A Potentiometric Analysis of Fluoride Ion in Toothpaste

In this laboratory exercise, we will analyze a toothpaste sample for its Fluoride Ion (F\textsuperscript{-}) content. This analysis will be performed potentiometrically (\(\varepsilon\); think voltage) using a Fluoride Ion selective membrane electrode (ISE). A Nernst-like relationship is expected to exist between the Fluoride Ion concentration \([\text{F}^-]\) and the Potential of the ISE. This relationship, which must be established via calibration, will allow us to determine the desired Fluoride Ion concentration from the measured Potential of the ISE.

Potentiometry involves the use of two electrodes, a Reference Electrode and an Indicator Electrode, to measure the Electric Potential (\(\varepsilon_{\text{cell}}\)) of an Electrochemical Cell constructed to include the Analyte Solution. A Cell Diagram for the system is:

Reference Electrode  |  Salt Bridge  |  Analyte Solution  |  Indicator Electrode

Schematically this can be pictured as:

```
                     Voltmeter
                     +--+-
                     |  |
                    Reference Electrode  Indicator Electrode (F\textsuperscript{-} Selective Membrane Electrode)
                     |
                     F\textsuperscript{-}
                     |
                     Analyte Solution
```
The Cell Potential $\epsilon_{\text{cell}}$ is measured using a typical Voltmeter in the limit of zero current flow.

$$\epsilon_{\text{cell}} = V \text{ in the limit } (I \sim 0) \quad \text{(Eq. 1)}$$

This limiting condition is fairly easily realized if a meter with an internal resistance of greater than $10^{11} \, \Omega$ is used. Modern pH meters are simply high internal resistance voltmeters meeting this requirement. Therefore, pH meters are capable of making the needed voltage measurements such that the Cell Potential can be determined.

A simple example of this type of measurement involves the use of a Calomel reference electrode ($\text{Hg}(l)\text{Hg}_2\text{Cl}_2(s)\text{KCl}(aq)$) connected via a salt bridge to a cathode consisting of a $\text{Cu}^{2+}$ analyte solution and a $\text{Cu}(s)$ indicator electrode.

![Diagram of a Voltmeter and Calomel Reference Electrode](image)

The oxidation reaction occurring at the Calomel reference electrode is:

$$2 \text{Hg}(l) + 2 \text{Cl}^{-}(aq) \rightarrow \text{Hg}_2\text{Cl}_2(s) + 2 \text{e}^- \quad \text{(Eq. 2)}$$

whereas the cathodic reduction is:

$$\text{Cu}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Cu}(s) \quad \text{(Eq. 3)}$$

The Cu indicator electrode is a metal electrode of the “first kind:” an indicating electrode used to determine the concentration of an ion derived from the electrode material.

**Ideally**, the Cell Potential is related to the $\text{Cu}^{2+}$ concentration via the Nernst Equation:

$$\epsilon_{\text{cell}} = \epsilon_{\text{Cu}^{2+}|\text{Cu}}^0 + (0.0592/2) \log \left( \frac{1}{a_{\text{Cu}^{2+}}} \right) - \epsilon_{\text{Calomel}} \quad \text{(Eq. 4)}$$
where \( a_{\text{Cu}^{2+}} \) represents the Activity of the Cupric Ion:

\[
a_{\text{Cu}^{2+}} = \gamma_{\text{Cu}^{2+}} [\text{Cu}^{2+}] \tag{Eq. 5}
\]

Thus, the Nernst equation forms the basis of the relationship between the analyte concentration and the measured cell potential.

In our laboratory exercise we will be using a Flouride Ion Selective Membrane Double-Junction Electrode, in which the Indicator and Reference Electrodes are built into a single probe, to construct the needed electrochemical cell. (See Diagram on Next Page.)

The built-in Reference is a Ag|AgCl electrode which operates according to the following oxidation half-reaction:

\[
\text{Ag}(s) + \text{Cl}^{-}(\text{aq}) \rightarrow \text{AgCl}(s) + \text{e}^{-} \tag{Eq. 6}
\]

The Indicator Electrode is constructed from another AgCl|Ag electrode and a Flouride Ion Selective Membrane which is inserted into the analyte solution.

The Flouride Ion (F\(^-\)) Membrane selectively binds Fluoride Ion to both its surfaces; the exterior surface being in contact with the Analyte Solution and the interior surface in contact with a reference Electrode Solution. Both the Analyte and Electrode solutions contain Fluoride Ion.

However, because the Activity of the F\(^-\) in the analyte solution \( (\alpha_a) \) on the outside of the membrane is distinctly different than that in the membrane’s interior solution \( (\alpha_e) \), different concentrations of F\(^-\) bind to the membrane’s two surfaces. This gives rise to a Potential Difference across the membrane. In our Fluoride Ion Selective Electrode, the active membrane is a single crystal of LaF\(_3\) doped with Europium (II) Ions to lower its electrical resistance and to facilitate ionic charge transport. F\(^-\) ions bind to this crystalline surface according to:

\[
\text{LaF}_3(s) + \text{F}^{-}(\text{aq}) \rightleftharpoons \text{F}^{-}(\text{aq}) \tag{Eq. 7}
\]
To BNC Connector to pH Meter

Ag/AgCl Wire

Inner Reference Chamber

Annular Reference Junction
(Allows Ref. Sol'n to Leak)

Ag/AgCl Wire

Outer Reference Chamber

Annular Reference Junction
(Allows Ref. Sol'n to Leak)

F<sup>-</sup> Selective Membrane
The LaF₃ crystal, sealed into the end of a plastic tube, is in contact with the external F⁻ analyte solution. Internal to the electrode is a solution that is 0.1M in both NaCl and NaF. The internal F⁻ activity controls the Potential on the inner surface of the crystal.

To complete the Indicator, the internal Cl⁻ activity controls the Potential of the AgCl|Ag electrode, operating reductively; in the reverse of that at the Reference.

\[
\text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq) \quad \text{(Eq. 7)}
\]

Diagrammatically, the entire Cell (Reference, Analyte, Indicator) can be represented as:

\[
\text{Ag} \mid \text{AgCl} \| \text{Analyte} [\rho_a] \mid \text{LaF}_3 \text{ Mem.} \mid \text{Internal Sol’n} [\rho_e] \mid \text{AgCl} \mid \text{Ag}
\]

(Reference) (Analyte) (Indicator)

The Potential of the Cell can be written as a composite of the Potentials of the Reference and Indicator:

\[
\varepsilon_{\text{cell}} = \varepsilon_{\text{ind}} - \varepsilon_{\text{ref}} + \varepsilon_{\text{jnc}} \quad \text{(Eq. 8)}
\]

where \( \varepsilon_{\text{jnc}} \) is the Potential which builds at the junctions between the Cell’s chambers and is the single largest source of error in most Potentiometric measurements. (Note the sign used for each contribution. This is done by convention.)

The response of the Indicator Electrode to the Fluoride Ion in the analyte solution is described by a Nernst Like equation:

\[
\varepsilon_{\text{ind}} = L - 0.0592 \log \rho_{F^-} \quad \text{(Eq. 9)}
\]

where \( L \) is a constant specific to the cell in question. Inserting (Eq. 9) into (Eq. 8) and rearranging, we obtain:

\[
pF = - \log \rho_{F^-} = \frac{(\varepsilon_{\text{cell}} - \varepsilon_{\text{jnc}} - \varepsilon_{\text{ref}} - L)}{0.0592} = \frac{(\varepsilon_{\text{cell}} - K)}{0.0592} \quad \text{(Eq. 10)}
\]

where \( K \) is a Cell constant that must be determined by calibration.

If interfering ions, like Hydroxide Ion (OH⁻), can bind to the Indicator’s membrane surface, these must also be included in the relevant activity:
\[ \varepsilon_{\text{ind}} = L - 0.0592 \log (\alpha_{F^{-}} + k_{F^{-},OH^{-}} \alpha_{PH^{-}}) \]  

(Eq. 11)

where \( k_{F^{-},OH^{-}} \) is the Selectivity Coefficient for the electrode toward interference by \( OH^- \).

Our ISE is somewhat sensitive to Hydroxide Ion (OH\(^-\)) and this must therefore be controlled with a buffer. The recommended buffer is TISAB (Total Ionic Strength Buffer) which not only controls the OH\(^-\) levels, it provides a constant Ionic Strength environment and a complexing ligand.

For the LaF\(_3\) crystal, OH\(^-\) becomes a problem when its concentration becomes greater than 10% of the F\(^-\) present. TISAB helps control the pH of the analyte solution so this does not occur.

Additionally, the buffering action of TISAB also prevents the pH of the solution from dropping below pH = 5, where F\(^-\) can protonate to form the weak acid HF (pK\(_a\) = 3.17):

\[ F^{-}(aq) + H^+(aq) \rightleftharpoons HF(aq) \]

Secondly, TISAB controls the Ionic Strength of the Analyte solution. This is important because (Eq. 10) relates the cell potential \( \varepsilon_{\text{cell}} \) to the Fluoride Ion activity \( \alpha_{F^{-}} \). However, we are most interested in the Flouride Ion concentration [F\(^-\)]. Because the activity coefficient \( \gamma_{F^{-}} \) is typically not determinable, the electrode must instead be calibrated against solutions of known concentration and not known activity. This only works if the ionic strength of the calibration standards and the analyte solution are the same. The TISAB buffer controls the ionic strengths of these solutions such that this is the case.

Finally, TISAB provides Complexing Agents for possible contaminants. Aluminium Ion (Al\(^{3+}\)) and Ferric Ion (Fe\(^{3+}\)) contaminants can complex with Fluoride Ions and therefore interfere with the potentiometric measurement:

\[ Al^{3+}(aq) + 4 F^{-}(aq) \rightleftharpoons AlF_4^{-}(aq) \]  

(Eq. 12)

TISAB contains the complexing agent CDTA (trans-1,2-cyclohexanedinitrilotetraacetic acid) which combines with Al\(^{3+}\) and Fe\(^{3+}\) up to concentrations of 5 ppm and renders them inert.

Thus, we will use a series of Standard Fluoride Ion solutions prepared using TISAB so as to generate a Calibration Curve of:
\[ \varepsilon_{\text{cell}} \text{ vs. } \log [F^-] \quad (\text{Eq. 13}) \]

which according to (Eq. 13) should be linear. The Cell Potential will be measured using a Fluoride Ion Selective Electrode attached to a pH meter. The resulting calibration curve can then be used to determine the F\(^-\) concentration in a solution prepared from a commercial toothpaste preparation.
Pre-Lab Calculations

1. TISAB buffers at pH = 5.25. What is the OH\(^-\) concentration in this buffer?

2. If 10 mL of the NaF Stock solution is to be diluted to prepare 100 mL a 0.01M Standard solution, what must be the concentration of the Stock solution?
Procedure

1. Fluoride Ion (F\textsuperscript{-}) can adsorb onto the surface of glassware, reducing its solution concentration. This is especially problematic at low concentrations. Since we will need to work at low concentrations to determine the Fluoride Ion in our toothpaste sample, make sure all handling of the Fluoride Ion solutions is conducted using plastic labware.

2. You are provided with a 0.1M NaF stock solution in 10% TISAB. Dilute the stock solution to make standards with the following concentrations:

\[
0.01\text{M} \\
0.001\text{M} \\
0.0001\text{M} \\
0.00001\text{M}
\]

All these solutions are prepared in 10% TISAB buffer.

(You may want to collaborate with your neighbors on preparing these calibration solutions.)

3. You should prepare a solution of Toothpaste by dissolving 5.00g of Toothpaste in 50.00 mL of 10% TISAB buffer. Record the concentration of Fluoride Ion in the Toothpaste as reported by the manufacturer.

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

5. **Caution:** The electrode is rather expensive and fragile. Please do not drop it or knock the tip against the countertop, or with the stir bar. Also, do not rub the tip with anything, such as with a Kimwipe during drying. Scratches can damage the LaF\textsubscript{3} crystal.

Attach the BNC connector of the Electrode to the input on the pH Meter.

6. Measure the Electrochemical Potential of each of the Sodium Fluoride standards and solutions. Try to work from the lowest to highest concentration and analyze the Toothpaste sample last. To make a measurement, place the electrode in a beaker containing the solution. Use a stir plate and stir bar to gently stir the solution. (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. ) Wait for the Potential to stabilize (~1-3 minutes) and record the reading in millivolts (mV). Rinse the electrode between each measurement.

7. Using a software package such as Excel, plot \( \varepsilon_{\text{cell}} \) vs. pF for the Standard Solutions. Here, pF is defined as:

\[
pF = - \log [F^-]
\]
Add a Linear Least Squares trendline and determine the slope and intercept as well as their associated uncertainties.

8. Use your calibration curve to determine the Fluoride Ion concentration in the Toothpaste. Report this as the wt% NaF in the Toothpaste. Be sure to determine the associated uncertainty in this measurement. Compare your result with that reported by the manufacturer. Be careful here.