

## Experiment: Ion-selective determination of fluoride

The development of ion-selective electrodes (ISE) makes possible the determination of the concentration of ions of choice using selectively sensitive electrode membranes. More than 20 ions can be determined by ISE, for example cations such as:  $\text{Ag}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and anions like:  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{CN}^-$ . The operation of a fluoride-selective electrode is based on the potential which develops across a single-crystal lanthanum fluoride membrane. This potential is proportional to the activity of  $\text{F}^-$  ions in contact with the membrane. This potential is measured against a convenient reference electrode and closely follows the Nernst Equation:

$$E = E^\circ + (0.059 \text{ volts/n}) \log[\text{ion}] \quad \text{where } n = \text{ionic charge.}$$

The above equation is valid for dilute solutions and for solutions whose ionic strength is kept constant. Ionic strength,  $\mu$ , is defined as

$$\mu = (1/2) \sum c_i z_i^2.$$

Where  $c_i$  = concentration of the  $i^{\text{th}}$  ion,  $z_i$  is the charge of the  $i^{\text{th}}$  ion. For example, solutions containing 1:1 electrolyte, like NaCl,  $\mu = [\text{NaCl}]$ . In this experiment, the fluoride content of (1) an unknown NaF solution, and (2) toothpaste will be measured by direct current potentiometry with a fluoride ion activity electrode in a high ionic strength medium.

In practical operation, a high ionic strength medium is necessary so that fluoride ion concentrations may be deduced from measurement of fluoride ion activities. A concept called TISAB (*Total Ionic Strength Adjustment Buffer*) has been introduced precisely for adjusting the conditions of fluoride analysis. The composition of TISAB is not critical when the same solution is used for standardization and unknowns. A typical composition is given in the Table below. TISAB is used to “swamp out” standard and sample differences in ionic strength. TISAB also minimizes the influence of polyvalent cation-fluoride complexes.

Table: Composition of TISAB

Sodium chloride	1.0 M
Acetic acid ( $\text{pK}_a=4.75$ )	0.25 M
Sodium acetate	0.75 M
Sodium citrate <sup>a</sup>	0.001 M
pH <sup>b</sup>	5.0
Ionic strength (approx.)	1.83 M

In this experiment, instead of TISAB, a 0.1M KCl solution will be employed.

Procedure:

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<sup>a</sup> Some citrate ion is added to complex preferentially with metal ions such as iron and aluminum to ensure that the fluoride ion is displaced into the solution as “free” fluoride

<sup>b</sup> The optimum pH range for the fluoride electrode is at pH 5.

Prepare the solvent: Prepare 750 mL of 0.10 M KCl. This will serve the same purpose as the TISAB. Note that all dilutions will be made using this 0.1M KCl solution and not distilled water.

Prepare the calibration solutions: Prepare a 100-mL stock solution containing 1000 ppm  $F^-$  using reagent grade sodium fluoride dried for 1 hour in the oven. (Show your instructor by a clear calculation that the grams of NaF required for this solution would be somewhere between 0.2 - 0.3 grams.). Dissolve the weighed NaF in a 100-mL beaker, add 50mL of 0.1M KCl. Transfer the solution to a 100-mL volumetric flask and fill it to the mark with 0.1M KCl and mix very well. (Depending on your instructor's discretion, this stock solution may be shared by all students doing the fluoride analysis on the same lab session). From this stock solution, prepare a 20-ppm  $F^-$  calibrating solution (for example, place 2-mLs of the stock in a 100-mL volumetric flask, add 0.10 M KCl and dilute it to the mark). From this 20-ppm calibrating solution, prepare 10, 5, 2.5 and 1.25 ppm calibrating fluoride solutions by serial dilution by taking 50-mL of the prior solution and diluting it to 100-mL with 0.1 M KCl in a 100-mL volumetric flask.

Obtain and prepare samples for analysis:

(1) Obtain a toothpaste sample from the instructor by submitting a clean, dry and preweighed 20-mL beaker to which 0.2-0.25 g toothpaste will be added by the instructor. A toothpaste sample is prepared as follows: weigh the beaker plus the sample of toothpaste to determine the net weight of the toothpaste sample. Transfer the toothpaste sample to a 250 mL beaker with a microspatula or stirring rod and add 50 mL 0.1 M KCl. Boil the solution gently for 2-3 minutes. Filter the suspension by gravity filtration using a #1 or #5 filter. After cooling, transfer the solution quantitatively to a 100 mL volumetric flask and make up to volume with 0.1M KCl.

(2) Obtain an unknown NaF sample from the instructor by submitting a clean 10-mL graduated cylinder. A 7.00-10.0 mL sample of an unknown solution of  $F^-$  will be supplied to you by the instructor. Transfer accurately (with a 5-mL transfer pipet), 5.0 mL of the solution and dilute it to 100-mL in a volumetric flask using the 0.1M KCl.

Measurement of  $F^-$ : The measuring system consists of the fluoride and reference electrodes and a pH meter in the mV mode. Note that although the fluoride electrode is a solid state which employs a rugged, epoxy-body construction, it is important to exercise proper care. The electrode is stored dry when not in use, with a protective end cap. Carefully remove the end cap so as to avoid any damage to the electrode.

Transfer approximately 20 mL of each solution into 50 mL beakers. Be sure that the solution is well stirred and record the observed emf (in mV) 3 minutes after the fluoride and reference electrodes have been immersed in the solution. Repeat for all the calibrating solutions as well as the sample solutions. Note: If the emf of the toothpaste falls outside the emf range of the standards additional calibrating solutions may be needed.

Analysis:

Plot the observed emf in mV vs logarithm of ppm F<sup>-</sup> to obtain a calibration curve. A negative slope of -59±4 mV (between 20°-30°C) indicates normal operation.

Determine the ppm F<sup>-</sup> in your unknown and in the toothpaste from the calibration curve.

The ppm unknown can be determined using the following equation:

$$\text{Ppm F}_{\text{unk}} = \text{ppm F}^{-} \text{ from graph} \times (100 \text{ mL}/5\text{mL}) = \text{ppm F}^{-} (\text{graph}) \times 20.$$

Express the fluoride ion concentration in the toothpaste as %F. The following equation can be used:

$$\%F = \frac{(\text{ppm F}^{-} \text{ from graph}) (0.100 \text{ L}) (100\%)}{(\text{mg toothpaste used})}$$

Further reading:

1. M.S. Frant and J.W. Rose, Jr. *Anal. Chem.* 40, 1169 (1968).

2. H. H. Willard, L. L. Meritt, J. A. Dean and F. A. Settle, "Instrumental methods of Analysis", D. van Nostrand Co., New York (1981).

3. <http://www2.truman.edu/~blamp/chem222/manual/pdf/ise.pdf>.

Informal Report

Experiment: Determination of Fluoride

Date submitted \_\_\_\_\_

Name \_\_\_\_\_

Time submitted \_\_\_\_\_

Locker # \_\_\_\_\_

Values obtained:

Unknown liquid \_\_\_\_\_ ppm F<sup>-</sup>

Toothpaste \_\_\_\_\_ % NaF

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mg of toothpaste used: \_\_\_\_\_ mg

mg of NaF dissolved \_\_\_\_\_ mg

ppm F<sup>-</sup> in stock solution = \_\_\_\_\_ ppm

% toothpaste =

ppm F<sup>-</sup> in unknown =