

# Ultra-High Precision Determination of Elements by ICP-OES – Matching the Internal Standard

## Introduction

ICP-OES is well known as a multi-element analysis technique and is used in many laboratories around the world. ICP-OES has the advantage that it suffers far less from matrix effects than ICP-MS, but that is not to say that there is none. Using an internal standard usually enhances the quality of the analysis results, though care should be taken to ensure the best performance.

## Internal Standardisation

The main reasons for internal standardisation is to reduce the effects of the matrix, changes in transport efficiency, and instrumental drift.

Transport efficiency can be influenced by the condition of the peristaltic pump tubing, but more so by the physical characteristics of the sample: surface tension, density, and viscosity. The equation from Japanese engineers, Nukiyama and Tanasawa<sup>[1]</sup>, explains the influence these three parameters have on the nebulisation of liquids.

Obviously, there are some requirements for internal standards – the most obvious is that it should be absent from the sample, or at least contained in minute quantities.

## Matching the Internal Standard

Different elements will emit varying amounts of light in the plasma, depending upon the plasma conditions and the position of the atoms in the plasma. It is possible to predict the behaviour of an element if three pieces of information are known beforehand: (a) the first ionisation potential, (b) the total excitation energy required to emit light at a given wavelength, (c) if the emission of the specific wavelength originates from an atom or an ion (indicated by I or II, respectively).

Matching these three parameters will ensure optimal matching of internal standard element to the analyte<sup>[2]</sup>, because if the three parameters are closely matched, both the internal standard element and the analyte element will behave very similarly in the plasma.

## Objective

The aim of the determination was to quantify very precisely the amount of boron present in a detergent – expected to be approximately 40,000 mg/kg. This analysis was previously performed by ICP-MS, but it produced poor quality results (poor precision and accuracy).

## Choosing the Internal Standard

The three parameters that need to match are:

- First Ionisation Potential
- Total Excitation Energy
- Atomic or Ionic Emission

The primary emission line for boron is B I 249.773 nm. The aim was to search for an internal standard element that will suit this emission line.

After careful consideration, it was decided to use antimony as an internal standard.

The detail regarding boron and antimony are shown in Table 1, below:

Table 1: Detail for Boron and Antimony

Parameter	B	Sb	Unit
Emission Line	249.773	217.581	nm
Emission Type	Atomic	Atomic	
First Ionisation Energy	8.298	8.644	eV
Total Excitation Energy	4.964	5.698	eV

## Internal Standard

The internal standard solution contained 40,000 mg/L Sb in 20 % HCl.

## Sample Preparation

The sample was prepared in duplicate by accurately weighing 1 g sample (to the nearest 0.0001 g) into a 50 mL plastic sample tube. Water and 5 mL HCl were added. 1,000 µL of internal standard was accurately added, using a syringe pump microdilutor. The sample was diluted further to approximately 50 mL with water and mixed properly. A further dilution of 1 mL to 10 mL was made in 5 % HCl matrix.

HCl was chosen as it effectively stabilises boron.

## Calibration Standards

Stock calibration standards were prepared gravimetrically in the range of 0 to 70 g/kg by weighing appropriate amounts of sodium tetraborate decahydrate (a primary material) into 50 mL sample vials and adding HCl. 1,000 µL of internal standard was accurately added, using a syringe pump microdilutor and made up to approximately 50 g with water and mixed properly. These standards were then further diluted (1 mL to 10 mL) exactly as the samples to create working calibration standard solutions.

## Instrumental Set-up

A SPECTRO ARCOS II Multiview (from SPECTRO Analytical Instruments GmbH, Kleve, Germany) was set up in radial view mode. The operating parameters are in Table 2, below.



Figure 1: SPECTRO ARCOS II Multiview, as used in this Application – Photo courtesy of SPECTRO Analytical Instruments GmbH – all rights reserved

Table 2: ICP-OES Operating Parameters

Parameter	Value	Unit
Plasma Power	1,400	Watt
Coolant Flow	12.00	L/min
Auxiliary Flow	0.60	L/min
Nebuliser Flow	0.70	L/min
Sample Flow	1.22	mL/min

The instrument was calibrated with the working calibration standard solutions. The calibration curve is shown in Figure 2, below. The correlation coefficient was 0.999996 and the detection limit 0.0017 mg/L.

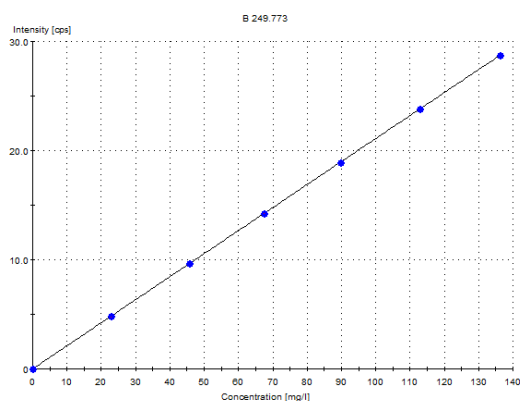


Figure 2: Calibration Curve for B I 249.773 nm

## Analysis Results

Three measurements were performed on each of the two solutions. The individual measurements and descriptive statistics are shown in Table 3, below:

Table 3: Analytical Results and Descriptive Statistics

Sample	Type	[B]
Solution 1	Measurement 1	39,258
	Measurement 2	39,263
	Measurement 3	39,211
	Average / (mg/kg)	39,244
	% RSD	0.074%
Solution 2	Measurement 1	39,217
	Measurement 2	39,206
	Measurement 3	39,226
	Average / (mg/kg)	39,216
	% RSD	0.025%
Overall	Average / (mg/kg)	39,230
	% RSD	0.050%
	% RMS	0.055%
	95 % CI (k=2) / (mg/kg)	55

## Conclusion

The precision of the three replicate measurements, expressed as % RSD, were 0.074 % and 0.025 % respectively. The precision on the duplicate samples, as % RSD, was 0.050 %.

The 95 % Confidence Interval (with Coverage Factor k=2) is 55 mg/kg, thus the result lies within the range 39,175 to 39,285 mg/kg.

If this analysis were performed on ICP-MS, a 95 % Confidence Interval (with Coverage Factor k=2) is expected to be approximately 3,300 mg/kg (assuming a standard deviation of 30 µg/L on a test solution of 1,000 µg/L, three replicate measurements, and duplicate samples).

It is thus possible to obtain very precise results on ICP-OES by carefully choosing an internal standard.

## References

[1] Nukiyama, S. and Tanasawa, Y., Experiment on Atomization of Liquid by Means of Air Stream, Transactions of the Society of Mechanical Engineers - Japan, vol. 4, no. 14, pp. 86-93, 1938.

[2] Harmse, M.J. and McCrindle R.I., The determination of antimony in lead-antimony alloys using ICP-OES and internal standardisation, J. Anal. At. Spectrom., 2002, 17, 1411-1414