

VAN LONDON

Est. 1961



pHoenix Co.



Fluoride Ion Selective Electrode



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GENERAL INSTRUCTIONS

Introduction

The Van London-pHoenix Company Fluoride Ion Selective Electrode is used to measure dissolved fluoride ion in aqueous solutions.

Required Equipment

1. An ion meter
2. Fluoride Ion Sensing Electrode
3. Polishing Paper to polish dirty or etched fluoride electrode crystals
4. Plastic syringe, pipets, volumetric flasks, 150 ml beakers

Required Solutions

1. Deionized or distilled water for solution preparation.
2. Ionic Strength Adjuster, TISAB 1, Cat.# F00IS01.
TISAB 1 is used to adjust the pH of the solution, de-complex fluoride and provide a constant background ionic strength.
3. Van London-pHoenix Company Fluoride Standard, 1000 ppm F⁻¹, Cat.# F00AS02.
4. Fluoride Electrode Reference Fill Solution, Cat.# R001013.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the reference electrode. Fill the combination 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 electrode to the proper terminals of the meter as recommended by the meter manufacturer. Store the black shipping cap for later use.

Electrode Slope Check (for Ion meters which display mV)

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 10 ml of TISAB 1. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Stir moderately. Remove air bubbles on the clear crystal membrane by redipping probe.
2. Using a pipet, add 1 ml of 1000 ppm fluoride standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm fluoride to the beaker. Stir moderately. After 1 minute, record the mV reading.
4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of 54-59 mV is found, assuming the solution temperature is 25°C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10.

Measurement using an Ion Meter (in the Concentration Mode)

1. By serial dilution of the 1000 ppm ammonia standard, prepare two ammonia standards whose concentration is near the expected sample concentration. (e.g 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers.
2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate. Add 10 ml of ISA to the solution and continue stirring.
4. After 1 minute, adjust the meter to the concentration of the more dilute fluoride standard and fix the value in the memory according to the meter manufacturer's instructions.

5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate. Add 10 ml of ISA to the solution and continue stirring.
7. After 1 minute, adjust the meter to the concentration of the more concentrated fluoride standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 100 ml of the sample and 10 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.
10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

Measuring Hints

As fluoride electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase. By using the meter's calibration controls this error can be corrected. If an electrode is able to be calibrated and is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

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

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

Constant, but not violent, stirring is necessary for accurate measurement.

Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.

A slow or sluggish electrode response may indicate surface contamination of the membrane. Use a toothbrush and some toothpaste to lightly scrub the membrane surface, then soak in deionized water for five minutes to restore proper performance.

Dilute concentrated samples (over 5000 ppm) before measurement.

Use fresh standards for calibration. Re-calibrate every few hours for routine measurement.

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.

The addition of TISAB 1 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 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.

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to $\pm 2\%$ can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility.

Interferences

The hydroxide ion, OH^- , is an electrode interference. Anions which make the sample more basic, such as CO_3^{2-} or

PO_4^{3-} would increase the OH^- interference, but do not interfere with direct electrode operation. Other anions commonly associated with fluoride, such as Cl^- , Br^- , I^- , SO_4^{2-} , HCO_3^- , NO_3^- , and acetate, do not interfere with correct electrode operation. Most cations do not interfere with the response of the fluoride electrode to fluoride ion.

Electrode drift and slow response could indicate the presence of high interferences. Use a toothbrush and some toothpaste to lightly scrub the membrane surface, then soak in deionized water for five minutes to restore proper performance.

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

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1°C temperature change for a 10 ppm solution.

The electrode can be used at temperatures from 0° - 80°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

Electrode Response

Plotting the electrode mV potential against the fluoride concentration results in a straight line with a slope of about 56 mV between 10 ppm and 100 ppm at 25°C.

For fluoride concentrations above 10 ppm F^- , the electrode exhibits good time response (95% of total mV reading in one minute or less). Response times are longer below this value.

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 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 0.2 ppm. 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^- in acid solutions with a pH below 5.

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. As the pH increases, the hydroxide interference becomes appreciable. At pH 10, no error is found in measurements of 200 ppm fluoride. At pH 10 and a fluoride concentration of 2 ppm, about a 10% measurement error appears. At a fluoride concentration of 0.2 ppm, considerable error exists in a pH 10 solution.

The addition of TISAB 1 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.

Electrode Life

The fluoride electrode will last one year 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.

Since fluoride electrodes have a limited shelf life, it is important to have a backup electrode which is in working condition when required.

Electrode Storage

The fluoride electrode may be stored for short periods of time in 10 ppm 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.

TROUBLESHOOTING HINTS

*Remember to remove the black protective shipping cap on the bottom of the electrode and expose the fill hole underneath the electrode cap. Fill the electrode with the Reference Filling Solution shipped with the electrode to a level just below the fill hole.

<u>Symptom</u>	<u>Possible Causes</u>	<u>Next Step</u>
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode operation	check electrode
	electrode not plugged in properly	unplug electrode from meter and reseal
	electrode reference chamber not filled	fill reference chamber as instructed in <u>Electrode Preparation</u>
	air bubble on membrane	remove air bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Reading (readings continuously or randomly changing)	insufficient reference filling solution	fill outer body of electrode with proper amount of reference filling solution
	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	air bubble on membrane	remove air bubble by redipping electrode

	meter or stirrer improperly grounded	check meter and stirrer for grounding
Drift (reading slowly changing in one direction)	electrode exposed to interferences	soak electrode in fluoride standard
	incorrect reference filling solution	refill outer body of electrode using filling solution shipped with electrode
	total sample level of dissolved species above 1M	dilute sample
	membrane failure (wet, perforation, discoloration)	replace electrode
	samples and standards at different temperatures	allow samples and standards to come to same temperature before measurement
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	TISAB 1 not used	use recommended TISAB 1
	standard used as TISAB 1	use TISAB 1
	membrane failure (wet, perforation, discoloration)	replace electrode
"Incorrect Answer" but calibration curve is good)	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: $10^{-3}\text{M} = 19 \text{ ppm as F}^{-}$
	TISAB 1 added to standards and not samples	add same proportions of ISA to standards and samples
	sample carryover	rinse electrodes thoroughly between samples

SPECIFICATIONS

Concentration Range:	saturated solutions to 0.02 ppm
pH Range:	5 to 8
Slope:	52 – 59 mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 80°C
Interferences:	OH^{-}
Reproducibility:	$\pm 2\%$
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store electrode in fluoride standard with TISAB added

ELECTRODE THEORY

Electrode Operation

The 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, 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, C_f, by the activity coefficient, \tilde{a} , by:

$$X = \tilde{a}C_f$$

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

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

where: C_x = concentration of ion X
Z_x = charge of ion X
∑ = 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, \tilde{a} , is constant and the activity, X, is directly proportional to the concentration.