Introduction
Gravimetric and titrimetric methods for the determination of particular analytes are very powerful in their application but they can sometimes be cumbersome, time consuming and inapplicable to certain analytic applications. One alternate method of nondestructive analysis that has found extensive use in the analytical laboratory is direct potentiometry. Direct potentiometry is the measurement of electrical potential (voltage) between two dissimilar chemical electrodes under the condition of zero external current flow to give the concentration of a particular ionic analyte (the “sensed ion”) in solution. The most important and common example of direct potentiometry is the pH meter where $[\text{H}^+]$ (hydrogen ion concentration) is measured. Using sophisticated design, electrodes can be created that display selectivity for a particular ion to the exclusion of others to a certain and quantifiable degree. Through the combination of such an Ion Selective Electrode (ISE), a suitable reference electrode and a sensitive voltmeter (a millivoltmeter) a very sensitive, direct, non-destructive method can be devised. The ISE falls into the category known as the indicator electrode.

An important difference between direct potentiometry and other analytic methods is that direct potentiometry provides a measure of the concentration of an analyte and not the total amount in a sample. Direct potentiometry is sensitive to a wide range of analyte concentration often from $10^{-1}$ to $10^6$ M.

The ability to measure concentration provides for a number of powerful chemical tools. One is the ability to determine the solubility and hence the solubility product constant ($K_{sp}$) of a sparingly soluble substance. Another involves the determination of the result of an enzymatic reaction, such as ammonia from urease, without having to perform any separation or purification steps.

In the present experiment, the potentiometric determination of fluoride ion involves a measurement of the potential difference of the cell comprised of a fluoride indicator electrode and a conventional silver-silver chloride reference electrode (with an electrolyte saturated with potassium chloride). The measured potential difference ($E_{\text{cell}}$) for the cell is given by the Nernst equation

$$E_{\text{cell}} = E_0 + S \log (A)$$  \hspace{1cm} (1)

$E_0$ is the reference potential which is a constant. $S$ is the ISE slope that is approximately -57 mV per decade of fluoride concentration. $A$ is the activity or “effective concentration” of fluoride in the solution. The fluoride activity is related to the fluoride concentration by the activity coefficient, $\gamma$

$$A = \gamma [F^{-}]$$  \hspace{1cm} (2)

The ionic activity coefficient is variable between zero and one and largely depends on the total ionic strength of the solution. If the total ionic strength of the solution is high and constant relative to the sensed ion concentration, the activity coefficient is constant and the activity is directly proportional to concentration. This is an important and very convenient simplification.

A Total Ionic Strength Adjustment Buffer (TISAB: 0.1 M nitrate, 0.1 M citrate, sodium counter-ion pH 5.0 ± 0.1) is added to all analytes so the background total ionic strength is maintained at a high and constant value. The TISAB also contains a buffer to maintain the analyte at a fixed value. Additionally, the TISAB contains a species that complexes with multivalent cations that can interfere with the fluoride determination.
A representative potentiometric calibration curve of fluoride is shown in Figure 1. This curve and figure differ from previously studied ones in that the x-axis, containing the fluoride concentration, is represented with a logarithmic rather than a linear scale. Included on this figure is a “curve fit” (via the method of linear regression) of the experimental data to a logarithmic expression (see equation 1) together with the derived values of slope and intercept with their uncertainties expressed as one standard deviation.

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E_{\text{cell}} = a + b \cdot \log([F^-])
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\[
a = -0.274 \pm 0.004
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b = -0.058 \pm 0.002
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**Procedures**

**Set Up of Measurement Apparatus:** A fluoride ion selective electrode (referred to as the indicator electrode), a reference electrode (either silver-silver chloride or double-junction), a voltmeter and an electrode stand are assembled as shown in Figure 2.

**Preparation of Solutions for a Standard Curve:** Prepare six solutions of varying fluoride concentration, from $10^{-3}$ to $10^{-6}$ M, each with a volume of 100 mL by ten-fold serial dilution and in TISAB. To a clean 100-mL volumetric flask, add 10.0 mL of 1.00 M sodium fluoride followed by 25 mL of 4x concentrated TISAB. Make up the mark with water. Transfer this solution in a labeled Erlenmeyer flask. Repeat this entire process five additional times, to make the six solutions.

**Potentiometric Measurement of a Solution:** Transfer the solution to be measured into a clean and dry beaker large enough to contain the two electrodes. Insert clean and dry indicator and reference electrodes into a solution and swirl gently. Record the potential difference on the meter using the voltage scale (rather than pH scale) after it has stabilized to within 10 mV and record $[F^-]$ of the analyte. There will often continue to be some drift in the potential with time but it will decrease after the initial stabilization if the electrodes are working well. Remove the electrodes and gently wipe the cylindrical surfaces dry using soft absorbent paper. Using the lightest touch, dab the end surface only once with the paper. The electrodes may be left in air during the laboratory session.

**Preparation and Potentiometric Measurement of Unknown Sample Solution:** Tare a clean and dry 250-mL beaker. Deposit approximately one gram of toothpaste in the beaker and record the mass accurately. Add 25 mL of 4x concentrated TISAB and 25 mL of water. Bring the solution to a boil using a hot plate set to 150 °C and boil for roughly five minutes to suspend the solids. Cool the beaker to room temperature and let the foam subside a bit. Quantitatively
transfer the beaker’s contents to a 100 mL volumetric flask and make up the volume with water (use the level between the liquid and the foam). At this point the solution will be cloudy, foamy and minty fresh. Measure the potential difference of this unknown sample solution as described above. Using your previously collected standard curve data estimate the concentration of fluoride ion in the unknown sample solution.

**Standard Addition with an Unknown Sample:** Perform an analysis of the unknown using the technique of standard addition. While continuously stirring the unknown sample solution using a magnetic stir bar added to the solution and a magnetic stir plate, (don’t whack the electrodes with the stir bar) make five or six additions of the $10^{-1}$ M [F] solution and record the potential difference after each addition (after stabilization). Select the volume of each the addition so to approximately double, triple, quadruple, etc. the unknown sample solution’s fluoride concentration.

**Results**

![Graph showing standard addition function](image)

**Figure 3.** A representative Standard Addition determination. Several aliquots of 0.1 M fluoride were added, in turn, to a 100 mL volume of unknown fluoride concentration and the potential difference was measured. The function was computed per Harris (2008) and plotted against the volume of added fluoride. The x-intercept, known fluoride concentration and unknown sample volume can be used to find the unknown concentration, in this case 84.7 µM.

Prepare a standard calibration curve figure showing the measured potential difference versus the fluoride concentration on a semi-logarithmic plot (plot [F] on a logarithmic axis not the logarithm of [F] on a linear axis, see Figure 2). Perform a logarithmic curve fit ($y = a + b \cdot \log(x)$) to the experimental data. Write a custom fitting function, if needed. Perform the fit on the visually linear section of potential versus log([F]) and include the best-fit straight line to the figure. Include the estimated regression coefficients and their estimated uncertainty.

Report your estimate of the unknown sample solution concentration using the standard calibration curve data.

Finally, report your estimate of the concentration of fluoride containing species in your selected toothpaste using the all the same units reported by the toothpaste manufacturer, either weight-weight, weight-volume percent or both.

**Discussion**

Estimate of the minimum detection limit for [F], the so-called Limit of Detection, using your calibration data and justify your choice. Estimate of the maximum detection limit for [F] similarly. It should be clear at this time that this estimate is meant to reflect the method only and to exclude consideration of the ability of the analyst to dilute the analyte.

**References**