1. Keep the final solution for checking the electrode calibration.
6. To a 150mL plastic beaker, add 50mL of sample and 50mL of low level TISAB. Place the beaker on the magnetic stirrer and begin stirring. After rinsing the electrode and blotting them dry, place the electrode tip in 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.

TABLE 3-2
LOW LEVEL MEASUREMENT CALIBRATION CURVE

STEP	PIPET	ADDED VOLUME (mL)	CONCENTRATION	
			ppm	M
1	A	0.1	0.01	$1.0 \times 10^{-6} \text{M}$
2	A	0.1	0.02	2.0×10^{-6}
3	A	0.2	0.04	4.0×10^{-6}
4	A	0.2	0.06	6.0×10^{-6}
5	A	0.4	0.10	$1.0 \times 10^{-5} \text{M}$
6	B	2.0	0.29	2.9×10^{-5}
7	B	2.0	0.48	4.8×10^{-5}

PIPET A = 1mL graduated pipet

PIPET B = 2mL pipet

Solutions: additions of standard/TISAB to 50mL of distilled water and 50 mL of low level TISAB.

3.3.4 Titration Procedure

The Fluoride Ion Electrodes can be used as highly sensitive end point 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% on the total fluoride concentration of the sample can be performed using lanthanum nitrate as the titrant.

Total fluoride concentration should be at least $1.0 \times 10^{-6} \text{M}$ for end point detection. Low results are given if aluminum, iron or trivalent chromium are present at a level of 1% or higher.

Use the following procedure for titration of fluoride with lanthanum nitrate.

1. Dissolve 43.3 grams of reagent grade lanthanum nitrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, in about 500mL 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 150mL plastic beaker, add exactly 9.0mL of fluoride standard and about 50mL of distilled water. Place the beaker on the magnetic stirrer and begin stirring. Lower the electrode tip into the solution.

3. Using a 10mL plastic burette, add the $\text{La}(\text{NO}_3)_3$ titrant in 0.5 - 1.0mL 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 volume until little change is noted in the mV reading even when adding 0.5-1.0mL increments.
4. Using linear graph paper, plot the mV readings (y-axis) against the volume (x-axis). The end point is determined at the steepest slope on the titration curve. Record the end point V_t^0 .
5. To a 150mL plastic beaker, add exactly 9.0mL of sample solution and about 50mL of distilled water. Place the beaker on the magnetic stirrer and begin stirring. Lower the rinsed, dried electrode tip into the solution.
6. Titrate the sample as in step 3. The end point is denoted as V_t^X .
7. Calculate the sample concentration, C_s^X

$$C_s^X = \frac{V_t^X}{V_t^0} \frac{V_f^0}{V_f^X} \times C_s^0$$

where:

C_s^X = concentration of sample

C_s^0 = Fluoride standard concentration (0.1M)

V_t^X = Volume of titrant added to achieve end point of unknown sample.

V_t^0 = Volume of titrant added to achieve end point in standardization.

V_f^X = Volume of sample used in sample titration (9.0mL)

V_f^0 = Volume of standard used in standardization titration (9.0mL)

A typical titration curve is shown in Figure 3-2.

3.4 APPLICATIONS

3.4.1 Fluoride in Water

The direct measurement procedure is used to determine fluoride in water. TISAB is added to standards and to samples in order to break fluoride complexes of ion and aluminum, since fluoride in water is determined in ppm of total fluoride concentration. An adjustment to the pH and a constant ionic strength is also accomplished by the addition of TISAB.

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 100 ppm fluoride standard. To each 50 mL of standard, add 50 mL of TISAB-1, or 5 mL of TISAB-2. Calibrate the meter as previously described by using the 2, 1 and 0.5 ppm fluoride standards. The calibration curve should be drawn on semi-logarithmic 2-cycle graph paper.

3.4.2 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 standards contain less than 10ppm fluoride.
4. Calibrate the electrode as described in the section Electrode Slope Check.
5. After diluting each unknown sample 10:1 with sodium acetate (as in step 3), measure the mV potential and determine the fluoride concentration.

3.4.3 Fluoride in Alkaline Solutions

Hydroxide ions interfere with fluoride measurements in basic solutions with a low fluoride content. At a fluoride concentration less than $1.0 \times 10^{-4}\text{M}$ 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 4.6).

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 section on Determination of Fluoride in Acid Solutions, prepare standards, calibrate the electrodes, and measure unknown samples.

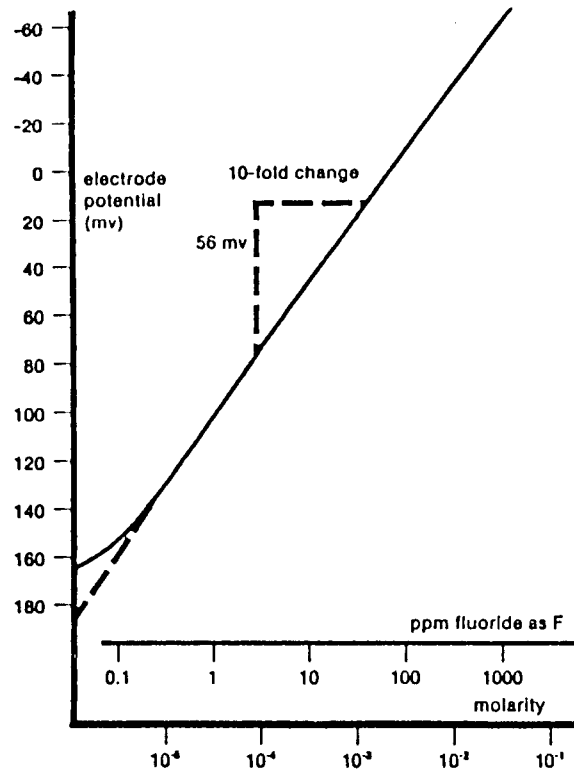


Figure 3-1 Typical Fluoride Calibration Curve

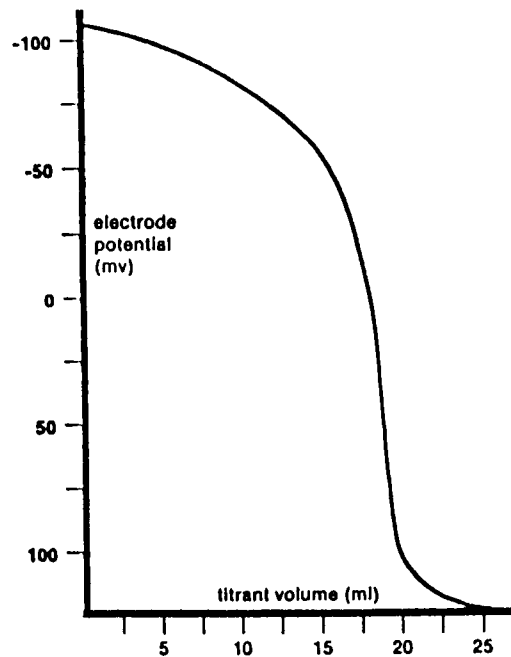


Figure 3-2 Titration of 0.114M F with 0.100 M $\text{La}(\text{NO}_3)_3$

SECTION 4 ELECTRODE CHARACTERISTICS

4.1 REPRODUCIBILITY

Direct 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 with the electrode's operating range.

4.2 INTERFERENCES

The hydrogen 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. Anions commonly associate with fluoride, such as Cl^{-1} , Br^{-1} , I^{-1} , SO_4^{-2} , HCO_3 , NO_3^{-1} and acetate, do not interfere with correct electrode operation. Most cations and anions do not interfere with the response of the fluoride electrode to fluoride ion.

4.3 TEMPERATURE INFLUENCES

Samples and standards should be within +/-1°C of each other, since electrode potentials are influenced by changes in temperature. Because of the 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 4-1 gives values for the "S" factor in the Nernst equation for the fluoride ion.

TABLE 4-1
TEMPERATURE VS. VALUES FOR THE ELECTRODE SLOPE

<u>T(°C)</u>	<u>S</u>	<u>T(°C)</u>	<u>S</u>
0	54.20	30	60.15
10	56.18	40	62.13
20	58.16	50	64.11
25	59.16	100	74.04

The temperature range for the Fluoride Ion Selective Electrodes is 0°-100°C, provided that temperature equilibrium has occurred.

If the temperature varies substantially from room temperature, equilibrium time up to one hour is recommended.

Only intermittent use is recommended at temperatures above 80°C.

4.4 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 56 mV per decade.

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from several seconds in highly concentrated solutions to several minutes near the detection limit. Refer to Figure 4-1.

4.5 LIMITS OF DETECTION

Fluoride concentration down to 1.0×10^{-6} (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 1.0×10^{-5} . Saturated fluoride solution is the upper limit of detection.

4.6 pH EFFECTS

Hydrogen complexes a portion of fluoride in solution, forming the undissociated acid HF and the ion HF_2^{-1} in acid solutions with a pH below 5. The proportion of free fluoride in acid solutions is shown in Figure 4-2.

When the level of hydroxide is greater than one-tenth the level of fluoride ion present, hydroxide ion interferes with the electrode response to fluoride. As an example, no hydroxide interference with fluoride measurements takes place at pH=7 when the hydroxide concentration is $1.0 \times 10^{-4}\text{M}$ or less. As the pH increases, the hydroxide interference becomes appreciable. At pH=10, the hydroxide ion concentration is $1.0 \times 10^{-4}\text{M}$ and no error is found in measurements of 1.0×10^{-2} fluoride. At the same hydroxide ion concentration and a fluoride concentration of $1.0 \times 10^{-4}\text{M}$, about a 10% measurement error appears. At a fluoride concentration of 10^{-5}M , considerable error exists in a pH 10 solution. Figure 4-3 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. Special TISAB adjusts the pH to about 8.5 and should not be used for very low level measurements.

4.7 COMPLEXATION

Aluminum, silicon, iron, and some other multivalent cations, as well as hydrogen, 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 concentration.

TISAB-1 and TISAB-2 complexes about 5ppm aluminum or iron in a 1ppm fluoride solution. TISAB-1 complexes higher levels of iron and aluminum.

4.8 ELECTRODE CLEANING/STORAGE

Inorganic solutions are removed from the electrode by rinsing with distilled water. Organic deposits on the sensing element will increase response time, especially in diluted fluoride solutions. The following procedure will remove most organic deposits without damage to the electrode. Take care not to overheat the electrode.

1. Prepare a solution containing 10 mL of concentrated NH_4OH , 10 mL of dishwashing detergent, and 180mL of water. Pour about 80 mL of this solution into each of two 100 mL plastic beakers. Add distilled water to a third 100mL plastic beaker.
2. Assuring that the electrode tip will not touch the bottom of the beaker, lower the electrode into one of the detergent-filled beakers. Heat all three beakers gently, and with occasional stirring, to 70-75°C.
3. After removing the beakers from the heat source, transfer the electrode to the second detergent-filled beaker. Allow the electrode to soak for 3-5 minutes.
4. Remove the electrode from the detergent and place it into the beaker with distilled water. Allow to cool to room temperature.
5. Immerse the electrode in 50% HCl for 20 seconds, stirring gently. Rinse with fresh distilled water.

The electrode is stored in air, after rinsing and blotting dry. For long-term storage, the sensing crystal should be protected from accidental damage by covering the electrode tip with the protective rubber cap.

The Fluoride Combination Electrode may be stored in fluoride standards for short periods of time. For long-term storage, drain and rinse the reference portion and store dry.

Neither electrode should be stored in distilled water.

4.9 THEORY OF OPERATION

The Fluoride Ion Electrode consists of a single crystal of lanthanum fluoride as the membrane, bonded into an epoxy body. The combination electrode also contains an internal reference. 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 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 (256mV0
- X = level of fluoride in solution

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

$$C_f = C_t - C_b$$

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

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

$$X = \zeta C_f$$

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

$$I = 1/2 \sum C_x Z_x^2$$

where:

- C_x = concentration of ion X
- Z = charge of ion X
- \sum = 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, ζ is constant and the activity, X, is directly proportional to the concentration.

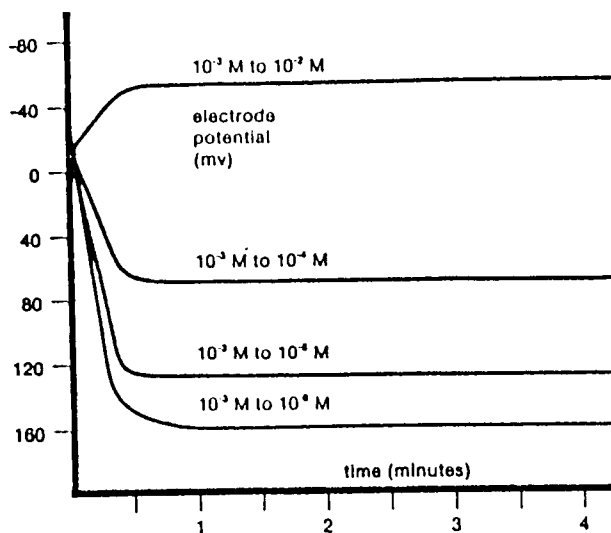


Figure 4-1 Typical Electrode Response to Step Changes in NaF Concentration

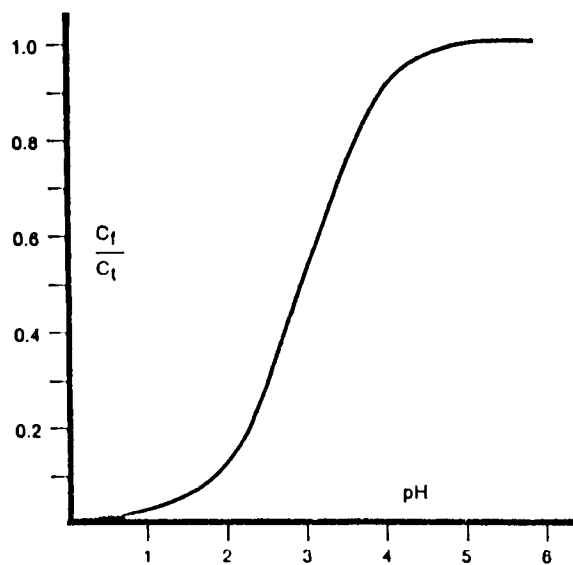


Figure 4-2 Fraction of Free Fluoride as a Function of Solution pH, where Hydrogen is the only complexing species

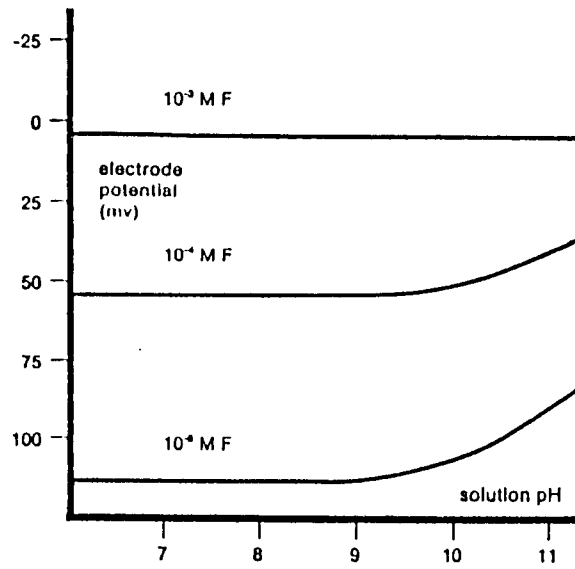


Figure 4-3 Electrode Response in Alkaline Solutions

SECTION 5 TROUBLESHOOTING

SYMPTOM	POSSIBLE CAUSES	NEXT STEP
Out of range reading	Defective meter	Check meter with shorting strap (See meter instruction manual)
	Electrode not plugged in properly	Reseat electrode
	Reference electrode junction is dry	Hold cap and lift outer sleeve to expel a few drops of filling solution
	Reference electrode not filled	Be sure reference electrode is filled
	Calibration control not turned far enough	Continue turning the calibration control
Noisy or unstable readings (changing randomly)	Defective meter	Check meter with shorting strap
	Wrong reference electrode	Do not use calomel or Ag/AgCl (frit or fiber type) reference electrode
	TISAB not used	Use recommended TISAB
	Meter or stirrer not grounded	Ground meter or stirrer
	Static electricity	Wipe plastic meter with detergent solution
	Reference electrode junction clogged	Clean out junction
Drift (reading changing in one direction)	Samples and standards at different temperature	Allow solutions to come to room temperature before measurement
	Incorrect reference	Use recommended filling solution
	Membrane dirty	Remove organic deposits
	Glassware used	Use plastic labware

SYMPTOM	POSSIBLE CAUSES	NEXT STEP
Low Slope or no slope	Standards contaminated or incorrectly made	Prepare fresh standards
	Standard used as TISAB	Use TISAB
	TISAB not used	Use TISAB if sample ionic strength is below 0.1M; if sample ionic strength is high, dilute sample
	Glassware used	Use plastic labware
"Incorrect Answer" (but calibration curve is good)	Incorrect scaling of semilog paper	Plot millivolts on the linear axis. On the log be sure concentration numbers within each decade are increasing with increasing concentration
	Incorrect sign	Be sure to note sign of millivolt reading correctly
	Incorrect standards	Prepare fresh standards
	Incorrect TISAB dilution	Add 50mL of TISAB-1 or 5 mL of TISAB-2, to each 50mL sample or standard
	Wrong units used	Apply correct conversion factor: $10^{-3} = 19$ ppm as F^{-}

SECTION 6 SPECIFICATIONS

CONCENTRATION RANGE: Saturated solutions to 1.0×10^M
(0.02 ppm)

pH RANGE: 5 to 7 at $1.0 \times 10^{-6}M F^-$ (0.01ppm F^-)
 ≤ 11 at $1.0 \times 10^{-1}M F^-$ (1900ppm F^-)

TEMPERATURE RANGE: 0° to $80^\circ C$ (80° to $100^\circ C$ intermittent
use)

RESISTANCE: 150 - 200 Kohm

REPRODUCIBILITY: +/-2%

STORAGE: In air (ISE-8790)
In air or standardizing solution
(ISE-8795)

SIZE: Length: 175mm (4.500 in.)
Diameter: 12mm (0.470 in.)
Cable Length: 100cm (3.3 ft.)

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TEMPERATURE

- Thermocouple, RTD & Thermistor Probes, Connectors, Panels & Assemblies
- Wire: Thermocouple, RTD & Thermistor
- Calibrators & Ice Point References
- Recorders, Controllers & Process Monitors
- Infrared Pyrometers

PRESSURE/STRAIN FORCE

- Transducers & Strain Gauges
- Load Cells & Pressure Gauges
- Displacement Transducers
- Instrumentation & Accessories

FLOW/LEVEL

- Rotameters, Gas Mass Flowmeters & Flow Computers
- Air Velocity Indicators
- Turbine/Paddlewheel Systems
- Totalizers & Batch Controllers

pH/CONDUCTIVITY

- pH Electrodes, Testers & Accessories
- Benchtop/Laboratory Meters
- Controllers, Calibrators, Simulators & Pumps
- Industrial pH & Conductivity Equipment

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