

ELEMENTAL ANALYSES USING EXTERNAL STANDARDS

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Basic principle of external calibration

There are many different ways to determine the concentration of an element in a rock sample. The approach here is to measure the signal intensity of an element in an unknown solution (**sample**) and reference it to the signal intensity of the same element in another solution, whose elemental concentrations are known. The solution whose concentration is known is called an **external standard**. For example, the concentration of an element in the sample solution C_{SA}^{Sol} is determined by

$$C_{SA}^{Sol} = I_{SA} \frac{C_{ST}^{Sol}}{I_{ST}} \quad (1)$$

where I_{SA} is the measured intensity in **counts per second** (cps) of the element in the sample solution, I_{ST} is the intensity in the standard, and C_{ST}^{Sol} is the known concentration in the standard.

Drift and the Internal Standard

In the ideal world, Eq. 1 suffices. However, in the real world, there are some complications. First, one never measures the sample at the same time the standard is measured. During the elapsed time between standard and sample measurements, it is possible that the **sensitivity** of the instrument has **drifted** (sensitivity is defined as the number of cps obtained for a given concentration unit, e.g. cps/ppm; for the Element 2, the sensitivity of ^{115}In is $\sim 1-2 \times 10^9$ cps/ppm). Drift can be caused by many factors. For our instrument, drift is usually caused by buildup of precipitates in the nebulizer, torch, and/or on the sampler cone. A second complication is that there may be **matrix** differences between the standard and the sample. The matrix is defined loosely as a property which describes the bulk composition of the solution, e.g., total dissolved solids, acidity, salinity, organic molecule content, etc. Variations in these matrices can give rise to variations in ionization efficiency; thus, that the signal of a given trace element in two solutions having identical concentrations of that element but different matrices could be different. In an ideal world, it would be best to match the matrices of the standard and sample. In practice, it is not possible to exactly match standard and sample matrices because in general we do not know the composition of the unknown sample! Matrix effects therefore represent another form of drift. Before applying Eq. 1, one must first correct all measured signals for drift – instrumental and matrix induced.

We correct for drift using the following principle. Let us assume that we spiked our sample and standard solutions with exactly the same concentration of a given element (not the particular element whose concentrations we are trying to determine!), which we call the **internal standard (IS)**. If there are no instrumental- and matrix-induced drifts,

the signal intensities of the IS in the sample I_{SA} and standard solutions I_{ST} should be identical. If there is drift, it follows that we should be able to correct for the drift. Thus, if we wish to drift-correct our sample intensities to our standard intensities, we multiply the intensity of the element of interest in our sample, I_{SA} , by a **drift correction factor**:

$$I_{SA} \left(\frac{I_{ST}}{I_{SA}} \right) \quad (2a)$$

In practice, we are often faced with the situation where we did not spike each solution with the identical amount of IS but we know exactly how much we put in to each solution. We can account for this by modifying Eq. 2a:

$$I_{SA} \left(\frac{I_{ST} C_{SA}^{IS}}{I_{SA} C_{ST}^{IS}} \right) \quad (2b)$$

where C_{SA}^{IS} is the concentration of the IS in the sample and C_{ST}^{IS} in the standard.

The element mass that is chosen for an internal standard is based on the following criteria:

- 1) The element mass chosen for an IS must be absent or present in negligible quantities in the sample and standard. Thus, we could choose an enriched isotope of an element or we can choose an element whose natural concentrations are extremely low. The former can be very expensive. In our lab, we typically use Indium (^{115}In). The natural abundances of In in most rocks is very small, and in addition, we spike at an amount that swamps the natural abundance signal (but remains comparable to the concentrations of the elements of interest).
- 2) The IS element must have negligible isobaric interferences.
- 3) The IS element should remain stable in solution for long periods of time.

Blank correction

Another complication in determining elemental concentrations in an unknown is the possibility for contamination. When using an **external rock standard (see below)**, one always processes a **procedural blank** through the same chemistry that the rock standard and sample unknowns undergo. The contamination it picks up represents the integrated contamination from the various dissolution steps. The assumption is that the procedural blank represents a constant background contamination that affects standards and samples identically. Therefore, in order to correct for the procedural blank, one must subtract out the intensities of the procedural blank. This is, of course, done after all intensities have been drift-corrected:

$$I_{SA}^* = I_{SA} \left(\frac{I_{ST} C_{SA}^{IS}}{I_{SA} C_{ST}^{IS}} \right) - I_{BL} \left(\frac{I_{ST} C_{BL}^{IS}}{I_{BL} C_{ST}^{IS}} \right) \quad (3)$$

where I_{SA}^* is the **blank-corrected and drift-corrected** intensity of the element of interest in the sample, I_{BL} is the intensity of the IS element in the blank, and C_{BL}^{IS} is the concentration of the IS element in the blank.

When using a **synthetic standard** (see below), we do not apply the blank correction at this stage. This is because the synthetic standard did not go through the

same procedure as the samples. It is also assumed that the synthetic standard has little or no blank problems (relative to the signal intensities of the synthetic standard, samples, etc.). The procedural blank concentrations are determined by treating the procedural blank as a sample and then subtracting the former from the latter at the very end of the data reduction protocol.

External standard normalization

There are two types of external standards used in this laboratory: a **certified rock standard** and a **synthetic standard**. The certified rock standard is a rock powder whose concentrations have been independently determined by many different laboratories. A synthetic standard is one that is prepared in our laboratory by mixing of certified single-element (and sometimes multi-element) solution standards purchased from various companies that make standards (e.g., Alfa-Aesar Johnson Matthey, NIST, Spex, etc.).

In general, we prefer to use certified rock standards to determine elemental concentrations in an unknown sample because it is much easier to match the matrix of our samples with a certified rock standard than a synthetic standard. The external rock standard is taken through the exact same process as all sample unknowns. An external rock standard only works if complete dissolution is achieved. In some cases, the matrix of the unknown sample may be so different from all of the rock standards in our laboratory. In such cases, we may use a synthetic standard to determine concentrations.

In all cases, one or more **quality standards** are analyzed in order to check the calibration. Quality standards are other certified rock standards.

Dilution effects

In general, the total amount of rock powder dissolved for the external standard and sample unknowns are not identical. In addition the total weight of the diluted standards and samples are also not identical. Therefore, appropriate corrections must be made. The actual concentration of the element of interest in the sample solution, C_{SA}^{Sol} , is given by:

$$C_{SA}^{Sol} = I_{SA}^* \frac{C_{ST}^{Sol}}{I_{ST}} \quad (4)$$

where C_{ST}^{Sol} is the actual concentration of the element in the standard solution and is given by

$$C_{ST}^{Sol} = \frac{C_{ST}^{Rock} M_{ST}^{Rock}}{M_{ST}^{Sol}} \quad (5)$$

where C_{ST}^{Rock} is the certified concentration in the rock standard, M_{ST}^{Rock} is the mass of the certified rock standard dissolved, and M_{ST}^{Sol} is the final diluted weight of the standard solution.

Similarly, in order to obtain the concentration in the sample powder, one needs to correct for the different amounts of sample powder dissolved and the total diluted solution weight. Equation 5 then becomes

$$C_{SA}^{Rock} = I_{SA}^* \frac{C_{ST}^{Sol}}{I_{ST}} \frac{M_{SA}^{Sol}}{M_{SA}^{Rock}} \quad (6a)$$

$$C_{SA}^{Rock} = I_{SA}^* \frac{C_{ST}^{Rock}}{I_{ST}} \frac{M_{ST}^{Rock}}{M_{ST}^{Sol}} \frac{M_{SA}^{Sol}}{M_{SA}^{Rock}} \quad (6b)$$

Multiple calibration points

In the above discussion, we have calibrated the sensitivity of our instrument using one external standard, e.g., we have a one-point calibration. To increase the accuracy of our results, we can generate a calibration curve using more than one point. For example, we can run two of the same rock standards, but at different dilutions. We can then do a linear regression through the data and empirically generate the best-fit calibration line. Treating the intensity of the standards as the y-variable and the concentration of the standards as the x-variable, we generate the following linear regressions $y = mx + b$ (or $y = mx$ if we force the regression through zero). The concentration of an element can then be determined by inverting the linear regression, e.g. $x = (y-b)/m$. In Eq. 6b, the first two terms on the right hand side would be replaced by

$$(I_{SA}^* - b) / m \quad (7)$$

Limit of detection and filtering of bad data

There are many ways to define the limit of detection. The most widely used definition in the ICP-MS community is the 3-sigma definition,

$$LOD = \frac{3\sigma_{Blank}}{S} \quad (8)$$

where σ_{Blank} represents 1 standard deviation of the signal intensities of the procedural blank and S is the sensitivity of the instrument. The **sensitivity** is the signal intensity obtained for a given concentration of a particular element in solution. Signal intensities above the LOD are considered to be resolvable from the blank. Those below the LOD are rejected.