Ion-Selective Electrode Determination of Fluoride Ion

I. Introduction

A. Ion-Selective Electrodes

The amount of a specific ion contained in an aqueous solution can be determined by direct potentiometric measurement of the voltage of a galvanic cell such as shown below.

reference electrode ‖ analyte solution | ion selective electrode

The most common example of this is a pH measurement using a glass membrane sensitive to H^+. The ion-selective electrode (ISE) typically consists of an inner reference electrode plus a membrane that provides the interface between the sample solution and the ISE. A potential develops across the membrane that depends on the difference in the activity of a specific ion on each side of the membrane. An internal solution with a fixed concentration (activity) of the analyte ion means that the potential developed across the membrane is related to the analyte activity in the sample solution.

The overall measured cell potential can be expressed as

$$E_{meas} = E_{outer\ ref} + E_{inner\ ref} + E_{junc} + E_{ISE}$$

where $E_{outer\ ref}$ is the potential of the outer reference electrode;

$E_{inner\ ref}$ is the potential of the inner reference electrode;

E_{junc} represents the various junction potentials that develop at liquid junction in the cell;

E_{ISE} is the potential developed across the ion-selective membrane.

If the measurements are made with very little current flowing in the cell, the reference electrode potentials are fixed, and if the sample solution is essentially the same matrix for all measurements the junction potentials are also unchanged. Then the measured cell potential can be expressed as

$$E_{meas} = constant - \frac{2.303RT}{nF} \log \frac{a_{ion\ inner}}{a_{ion\ outer}}$$

where R is the gas constant, T is the temperature (K), F is the Faraday constant, n represents the charge on the analyte ion and a is the activity of the analyte ion.

The ISE filling solution contains a large concentration (activity) of the analyte ion and is essentially unchanged during operation of the electrode ($a_{ion\ inner}$ is fixed). Thus, at 25°C,

$$E_{meas} = constant + \frac{0.05916}{n} \log a_{ion\ outer}$$

For fluoride ion solutions at 25°C and constant ionic strength,

$$E_{meas} = constant - 0.05916 \log \gamma_{F^-} - 0.05916 \log [F^-]_{sample} = constant - 0.05916 \log [F^-]_{sample}$$

Thus, for an ideal fluoride ISE, the cell potential is linearly related to the logarithm of the fluoride ion concentration and should increase 59.16 mV for every 10-fold decrease in the $[F^-]$. When the ionic strength of all standards and samples is constant, the response of a real fluoride ISE is described by a similar relationship

$$E_{meas} = constant - \beta(0.05916) \log [F^-]_{sample}$$

where β is the electromotive efficiency and typically has a value very close to unity (> 0.98).

B. Direct Potentiometric Measurement

To check if the electrode is working properly, you will measure the the cell potential of three fluoride standards prepared in a total ionic strength adjustment buffer (TISAB). The TISAB contains an acetic acid/acetate buffer that fixes the pH of the solution at about 5. At this pH the formation of HF is negligible and the concentration of OH^-, the only other anion that the electrode responds to, is insignificant. It also contains NaCl to establish a high and constant ionic strength, and a complexing agent that removes cations that could interfere by forming complexes with fluoride. From a linear least-squares fit to a plot of E_{meas} versus $\log[F^-]$ you can obtain the slope [$S = \beta(0.05916)$]. Typically S equals 56 ± 2 mV.

C. Method of Standard Addition

The method of variable volume standard addition will be used to determine the fluoride content of an unknown solution. In this approach, a solution containing fluoride will be mixed with the TISAB and the potential will be measured. Then successive amounts of a fluoride standard solution will be added and the potential will be measured after each addition. The following describes how the unknown fluoride concentration can be obtained from these measurements.

The measured potential (E) can be represented by

$$E = K + S \log C$$

where K is a constant;

S is the slope of the calibration curve and equals β(0.05916);

C is the analyte ion (F^-) concentration.

This equation can be rearranged to give

$$C = 10^{\frac{E-K}{S}} = \frac{10^{\frac{E}{S}}}{10^{\frac{K}{S}}}$$

The analyte ion concentration after any addition of the standard is given by

$$C = \frac{C_0 V_0 + C_{std} V_{std}}{V_0 + V_{std}}$$

where C_0 is the analyte concentration before any standard is added;

V_0 is the volume of the solution before any standard is added;

C_{std} is the concentration of the standard solution;

V_{std} is the volume of standard solution that is added.

Substituting this expression for C in the previous equation gives

$$\frac{C_0 V_0 + C_{std} V_{std}}{V_0 + V_{std}} = \frac{10^{\frac{E}{S}}}{10^{\frac{K}{S}}}$$

This equation can be rearranged to give

$$10^{\frac{E}{S}} (V_0 + V_{std}) = 10^{\frac{K}{S}} C_0 V_0 + 10^{\frac{K}{S}} C_{std} V_{std}$$

A plot of $10^{E/S}$ ($V_0 + V_{std}$) versus $C_{std}V_{std}$ will give a linear plot with an x-intercept (y = 0) equal to the negative of the amount (µg) of analyte in the solution before addition of the standard.

$$x\text{-}intercept = -\frac{b}{m} = -\frac{10^{\frac{K}{S}} C_0 V_0}{10^{\frac{K}{S}}} = -C_0 V_0$$

The analyte concentration (µg/mL) in the original unknown solution (C_{unk}) can then be determined by dividing by the volume of the unknown fluoride solution (V_{unk}).

$$C_{unk} = \frac{C_0 V_0}{V_{unk}}$$

II. Procedure

A. Preparation of Fluoride Standard Solutions

1. By serial dilution of the 1000 µg/mL fluoride standard solution, prepare 50 mL each of 200, 20 and 2 µg/mL fluoride standards in 50-mL volumetric flasks. After thorough mixing, transfer each diluted standard solution to a labeled plastic reagent bottle for storage. Calculate the concentration of each diluted standard using the exact concentration of the stock solution.

B. Calibration Check of Electrode

1. Carefully pipet 25.00 mL of the most dilute fluoride standard into a 50-mL volumetric flask and dilute to the mark with the TISAB. Stopper the flask and thoroughly mix the solution.

2. Transfer this solution to a 100-mL plastic beaker. Place the beaker on a stirring plate, add a magnetic stirring bar and begin stirring at a constant rate.

3. Connect the fluoride ISE to a pH meter and set the meter to the mV mode. Rinse the electrode with dionized water and blot dry.

4. Lower the electrode into the standard solution. When the reading is stable record the mV value.

5. Repeat steps II.B.1-4 for each of the remaining fluoride standards.

6. Estimate of the slope (S) from the difference in the mV readings for each factor of ten increase in the fluoride ion concentration. If your value is outside the expected range, consult with your lab instructor.

C. Analysis of Unknown

1. Prepare a 500 µg/mL fluoride standard by pipeting 5.000 mL of the 1000 µg/mL fluoride standard solution into a 10-mL volumetric flask and diluting to the mark with the TISAB.

2. Carefully pipet 50.00 mL of your fluoride unknown, which contains the TISAB at the same concentration as used for the standard calibrations, into a 100-mL plastic beaker. Place the beaker on a stirring plate, add a magnetic stirring bar and begin stirring at a constant rate.

3. Rinse the ISE with deionized water and blot dry.

4. Lower the electrode into the unknown solution. When the reading is stable record the mV value.

5. Pipet 1.000 mL of the 500 µg/mL F^- standard solution into the unknown solution. When the reading is stable record the mV value.

6. Make three additional 1.000 mL additions of the standard solution and record the mV reading after each addition as before.

7. When finished, rinse the ISE with deionized water and place it in the storage container.

III. Calculations

A. Determination of Calibration Slope

1. Using EXCEL, plot the mV reading for the diluted fluoride standards versus the log of the actual fluoride ion concentration.

2. Fit the data points with a linear least-squares line and from the equation for the line obtain the slope (S).

B. Determination of Unknown Concentration by Standard Addition

1. Using the slope determined in III.A, plot $10^{E/S}$ $(V_0 + V_{std})$ versus $C_{std}V_{std}$. Remember to include the initial reading with no added standard.

2. Fit the data points with a linear least-squares line and obtain the equation for the line.

3. Use the equation for the line to determine the x-intercept and from this calculate the fluoride ion concentration in the unknown solution.

IV. Results

Report the fluoride ion concentration (µg/mL) in the unknown solution.