

## DETERMINATION OF CHLORIDE AND FLUORIDE WITH ION SELECTIVE ELECTRODES

Chloride and fluoride are easily and rapidly determined in liquid samples using chloride and fluoride selective electrodes. The described method involves only a simple, one-step dilution, and it completely eliminates the need for tedious and complicated methods.

The chloride electrode responds directly to the activity of chloride ions. Linear response for this type of electrode extends down to approximately  $10^{-4}$  mol/l (3.5 ppm in chloride). The fluoride selective electrode exhibits linear response to concentrations ranging from  $10^{-5}$  mol/l to saturated and will give analytically useful results down to  $10^{-7}$  mol/l. The electrodes can be used for direct potentiometric determinations, or as end-point indicators for titrations. Some parameters for ion-selective electrodes are in tables in your textbook on pages 673 and 676.

### **Interference Effects**

In using an ion selective electrode, the approximate concentration of interfering ions present in a sample must be known. The ratio of the interfering ion concentration to the concentration of the species of interest must be kept within allowable limits. By arranging a test procedure so that the ratio of concentrations of interfering ions to the ion of interest does not exceed the tabulated limits, no irreversible damage will be done to the crystal sensing element, and errors of 1% or less will be introduced by the interfering ions. In general, the greater the concentration of the ion to be measured, the greater the level of interfering ions that may be tolerated.

### **Operation Notes:**

**Electrode preconditioning** - The ion selective electrodes (ISE) are ready for use immediately upon removal from the shelf. Soaking prior to use is unnecessary and possibly harmful. The electrodes may be stored dry. The reference electrodes, on the other hand, should be soaked prior to use.

**Stirring** - The response time of an electrode is generally enhanced by moderate stirring of the sample solution. However, streaming potentials at the reference electrode's liquid junction become apparent when vigorous stirring is employed. The potential observed for stirred samples usually differs slightly from that for unstirred samples.

**Electrode handling between samples** - The electrode pair (the ISE and the reference electrode) may be rinsed with distilled water and blotted gently to prevent cross contamination between samples. Rinsing the electrode pair with the next solution is preferable, since it avoids the necessity of wiping the electrode, thereby eliminating the possibility of scratching the sensing element surface.

**Storage** - The halide electrodes can be stored dry without affecting their response. The electrodes should be cleaned before storage to insure that residues of dilute solutions containing interfering ions do not become concentrated by evaporation on the electrode

sensing element.

## **SOLUTIONS**

**Fluoride Standards:** Prepare 1 l of 200 ppm  $F^-$  solution by weighing exactly approximately 0.442 g of NaF into a 1-l volumetric flask. Fill to mark with distilled deionized water. Prepare 100 ml solutions containing 10.0, 20.0, 50.0 and 100.0 ppm  $F^-$  standards by appropriate dilution of the 200 ppm standard.

**Chloride Standards:** Prepare 1 l of 200 ppm  $Cl^-$  solution by weighing exactly approximately 0.33 g of NaCl into a 1-l volumetric flask. Fill to mark with distilled deionized water. Prepare 100 ml solutions containing 10.0, 20.0, 50.0 and 100.0 ppm  $Cl^-$  standards by dilution of the 200 ppm standard.

**Total Ionic Strength Adjustor Buffer (TISAB):** Place approximately 500 ml of distilled water in a 1-l beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 0.30 g of sodium citrate. Stir to dissolve. Place beaker in a water bath (for cooling), insert a calibrated pH electrode and reference electrode into the solution, and slowly add approximately 5 mol/l sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature. Pour into a 1-l volumetric flask and add distilled water to the mark.

**Nitrate Ion Solution:** Prepare one liter of 0.02 mol/l  $HNO_3$  by adding 1.25 ml of concentrated  $HNO_3$  to a 1-l volumetric flask.

**Iodide Interference Solution:** Place 0.13 g of KI to a 100 ml flask. Add distilled water to the mark.

## **PROCEDURE**

1. Connect a chloride ISE and a reference electrode to the pH meter. Set the pH meter to read in volts (or mV). For each chloride standard, pipette 20 ml of nitrate ion solution and 20 ml of the chloride standard into a 50-ml beaker (each standard done separately). Measure the electrode potentials developed in each calibration solution. For the calibration graph, plot electrode potentials in millivolts (linear axis) versus the log of the halide concentration in ppm.
2. Connect a fluoride ISE and a reference electrode to the pH meter. Set the pH meter to read in potential units. For each fluoride standard, pipette 20 ml of TISAB and 20 ml of the fluoride standard into a 50 ml beaker (each standard done separately). Measure the electrode potentials developed in each calibration solution. For the calibration graph, plot electrode potentials in millivolts (linear axis) vs. the log of the halide concentration in ppm.
3. Record the electrode potentials developed in the unknown solutions and determine the chloride and fluoride concentrations from the calibration curve.
4. Determine the concentration of  $F^-$  or  $Cl^-$  in your unknown (the specific unknown is indicated on the unknown).
5. To study interference effects, add 10 ml of the KI solution to the 10.0 and 50.0 ppm solutions of chloride and fluoride. Add 20.0 ml of TISAB or nitrate ion. Measure the electrode potentials developed in each calibration solution.
6. Make a calibration plot of the interference effects and compare to original calibration

plot. How does the slope change? Why do you think this is?

**Procedure Notes:**

1. Standards and unknowns should be at the same temperature.
2. Many magnetic stirrers warm the solution being measured and cause a slow drift in electrode reading. A dry cork or asbestos (Though, where do you find asbestos in 2009?) sheet under the beaker minimizes the problem.
3. Perform readings on at least 3 samples of the unknown.

**Results**

Report the concentrations of  $\text{Cl}^-$  and  $\text{F}^-$  in the unknowns in ppm. Present all of the calibration curves and explain the extent of interferences. Can  $\text{Cl}^-$  and  $\text{F}^-$  be determined simultaneously?

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