

Experiment 24 Determination of Fluoride with Ion Selective Electrode

Introduction

The invention of the fluoride ion selective electrode (ISE) approximately 40 years ago by Frant and Ross (*Science* 1966, 154, 1553; Harris, pages 80, 332) immediately found an application to this problem. Today the potentiometric determination of fluoride using an ISE/reference electrode pair is performed routinely in water analysis laboratories throughout the world.

The basic idea of ion selective electrodes is to measure electrode potentials (voltages) and from that determine analyte concentrations in solution. Measuring voltages requires two electrical contact points. One is a reference electrode whose potential is constant. The other is a sensing electrode, whose potential varies with analyte concentration. $E_{\text{sensing}} - E_{\text{reference}}$ is the measured potential. For fluoride the sensing electrode surface is a crystal of LaF_3 doped with a little EuF_2 . The crystal has some fluoride vacancy sites (due to the EuF_2), allowing a response to external fluoride.

The potential of an F^- ISE/reference electrode cell is given by the Nernst equation:

$$E_{\text{ISE}}(\text{vs } E_{\text{ref}}) = \text{Constant} - \frac{RT}{nF} \ln(a_{\text{F}^-}) + E_{\text{lj}} \quad (\text{Eqn. 1})$$

where R is the gas constant (8.314 J/(mol·K)), T is the absolute temperature, n is the number of equivalents per mole ($n=1$ eq/mole for the fluoride electrode), F is the Faraday (96485 Coul/eq), and E_{lj} is the liquid junction potential developed at the reference electrode salt bridge. (Note: 1 Joule/Coulomb = 1 Volt.) The activity of the fluoride ion is given by:

$$a_{\text{F}^-} = \gamma_{\text{F}^-} C_{\text{F}^-} \quad (\text{Eqn. 2})$$

where γ_{F^-} is the activity coefficient and C_{F^-} is the concentration of the analyte. If the experimental conditions are adjusted so the activity coefficient is constant, we can express equation 1 as:

$$E_{\text{ISE}}(\text{vs } E_{\text{ref}}) = \text{Constant} - K \ln(C_{\text{F}^-}) + E_{\text{lj}} \quad (\text{Eqn. 3})$$

where the new constant K now contains the activity coefficient γ_{F^-} . The fluoride

concentration C_{F^-} is a function of pH since HF is a weak acid with a pK_a equal to

3.17 at 25 °C.

In view of the above theory, a **Total Ionic Strength Adjustment Buffer (TISAB)** solution is used for several reasons in the potentiometric determination of fluoride.

1. The TISAB keeps solution pH at 5.50. Since changing pH changes the concentration of fluoride in solution, it is important to keep pH constant. (*Note: HF is a hazardous, toxic compound – it is important to work at a pH well above the pK_a of HF!*)
2. The TISAB maintains constant ionic strength so the $\log(\gamma_{F^-})$ and the K terms in equation 3 are constant during the experiment.
3. The TISAB maintains the liquid junction potential ($E_{l,j}$) approximately constant.
4. The TISAB masks any aluminum or iron ions in the unknown by tightly complexing those ions with 1,2-cyclohexyl enediaminetetracetic acid, which is part of the ISA solution. These metal ions would otherwise form fluoride complexes and decrease the concentration of free fluoride.

Determining the concentration of unknown samples requires calibration of some sort. In analytical work, it is common to prepare a graph of measured signal versus concentration, and use that to determine concentrations. For ISE's, that graph would plot measured **potential versus log[analyte]**, with a linear response expected, based on the form of the Nernst equation.

Procedure

1. Preparation of TISAB (Total Ionic Strength Adjustment Buffer)

Add 11.4 ml glacial acetic acid , 11.6 g sodium chloride , 6.2 g sodium hydroxide and 0.4 g 1,2-cyclohexyl enediaminetetracetic acid (CDTA) to approximately 165 ml distilled deion water. Stir and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5 M NaOH. Transfer this solution to a 200 ml volumetric flask and dilute to the mark with distilled deion water.

2. Preparation of fluoride standards

Prepare 10.0 ml of 50 ppm F^- standard solution from the 1000 ppm F^- stock solution. Then, prepare each of the following standard solutions: 0.5 ppm, 1.0 ppm, 2.0 ppm, and 5.0 ppm, by pipetting an appropriate volume of the 50 ppm standard solution to individual 25 ml volumetric flask. Adjust the standard F^- solutions to the same ionic strength by pipetting 12.5 ml of TISAB into each volumetric flask and dilute to the mark with distilled deion water.

3. Preparation of Toothpaste Sample

A weighed sample of toothpaste of approximately **200 mg** is placed in a 100 ml beaker containing 25 ml of TISAB. The mixture is then boiled for 2 minutes. After cooling, the solution is quantitatively transferred to a 50 ml volumetric flask and diluted to the mark with distilled deion water.

4. Preparation of Tea Sample

Pipette 12.5 ml tea sample into 25 ml volumetric flask and dilute to the mark with TISAB.

5. Measurement of ISE Potentials

Starting with the most dilute fluoride standard, immerse the fluoride electrode into the standard solution. The solution should be stirred at a non-turbulent rate. This stirring rate should be constant for all measurements. Turn the knob on the pH/mV meter from standby to mV. Allow at least 10 minutes for the potential reading to stabilize and record the potential. Readings for **higher** concentrations take a **shorter** time to come to equilibrium. Rinse the electrode with distilled water and pat dry with a kimwipe. Repeat the above measuring step for all standard solutions and samples.

Results

1. Plot potential in mV versus pF^- (**-log** of fluoride concentration , **ppm**) of the standards. Use the method of least squares to find the best fitting line to the data.
2. Determine F^- concentration ($\mu\text{g/g}$) of the toothpaste.
3. Determine F^- concentration (ppm) of the tea sample.
4. What is the **slope** of your calibration curve and how is this related to the Nernst equation? Compare your **slope** with the **Nernstian slope** and comment on its closeness to theory.