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Internal Standardization for ICP-OES and ICP-MS

Jerry Dulude, Glass Expansion Inc., 4 Barlows Landing Road, Unit #2, Pocasset MA 02559, USA.

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INTRODUCTION

Internal standardization has long been used to effectively compensate for matrix based interferences. It is similar to the method of standard additions (MSA) in that the response of an element in a sample as opposed to the standard is used to calculate concentration. In MSA, one or more additions of the analyte are added to the sample and the in-sample calibration curve is used to calculate concentration. MSA is typically used with atomic absorption spectrometry (AAS) determinations (particularly with a graphite furnace) since the matrix effects differ in severity between elements. For ICP-OES, it is generally assumed that matrix effects are similar for all elements (an assumption that is not rigorously valid, as will be discussed below). For ICP-MS, matrix effects can be reasonably accurately predicted based on the mass/charge of the analyte. Therefore, concentration is corrected based upon the response of an added element (or elements) not otherwise present in the sample (see Figure 1 below). All commercially available ICP spectrometers have the capability of performing this correction automatically.

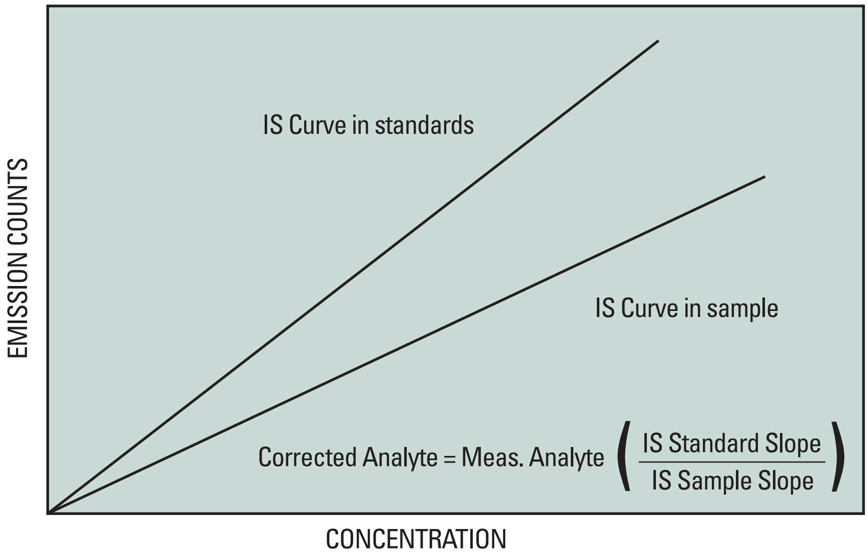
It should be recognized that internal standardization does not correct for all interferences. For example, it does not correct for background or spectral/mass overlap interferences.

In ICP-OES, matrix interferences stem from several mechanisms as follows:
1. Differences between the viscosity or surface tension of the sample and standards can alter the transport efficiency of the sample introduction system.

2. The presence of high concentrations of dissolved solids is quite common and may result in “plasma loading” such that the amount of energy available is decreased. The effects of this tend to be more severe on those “hard” lines that require more energy for efficient excitation. It should also be noted that this type of interference predominantly affects ion lines. Atom lines are more robust (except in the case of the easily ionizable elements discussed below), while the ion lines tend to be suppressed. It is therefore important to link analyte ion lines with internal standard ion lines and similarly for atom lines. Commonly employed internal standard lines for Yttrium and Scandium are ion lines. Experience has shown that atom lines often do not require an internal standard to compensate for plasma loading effects. Indeed, linking an analyte atom line to an internal standard ion line may result in an erroneously high concentration.

3. Easily ionizable element (EIE) effects are more pronounced for axially viewed plasmas where a small slice of the plasma is not easily isolated. Elements such as sodium, potassium, lithium, and cesium exist predominantly as ions in an ICP. However, the only intense emission lines are for atomic species, the population of which is fragile and can be altered by the presence of other easily ionizable elements. Rather than an internal standard, an ionization suppressant consisting of a high concentration of an easily ionizable element that is not of analytical

Figure 1. Internal Standard Calculation



$$\text{Corrected Analyte} = \text{Meas. Analyte}\left(\frac{\text{IS Standard Slope}}{\text{IS Sample Slope}}\right)$$

interest can be added to all solutions to serve as a buffering agent. Often, the ionization suppressant is mixed with the internal standard(s) and added simultaneously.

In ICP-MS, interferences are similar with some distinctions. EIE effects are dramatically reduced in comparison to axial ICP-OES since for ICP-MS, the ion populations are of analytical interest and these are not significantly affected by the presence of other easily ionizable elements. However, ICP-MS does suffer from mass related interferences which occur at the sampling interface and thus are not seen in ICP-OES. In essence, the presence of high concentrations of high mass ions has a suppressive effect on elements of lower mass. To compensate for this type of interference, a multiple element internal standard solution is used to cover the mass range of interest.

CHOOSING INTERNAL STANDARDS

The rules for choosing internal standards are as follows:

- Choose an element that is not of analytical concern.
- Choose an element which is extremely unlikely to be present in the samples. Precious metals or rare earths are often selected as internal standards for this reason.
- Choose an element that behaves similarly to the elements to which it will be linked.
- Choose an analytical wavelength or mass for the internal standard that behaves similarly to that to which it will be linked and one that has a clean background in the sample type of interest.
- Choose an internal standard element concentration that gives a signal that is within a high precision range.

MANUAL VS. IN-LINE ADDITION

Manual Addition

Certain types of samples incorporate a significant and consistent dilution as part of the workup, for example metals and oils. In these cases, it is easy and accurate to add the internal standard(s) to the diluent. When sample dilution is undesirable, individual small volume additions to each solution must be performed. For multiple internal standard additions, a "soup" may first be prepared of all elements and then an aliquot of this added to each analytical solution. Some concerns are as follows:

- If sample volumes are small, the degree of dilution will be greater.
- As internal standard aliquots become smaller, the accuracy of addition suffers.
- Each addition carries a finite error which is the propagation of the errors of sample and internal standard volume and concentration measurements.
- Use of micropipettes to add internal standard may result in the uptake of an air bubble which will adversely affect accuracy.

Furthermore, manual addition can be quite time consuming and labor intensive. For these reasons, many analysts elect to add internal standard automatically via an in-line system.

In-Line Addition

Automatic addition of internal standard is usually accomplished by teeing the internal standard solution into the sample line using an available position on the existing peristaltic pump (see figure 2 below).

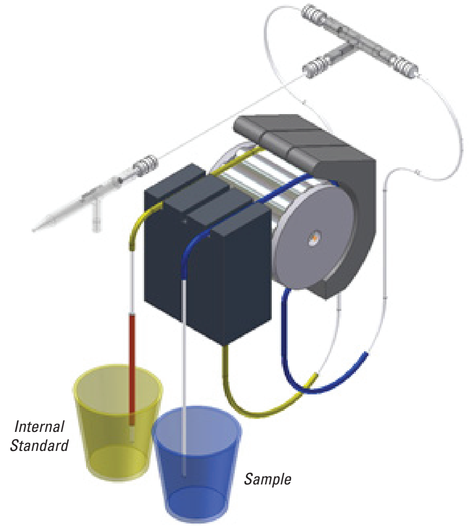


Figure2. Schematic of In-line Internal Standard Addition

Concerns regarding the in-line addition approach are as follows:

- The ID of the pump tubing used for the two solutions (sample and internal standard) will determine the degree of dilution of both the solutions.
- The combined solution flow of sample and internal standard should not exceed the uptake rate for which the nebulizer is designed.
- Accurate matrix compensation often requires intimate mixing of the internal standard with the sample.
- The addition of the mixing tee increases the washout time of the sample.

In order to provide a general recommendation, two examples will be given, one for ICP-OES and the other for ICP-MS.

ICP-OES

First, standard conditions without using in-line addition will be described. Typically, uptake rates of between 1 and 3 ml/min are employed and therefore 2ml/min will be used in this example. To accomplish this, 0.76mm ID pump tubing is used at the appropriate pump speed. A commonly used internal standard element is either Scandium or Yttrium at a concentration of 1ppm in the analytical sample.

For in-line addition, to minimize dilution of the sample, a pump tube of 0.19mm ID is recommended for the internal standard (see the System-Set-up section on how to connect small ID pump tubing). Since volume (and hence flow rate) vary as the square of the radius, this would result in 6% dilution of the sample and 94% dilution of the internal standard. The sample dilution is negligible with respect to the effect on detection limits and on appropriate nebulizer consumption and therefore the pump speed can remain unchanged. The internal standard reservoir should be prepared at 15ppm to deliver approximately 1ppm in the sample.

ICP-MS

Conditions without in-line addition are as follows. Lower uptake rates are commonly employed in ICP-MS to both reduce oxides and enhance ionization. For this example, an uptake rate of 0.4ml/min will be used. For this uptake rate, a low-flow nebulizer is recommended such as the Glass Expansion MicroMist or PFA OpalMist models. To achieve the desired uptake rate in a pumped mode, the 0.38mm ID pump tubing can be used at the appropriate pump speed for the sample.

For in-line addition, and again to minimize sample dilution, a pump tube of 0.13mm ID is recommended for the internal standard (see the System-Set-up section on how to connect small ID pump tubing). In this case the sample will be diluted by 10% and the internal standard by 90%. To maintain optimum nebulizer performance, it is recommended to decrease the pump speed by 10%. The internal standard reservoir should be prepared with each element at a concentration that is a factor of 10 times greater than that desired in the sample.

System Set-up

Standard supplies are available from most lab supply houses to allow the assembly of a "home made" internal standard in-line addition kit. The following components are recommended:

- A merging tee. Inexpensive plastic tees are available. Exercise care in the handling of these as they can be somewhat fragile and susceptible to leaks if handled harshly.
- Appropriate pump tubing, either 2 tab or 3 tab as your pump dictates. For the small ID pump tubing recommended above, some type of stretching tool is recommended to enable the connection of the pump tubing to the capillary tubing (for example, a 1.3mm OD capillary needs to be inserted into a 0.13mm ID pump tube). Care must be exercised to avoid contamination of the tubing. Alternatively, flared-end pump tubing is available which obviates the need for tube stretching (see below).
- A mixing chamber; often a small length of larger bore tubing that allows the merged solutions to intimately mix.
- Air-tight connections for the four junctions as follows:
    - Sample to tee
    - Internal standard to tee
    - Tee to mixing chamber
    - Mixing chamber to nebulizer
- Capillary tubing to connect all components.

To facilitate the creation of this kit, Glass Expansion offers a ready-to-use modular in-line addition kit (see Figure 3) that has the following attributes:

- Combination merging tee and mixing chamber. Made from borosilicate glass, this component combines zero dead volume ports for the sample and internal standard with a measured mixing chamber on the outlet side of the tee. This guarantees minimal washout times along with intimate mixing of the solutions. This mixing tee is also available in HF resistant plastic.
- All capillary tubing is included and equipped with EzyFit connectors for air-tight seals to the mixing tee and nebulizer.
- A sipper probe with integrated capillary is included to facilitate uptake of internal standard solution.
- Squares of sandpaper are included to facilitate the connection of the pump tubing to the capillary tubing.
- The kit is compatible with Glass Expansion's line of trace metal free flared-end pump tubing so that even very small ID tubing can easily be mated to the capillary tubing.

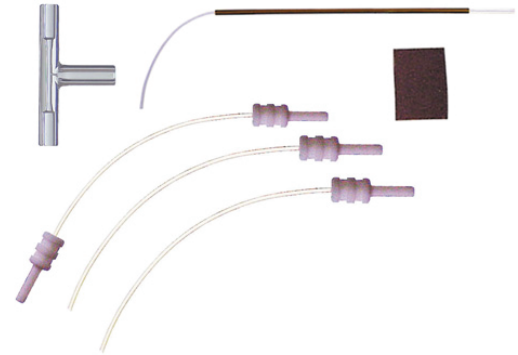


Figure 3: Glass Expansion In-line Internal Standard Kit

CONCLUSION

For both ICP-OES and ICP-MS internal standardization is a useful and often necessary tool to help achieve a high level of accuracy. The automatic in-line addition of internal standards to every sample, standard, blank and control is an effective method to achieve high accuracy of addition and minimize sample dilution while reducing labor and saving time.

For more information or to contact Glass Expansion, please visit www.geicp.com.

Glass Expansion (Australia)
15 Batman Street
West Melbourne VIC 3003
Australia
Telephone: +61 3 9320 1111
Facsimile: +61 3 9320 1112
Email: enquiries@geicp.com
Web: www.geicp.com

Glass Expansion Inc.
4 Barlows Landing Road
Unit #2
Pocasset, MA 02559
USA
Telephone: 508 563 1800
Facsimile: 508 563 1802
Email: geusa@geicp.com