Remember to bring in your own drinking water sample to be tested for Fluoride. Ahead of the actual laboratory work, you need to sign-out from the stockroom a 500 mL plastic bottle in which to store your drinking water sample. Note valuable laboratory time can be saved if your group has read this experiment ahead of time. It is suggested that one of the partners start to dissolve the toothpaste sample at the start of the experimental work.

ABSTRACT

In this experiment, a fluoride, solid-state type, ion selective electrode is used to measure the potential that arises when it is immersed in aqueous solutions having different fluoride activities. Using a simple millivolt/pH meter, first the potentials of a series of aqueous standards having known fluoride activities (really concentrations as each solution has the same ionic strength) are measured with the fluoride ion selective electrode, versus a standard calomel (reference) electrode (SCE). A plot of these potentials vs. the log of the concentrations of fluoride ion, usually over the 100 to 1.00 ppm fluoride concentration range, gives a straight line whose slope approximates a 0.0592 volt change per decade. Below 1.0 ppm the data points are found not to be as linear but are still needed in order to measure the fluoride ion concentration typically found in most fluorinated drinking waters. Diluted samples of fluorinated mouth wash, toothpaste, an unknown fluoride solution received from the instructor, and either your home (or dormitory) tap water are measured using the fluoride ion selective electrode. The fluoride concentrations of those solutions are read from the standard curve. In the case of the mouth wash and toothpaste, appropriate dilution equations are needed to obtain the actual per cent fluoride in the weighed sample.

Background Reading:


Equipment Required: Millivolt/pH Meter (Digital with three digits) or expanded scale analog millivolt/pH meter; Fluoride ion selective electrode, (Orion Part No. 94-09 or equivalent); Saturated Calomel (reference) Electrode (SCE); Magnetic stirrer with stirring bar; Stirring bar retriever; Thermometer; Hot plate to hasten the dissolving of
the toothpaste; Analytical balance, readable to 0.1 mg; Semi-log paper, 3 cycles of log by 10 units for each inch. (National 12-183 or Keuffel & Esser 359-72).

**Chemicals:** NaF, NaCl, NaOH, and 1,2-diaminecyclohexane-N,N,N’,N”-tetracetic acid monohydrate (CDTA).

**Solutions:** 400 and 100 ppm Fluoride solutions (as NaF) stored in plastic bottles. The NaF should have been dried at 110 °C before weighing. The Total Ionic Strength Adjustment Buffer (TISAB) solution is prepared by starting with 1.0 L of deionized water in a 2L beaker, adding 115 mL (1.00 M) glacial acetic acid, 116 g (1.00 M) NaCl and 8.0 g (11.5 mM) of CDTA. Stir and to completely dissolve this mixture slowly add about 300 mL of 5.0 M NaOH until the pH is between 5.0 to 5.5 as read on a pH meter. Transfer and quantitatively dilute to 2.00 L in a 2 L volumetric flask. Unknown fluoride solution to be issued by the Laboratory Instructor or Teaching Assistant.

**Commercial Samples:** Fluorinated toothpaste and mouth wash.

**Glassware and other Containers:** to be checked-out from the stockroom as a kit.

Short medicine dropper or Pasteur pipet to deliver the 20 drops of mouth wash; Plastic bottles (32 oz, 1000 mL) to store the concentrated NaF standard and to be issued to students for them to sample their own drinking water samples; Beakers: 15-30 mL, 1-400 mL beaker, 1-250 mL beaker; Volumetric flasks: 8-100 mL, 1-500 mL; Volumetric Pipets: 1-50 mL, 1-25 mL, 3-10 mL; Graduated pipet: 1-10 mL; and 1-pipet bulb.

**INTRODUCTION**

In recent years a number of measuring electrodes, which possess selectivity toward some particular ion, have increased in popularity among many fields of science. These electrodes have been used in such applications as pollution control, biomedical research, clinical medicine, food processing, and metallurgy, to name a few. Various ion selective electrodes give direct measurement of the activity of many common anions and cations such as sodium, potassium, calcium, chloride, nitrate, sulfide, as well as fluoride and many more. There are about twenty of these types of electrodes. Some electrodes measure dissolved gases such as ammonia, sulfur dioxide, and carbon dioxide. In addition, several enzyme selective electrodes have been developed.

Potentiometric methods are simple and, besides the ion selective electrode, and an ordinary SCE reference electrode, only an expanded scale pH/millivolt meter is needed. Potentiometric analyses are quick and simple; many solutions can be analyzed directly with little prior solution preparation. The entire electrode assembly may be easily transported to the sites of the analysis, as in the case of environmental measurements. In addition potentiometric methods are sensitive; most ion selective electrodes being capable of measurements in the parts-per-million range.

Several limitations must be kept in mind when using ion selective electrodes. First, activity and not concentration is being measured. Because the activity coefficient is dependent upon the total ionic strength of the solution, the activity will deviate from the concentration to a greater extent as the solution concentration increases. Also, the variation in concentration of any other ionic species that happens to be in the solution will affect the total ionic strength and change the activity of the ion being measured. These effects may be swamped by adding high and constant concentrations of non-
interfering ions, such as sodium chloride that are available in the Total Ionic Strength Adjustment Buffer (TISAB).

Second, the electrode responds only to free ions. The presence of any species which complexes with the ion being measured will lower its activity and therefore the electrode response. Finally, the electrode response is selective, not specific. Selectivity means interference from competing ions is possible.

The Fluoride Selective Electrode

The fluoride selective electrode is a solid-state type electrode consisting of a lanthanum fluoride crystal sealed over the end of an inert plastic tube which contains an internal electrode and filling solution usually of 0.1M NaCl and 0.1M NaF. A potential arises because of the difference in fluoride activity on either side of the crystal.

The pH range for the fluoride selective electrode is limited at the acid end by the formation of HF and at the basic end by hydroxide interference. Polyvalent cations of Si+4, Fe+3, and Al+3 also interfere by forming complexes with fluoride. To avoid problems arising from these possible interferences, TISAB (total ionic strength adjustment buffer) is added in excess and in exactly the same amount to each of the solution that will be measured. This TISAB buffer renders all of the solutions to about a pH of 5.0 and contains a complexing agent to complex polyvalent cations. Most importantly, however, it contains a high concentration of NaCl to provide a constant ionic strength to each solution.

Potential Measurements

The potential of the ion selective electrode (ISE) arises when there are solutions of a given ion, X, on either side of a membrane. The type of membrane categorizes the electrode: there are glass membranes (H+, Na+, K+, Ag+ selective), crystal membranes (F-, Ce3+, Pb2+ selective), liquid ion-exchange membranes (NO3-, K+, Ca2+ selective), and so forth. The measured potential of an indicator electrode (EIND) is presented in equation 1.

\[
E_{IND} = E' - \frac{RT}{nF} \ln \left( \frac{a_X \text{ unk}}{a_X \text{ int}} \right)
\]

Equation 1

where \( E' \) is a constant similar but not equivalent to \( E^\circ \) for a redox couple; \( R \) is the gas constant with the value of 8.314 volt coulombs °K⁻¹ mole⁻¹; \( T \) is the temperature in degrees Kelvin; \( n \) is the charge on the ion; \( F \) is the Faraday which has a value of 96,487 coulombs/equivalent. Upon conversion from the natural log to the log of base 10 (2.303), and when the temperature is 298.16 °K (25.0 °C), the \( \left( \frac{RT}{F} \ln \right) \) term becomes (0.0592 log). Then the potential measured, \( E_m \), at the indicator electrode with respect to a reference electrode (EREF) at a temperature of 25.0°C, can be expressed as:
\[ E_m = E_{IND} - E_{REF} = E' - 0.0592 \log \left[ \frac{a_x \text{ unk}}{a_x \text{ int}} \right] - E_{REF} \quad \text{Equation 2} \]

Normally, it is the concentration of a solution which is of interest, not the activity. The activity is related to the concentration through the activity coefficient as shown in Equation 3. Making use of this relationship,

\[ a_i = f \ C_i \quad \text{Equation 3} \]

while separating the log terms, Equations 4 and 5 are obtained.

\[ E_m = E' - 0.0592 \log \left[ \frac{f \ C_x \text{ unk}}{a_x \text{ int}} \right] - E_{REF} \quad \text{Equation 4} \]

\[ E_m = E' - 0.0592 \log [C_x \text{ unk}] - 0.0592 (\log f - \log [a_x \text{ int}]) - E_{ref} \]

\[ \text{(constant)} \quad \text{(Constants)} \]

Since the activity coefficient, \( f \), is a function of only the ionic strength, then if the ionic strength is held constant by adding a constant volume of the TISAB solution, Equation 5 reduces to a simple linear equation of the form \( y = mx + b \).

\[ E_m = K - 0.0592 \log [C_x \text{ unk}] \quad \text{Equation 6} \]

Thus if the potentials of a set of standards of known concentrations are measured, a plot of potential, \( E_m \), vs. log concentration should give a straight line whose slope should approximate \( -0.0592/n \) volts/unit charge, remembering that the equation holds for 25.0 °C.

**pH Measurements**

The measurement of pH is the most common measurement for an ion selective electrode. Equation 7 can be easily obtained from Equation 2. Verify from Equation 7 that a unit change in pH (for example from 3 to 4) should result in a potential change (at 25.0°C) of 0.0592 volts or 59.2 millivolts.

\[ E_m = K' + 0.0592 \ \text{pH} \quad \text{Equation 7} \]

In principle, \( H^+ \) could be measured exactly as are other ions that were previously described. The potential of standards of known pH could be measured to obtain a calibration curve of potential vs. pH. The curve could then be used to find the pH of unknown solutions. However, because pH is such an important value, and because so many standards are available, potential measuring meters are calibrated directly in pH where one pH unit is equivalent to 0.0592 volts (at 25°C). The instrument then simply has to be standardized.
by putting it in the measuring mode and setting it to the known pH of a standard buffer. Subsequent measurements will then give the pH of other solutions.

**Preparation of Standard Solutions**

Prepare the following standard solutions of fluoride by first diluting the 400 ppm to a 100 F\(^-\) solution (See note 1 in the appendix). Next prepare 100 ml of the 40 ppm F\(^-\) standard by diluting the 100 ppm F\(^-\) standard using deionized water. (Note the deionized water needs to be free of fluoride ions)!

Second, use the 40 ppm F\(^-\) standard and dilute as follows in other 100 ml volumetric flasks:

<table>
<thead>
<tr>
<th>Starting with the 40 ppm F(^-)</th>
<th>resulting ppm F(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.00 ml. dilute to 100 ml.</td>
<td>20.0</td>
</tr>
<tr>
<td>25.00 ml. dilute to 100 ml.</td>
<td>10.0</td>
</tr>
<tr>
<td>10.00 ml. dilute to 100 ml.</td>
<td>4.00</td>
</tr>
<tr>
<td>5.00 ml. dilute to 100 ml.</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Prepare the following standard solutions of fluoride by diluting the indicated volumes of 10 ppm F\(^-\) solution, prepared above,

<table>
<thead>
<tr>
<th>Starting with the 10 ppm F(^-)</th>
<th>resulting ppm F(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00 ml. dilute to 100 ml.</td>
<td>1.00</td>
</tr>
<tr>
<td>5.00 ml. dilute to 100 ml.</td>
<td>0.500</td>
</tr>
<tr>
<td>2.50 ml. dilute to 100 ml.</td>
<td>0.250</td>
</tr>
</tbody>
</table>

Into the nine, 30 ml labeled beakers, pipet 10.0 ml of 0.250, 0.500, 1.00, 2.00, 4.00, 10.0, 20.0, 40.0, and 100.0 ppm F\(^-\) solution, respectively. Then into each of these nine beakers, carefully pipet, exactly 10.00 ml of TISAB (See note 2 in the Appendix).

**Adjusting the Zero of the Millivolt Meter**

Have the Instructor or the Teaching Assistant show you how to zero the Millivolt meter to 0.0 mv. At the same time, using the thermometer provided, measure the temperature of the 100.0 ppm F\(^-\) solution. Have the instructor explain to you how to adjust the temperature compensation dial (circuit) of the millivolt meter so that it corrects for the difference in temperature in the slope (the Nernst term factor).

**Cautions Concerning Use of Electrodes and Meters**

The fluoride electrode is used with a saturated calomel electrode. The former is stored in a fluoride solution and the latter in a KCl solution. Be sure to return them to the correct solution at the end of the experiment.
Remove each electrode from its storage flask and rinse with deionized water. **BLOT** each electrode with a Kimwipe®. Do not rub the surface of the fluoride electrode since this sort of treatment could damage it (the fluoride electrode costs about $250; the SCE reference electrode costs about $50). Place each electrode in the electrode holder and immerse the electrode system in the first solution to be measured.

Each solution must be stirred at the same rate with the magnetic stirrer and with the same electrode configuration. Take care not to allow the stirring bar to hit the electrodes since this may cause damage. A stirring bar retriever is provided to withdraw the stirring bar from the solution after measurement. Rinse the stirring bar with deionized water. After removal, dry with a Kimwipe®, and drop it into the next solution to be measured. **BEFORE BEGINNING THESE MEASUREMENTS, READ THE NEXT SECTION.**

**Determination of Potentials for the Calibration Curve**

Measure the potential of all the standard solutions starting with the highest fluoride concentration, 100 ppm, and working down to the lowest, 0.250 ppm. (Record the sign: positive or negative) of the resulting millivolt readings as measured against the reference electrode. Unlike a pH electrode, the fluoride electrode does not reach equilibrium immediately, and it may be necessary to wait a minute or so before the potential stops drifting. The drift will be more pronounced as the concentration decreases.

While still on this laboratory experiment, before discarding the known solutions or dismantling the measuring equipment, make a rough plot of mV vs. log F⁻ (ppm) using the semi-log paper provided. Make sure the electrode is behaving linearly (Note 2). If there are some obvious data points deviating from the expected linear relationship you might want to recheck one or more of the potential readings.

**Determination of Fluoride in Toothpaste** (Remember to record the brand name in your laboratory notebook). As rapidly as possible, since volatile materials are lost from the toothpaste sample, weigh about \(2\,\text{mg} \pm 0.1\,\text{mg}\) of toothpaste into the 250 ml beaker provided. Add about 50 ml of distilled water and gently boil this mixture on the heating plate provided for about five minutes. Cool. Transfer to a 50 ml volumetric flask and dilute to the mark using distilled water. Pipet 10.0 ml of the toothpaste solution and 10.0 ml of TISAB into a 30 ml beaker. While stirring with the magnetic stirrer, insert the electrodes into the sample and when the potential stops drifting perceptibly read it.

**Determination of Fluoride in the Mouth Wash** (Again remember to record the brand name in your laboratory notebook). Weigh an empty 30 ml beaker of the analytical balance. Carefully deliver into this weighed beaker exactly 20 drops (about 1.00 mL) of the Mouthwash using the Pasteur pipet (as a medicine dropper). Rapidly reweigh the beaker to obtain an accurate weight of the Mouthwash delivered. Add exactly 9.00 ml of deionized water and 10.00 ml of TISAB. Determine the potential as discussed in the previous section.

**Determination of Fluoride in Water Samples**
Use your own tap water, either from your home or dormitory. Pipet 10.00 ml. of water to be tested and 10.00 ml. of TISAB into a 30 ml. beaker. Determine the potential as discussed previously.

**Determination of Fluoride in Unknown**

Obtain a sample of unknown fluoride from your instructor. Be sure to record the number of this unknown. Into a 30 ml. beaker pipet 10.00 ml. of unknown and 10.00 ml. of TISAB. Measure the potential as discussed previously.

**Data Work-Up**

1. Construct a calibration curve by plotting mV vs. log ppm F\(^-\) of the standard solutions. The plot should be constructed on semi-log paper by putting ppm F\(^-\) or fluoride concentration on the log axis and the recorded mV on the regular (X) axis. (You will need semi-log paper having three orders of change on the log. axes). Using those data points that clearly fall in the linear portion of the plot, usually in the 2 to 100 ppm range, determine the slope of the curve in mV/decade. Do not report the calculated slope from just a linear regression calculation; but, calculate the differences in mV measured, for example from the 100 and 10.0 ppm fluoride standards or the difference in mv measured for the 40 and 4.0 ppm fluoride standards. Does the electrode exhibit Nernstian or near Nernstian behavior? Manufacturer reported value is a difference of 54 to 58 mv per decade (Note 3).

2. From the calibration plot, read off the concentrations in ppm of F\(^-\) for all of the solutions measured; toothpaste, mouthwash, water sample, and unknown. Express your answer to 3 significant figures. Three significant figures are justified since there will be over a 100 mv. difference in mv. readings between the 100 and 0.25 ppm fluoride standard. Since both the standard solutions and the solutions measured were diluted by half with TISAB, the concentrations of the 10.0 ml. samples can be read directly from the calibration curve (Note 2).

3. Using the equation presented on page 8-9, calculate the concentration of fluoride, expressed as % by weight of fluoride in the toothpaste. Depending upon brands, usually a 0.07 to 0.20 % fluoride value is usually obtained. Remember in your lab report to specify the brand name used.

4. Again using the other equation presented on page 8-9, calculate the concentration fluoride in the mouthwash sample. Express this as a % fluoride by weight. Depending upon brands of fluorinated mouthwash, a value of 0.02 to 0.05% is usually obtained. Remember in your lab report specify the brand name used.

5. Report the value, in ppm of F\(^-\), directly read from the calibration plot for the amount of fluoride in your unknown measured and in the drinking water tested. Remember in your lab report to properly document the number of your fluoride unknown and the nature of your drinking water sample. Do the potential values measured for the amount of fluoride in the drinking water sample fall in the linear portion of the calibration plot? If not, would you expect those values to be as accurate as if they were in the linear portion of that plot?

APPENDIX 1
1. **Concentration Units**

The standard fluoride solutions are given in parts per million (ppm) fluoride; this is mg. F\(^{-}\) per liter or µg. F\(^{-}\) per ml.

2. **Calibration Curve**

The calibration curve is obtained by plotting mV vs. log ppm F\(^{-}\). In fact, each standard solution of F\(^{-}\) was diluted in half because 10.00 ml. of TISAB was added to 10.00 ml. of standard F\(^{-}\) solution. However, since each standard received the same treatment, the calibration curve can be used with the undiluted standard concentrations. Otherwise, we would simply divide by two to get the concentrations for the calibration curve and multiply by two to obtain the concentration of the measured solution.

3. **Nernstian Behavior**

Because all of the solutions are at a constant ionic strength, Equation 6, shown on page 8-4 can be rewritten as follows:

\[
E = \text{constant} - 0.059 \log[F^{-}]
\]

(8-9)

From this equation, if \(E\) is plotted against log F\(^{-}\), the slope should be 59.2 mV per decade change in fluoride concentration. This means that for every ten fold decrease in F\(^{-}\) concentration, increasing by one unit in terms of - log, the potential should change 59.2 mV.

4. **Equations to be Used.**

**To calculate the per cent fluoride in the toothpaste.** Realizing the concentration measurement of the toothpaste solution was done on 10.0 ml of solution and one-fifth of the total solution was used, then the weight and percentage, of fluoride in the toothpaste is calculated as follows.

\[
\frac{\text{ppm or } \mu g/ml}{\text{of fluoride}} \times 10.0 \text{ ml} \times \frac{50.0 \text{ ml}}{10.0 \text{ ml}} \times \frac{1 \text{ mg}}{1000 \mu g} = \_\_\_\_ \text{ mg}
\]

percent of fluoride = \[
\frac{\_\_\_\_ \text{ mg}}{200.\_ \text{ mg}} \times 100 = \_\_\_\% \]

(usually a value of 0.07 to 0.20 % fluoride expressed as % NaF is obtained depending upon brand of toothpaste).

**Equation to calculate the per cent of fluoride in the mouth wash.**

ppm or
\[
\text{\( \mu g/g \) of solution} \times 10^{-6} \text{ g} \times 10.0 \text{ ml} \times 100 \text{ } = \text{ } 0.\_\_\_\_%
\]

(usually a value of 0.02 to 0.05 % fluoride expressed as % NaF is obtained depending upon the brand of mouth wash).