Determination of Fluoride Ion Using an Ion Selective Electrode

INTRODUCTION

In recent years direct potentiometry has become important as an analytical technique largely because of the development of ion-selective electrodes (ISE). This type of electrode incorporates a special ion-sensitive membrane which may be glass, a crystalline inorganic material or an organic ion-exchanger. The membrane interacts specifically with the ion of choice, in our case fluoride, allowing the electrical potential of the half cell to be controlled predominantly by the F- concentration.

The potential of the ISE is measured against a suitable reference electrode using an electrometer or pH meter. The electrode potential is related to the logarithm of the concentration of the measured ion by the Nernst equation.

$$E = E^{o} + 2.303\frac{RT}{nF}\log[M]$$

where n is the ion charge (negative for anions). The factor 2.303 RT/F has a theoretical value of 59 mV at 25 °C. The equation is only valid for very dilute solutions or for solutions where the ionic strength is constant. Ionic strength is defined by

$$I = \frac{1}{2}\sum Z_i^2 C_i$$

where Z_i is the charge on an ion and C_i is its concentration. ISEs are available for measuring more than 20 different cations (e.g., Ag^+, Na^+, K^+, Ca^{++}, Cu^{++}) and anions (e.g., F^-, Cl^-, S^{-2}, CN^-).

In this experiment you will use a fluoride sensitive electrode and either a saturated calomel electrode (SCE) or Ag/AgCl external reference electrode to measure the fluoride-ion content of a solution. Fluoride is added to drinking water and toothpaste to inhibit dental caries; it is also present in effluents from many industrial processes, e.g., manufacture of fluoro-polymers. Flouride ISEs only respond to free ionized F- in solution and can thus be used to measure this ion in the presence of other fluorine compounds, e.g., AlF_6^{3-} or organofluorine compounds. In other words, the electrode responds to F^- activity.

REAGENTS AND EQUIPMENT

- NaF, dried at 100 °C for 1 hour.
- Liquid NaF unknown.
- KCl (7.55 g)
- Fluoride ISE and Ag/AgCl or SCE reference electrode.
- Multimeter or pH meter capable of displaying mV potentials

ATTENTION:
DO NOT Store fluoride solutions in volumetric flasks!!! Transfer solutions to plastic bottles if you are unable to complete the experiment in one lab period

PROCEDURE

Preparation of Standards

1. Dry the NaF solid for 1 hour at 100 °C.
2. Accurately weigh out about 0.42 g of NaF, dissolve in deionized water, dilute to 100 mL in a volumetric flask and mix well. This solution is about 10^{-1} F in NaF.
3. Transfer 10.00 mL of the solution prepared in (2) to a 100 mL volumetric flask using a pipet, dilute to volume with deionized water and mix well. This solution is about 10^{-2}F in NaF.
4. Weigh out 7.55 g of KCl on a top-loading balance and dissolve in 100 mL of deionized water. This solution is 1 F in KCl.
5. Prepare standard solutions in four 100 mL volumetric flasks as follows:

	mL 10^{-2} F NaF (from 3)	mL 1 F KCl
(I)	1.00	10.00
(II)	2.00	10.00
(III)	5.00	10.00
(IV)	10.00	10.00

Dilute each flask to volume with deionized water and mix well.

Instrument Setup and Operation

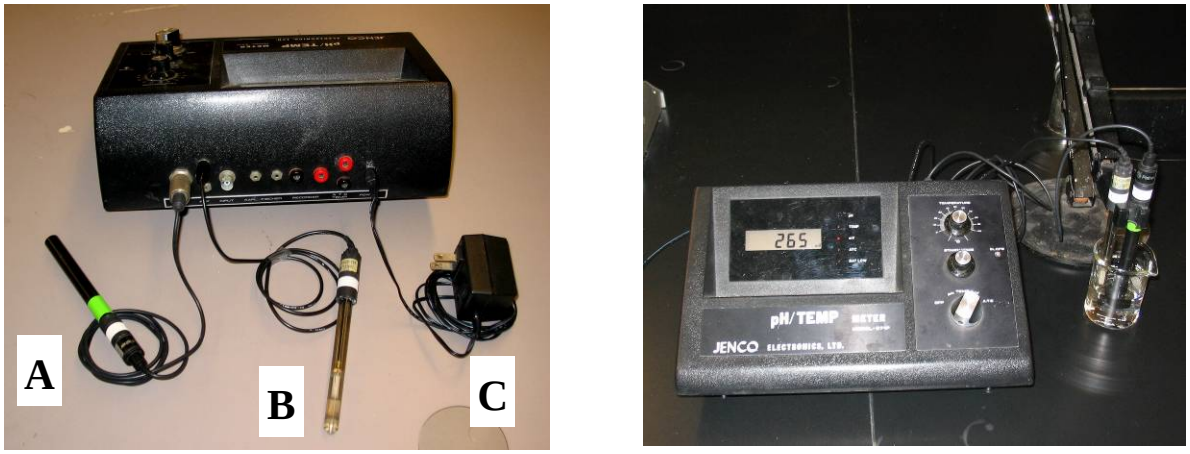


Figure 1. Instrument setup for ISE measurements. Left: Back of pH/mV meter showing ISE (A), reference electrode (B) and power (C) connections. Right: Front view showing typical arrangement for mV measurements. Note that electrodes are suspended off the bottom of the beaker that holds the sample.

NOTE: When the electrodes are not immersed in solution, be sure to set the meter to the "OFF" position to avoid polarizing the electrodes. During measurement, set the meter to the "mV" position, making sure that the "mV" indicator light is illuminated.

Analysis of Unknown

Your unknown for this experiment is a solution. When you obtain your unknown, you need to quantitatively transfer it to a 100 mL volumetric flask and dilute it to the mark, resulting in the

"prepared" unknown solution. You are to report the results of this "prepared" unknown.

1. Add 1 mL of your prepared unknown, then 10 mL of KCl to a 100 mL volumetric flask. Dilute to the 100 mL mark with deionized water.
2. Measure the potential in mV of the fluoride ISE vs the reference electrode for each of the four standards and unknowns.

C A U T I O N: Do not touch the ISE ion sensitive membrane. Rinse it with deionized water between measurements and then with a small volume of the new solution. Do not wipe it dry.

3. Pour about 30 mL of each standard or unknown solution into a clean, dry 100 mL beaker and immerse the electrodes in the solution to a depth of not more than 2 cm, as shown in Figure 1. Measure the electrode potential, taking care to note both the sign and the magnitude of the potential.
4. When you finish, rinse the electrodes with deionized water. Leave the reference electrode in the appropriate storage solution. The F^- ISE should be stored dry and loosely capped. DO NOT force the cap onto the electrode tip!

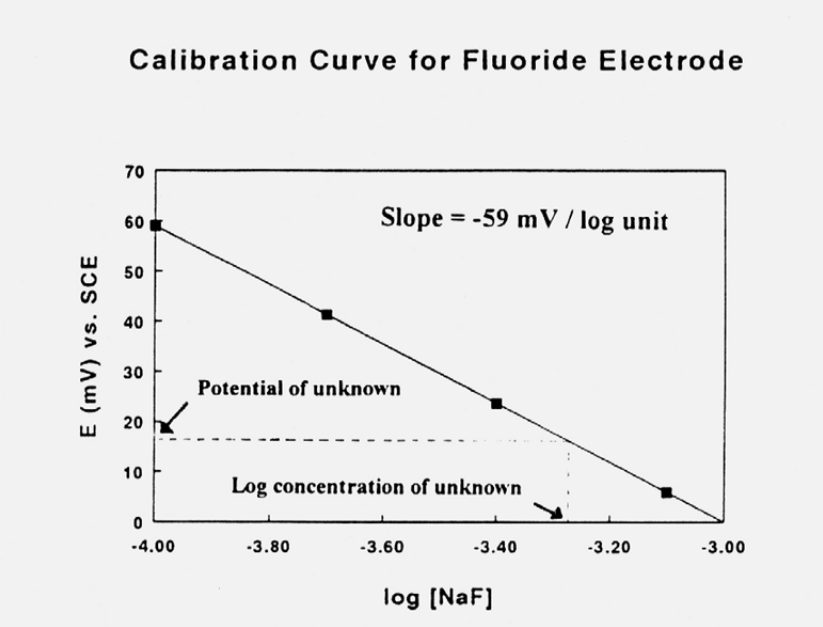
Analysis of Fluoride in Toothpaste

The toothpaste sample should be prepared and analyzed at the same time the standards and your prepared unknown.

1. Accurately weigh about 0.2 g of toothpaste into a 100 mL beaker. Add 10 mL of 1F KCl and about 40 mL of water to the beaker.
2. Boil the mixture gently for 3-5 minutes, breaking up the toothpaste with a stirring rod if necessary.
3. Cool the solution, quantitatively transfer the liquid to a 100 mL volumetric flask and dilute to volume.
4. Analyze this sample when you perform the analysis on your standards and unknown. Report your results in terms of the % (w/w) F^- in the toothpaste. Report this on your unknown card in addition to the unknown sample results that you turn in.

TREATMENT OF RESULTS

1. Accurately calculate the molarity of NaF for each of the standard solutions.
2. Plot a graph of the logarithm of [NaF] in the standard solutions vs E. Determine the best line through the four standard solution experimental points. Calculate the slope of the calibration curve, and its associated uncertainty. How nearly does it equal the theoretical slope, -59 mV? (Slope = dE/ dlog[NaF]).



3. Utilizing the calibration curve, determine the concentration of NaF in your "prepared" unknown solution. Report this as percent fluoride (% w/v) in the "prepared" unknown. Report the 95% confidence interval for your results.