# Calibrations III – Internal Standards

## Overview

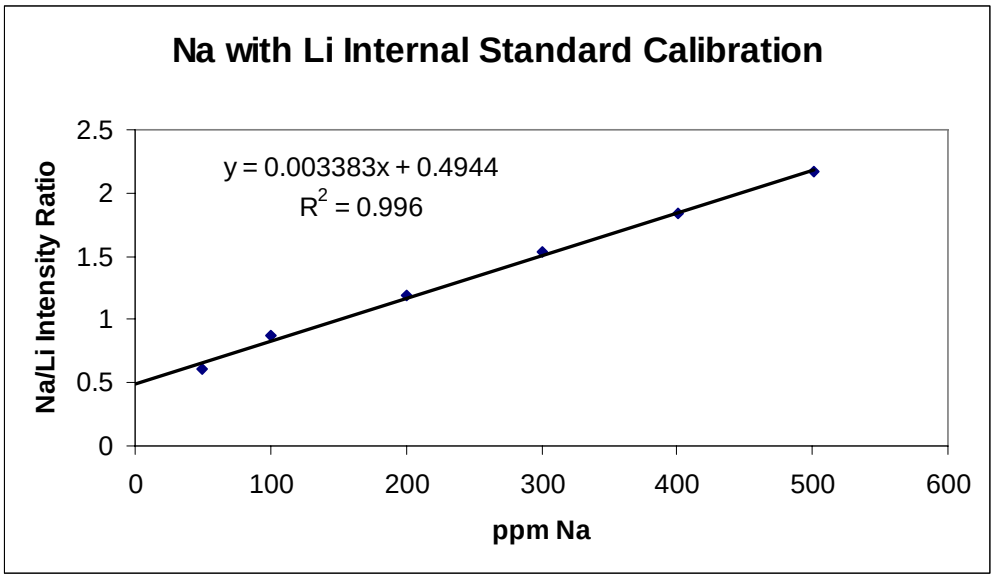
This is the third of three labs which demonstrate different ways to calibrate instrumental methods for quantitative analyses. The first lab was a direct calibration with no twists. The 2nd lab involved a standard additions procedure; useful when the sample composition (matrix) is unknown, complex, and affects the analytical signal. This 3rd lab utilizes an internal standards procedure. Whereas a standard additions method spikes the sample with additional analyte, an internal standards method involves addition of a detectable compound that is different from the analyte. The internal standards calibration solves common problems such as when the quantity of sample analyzed cannot be precisely controlled (as in this experiment), or the instrument response is variable from run to run. The internal standard method is described in general in Skoog Section 1D-4, pp. 17, and Harris Section 5-4, pp. 90-91. Please note that the Harris text describes a 1-point calibration, which is not advisable and therefore not done in this lab, but the idea is the same.

## General Procedure

Although this experiment utilizes the same Ocean Optics array spectrometer, it is being used in a very different way. In the previous two laboratories absorbance measurements were acquired with the application of Beer's Law. This is an emission experiment, and although one again hopes to obtain a linear calibration, Beer's Law is only applicable to absorbance not emission measurements.

Most students by this point in their careers have been asked to perform a qualitative analysis for Na using the flame test. In this procedure a thin nichrome wire is placed in a sample, then placed in a Bunsen burner flame. A persistent yellow flame, resulting from Na emission at 589 nm, positively identifies Na in the sample. The array spectrometer equipped with a fiber optic probe can be used to detect sodium and other elemental emissions in the flame (J. Chem. Educ. 2006, 83, 277-279). To obtain quantitative data using this method a 2nd element must be added (the internal standard) to all samples and standards, since it is not possible to precisely control the amount of sample in the flame at any one time without expensive hardware called an aspirator. By taking the ratio of the analyte (sodium) emission intensity to the internal standard (lithium) emission intensity, the signal is normalized and independent of the quantity of sample in the flame at any given time. We will construct a poor person's aspirator, indeed a poor person's flame emission spectrometer for quantitative analysis, by attaching a chromatographic sprayer to a compressed air tank. The sample solution will be sprayed into the air holes of a Bunsen burner flame partially enclosed with the top of a PET 2-gallon soda bottle. The fiber optic probe of the spectrometer will be pointed at the flame, and you will collect data using the CCD array spectrometer in kinetics mode for replicate measurements.

The internal standards calibration line is a plot of this band intensity ratio on the y-axis vs. analyte concentration on the x-axis. In this laboratory lithium is used as an internal standard since it is detectable, is also an alkali metal and thus behaves similarly to sodium, and is not commonly found so the sample matrix is unlikely to interfere with this internal standard. An internal standards calibration line is shown below using this method.




Here is some specific information:

- You are advised to make stock sodium and lithium solutions for use to prepare all of the standard solutions for calibration. Dry, solid primary standard NaCl and $Li_2CO_3$ is available. The $Li_2CO_3$ will require HCl for dissolution. Thought should be put into reasonable concentrations for these stock solutions and how the dilutions will be done. Valuable time can be saved if thought is put into this beforehand, you should have all the information required.
- All of the samples in the above internal calibration had approximately 320 ppm Li.
- Acquiring the data will be a 2-person operation. One person will aim the aspirator through the cut-out at the base of the Bunsen burner, while the other person will monitor the spectrometer. Once the spectrometer is set up in kinetics mode with the proper settings and wavelengths for data acquisition, the person operating the spectrometer will click the start button and count the data acquisitions. Data acquisition can be stopped after about 10 replicate measurements, which will only take a few seconds. The file name will need to be changed to avoid being overwritten, then exported to a diskette or flash drive for data workup off line.
- Signals approaching 50000 counts are considered off scale since 60000 is the top of the scale.

Two unknowns will be analyzed. The first is a NaCl solution made by the stockroom. The second will be a salty snack such as pretzels provided by the stockroom or yourselves. (Hint: oily snacks like potato chips cause difficulties in sample preparation. Stick to salty snacks which do not have excessive oil; that

is avoid things that are deep fried, lean towards things that are baked. Not bad advice outside of the chemistry lab either!) In this case the amount of sodium should be calculated on a mass basis such as mg Na/g food. This sample should be placed in 3M HCl and boiled gently for 15 minutes in the hood. Insoluble components should be filtered and washed. The recovered, filtered solution must be prepared for analysis. Think hard about what data is required to calculate the sodium content in mg/g, and do the experiment such that the data is obtainable. Compare these results to the amount of Na in the food reported by the manufacturer on the package.