



Investigation of a measure of robustness in inductively coupled plasma mass spectrometry



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ABSTRACT

In industrial/commercial settings where operators often have minimal expertise in inductively coupled plasma (ICP) mass spectrometry (MS), there is a prevalent need for a response factor indicating robust plasma conditions, which is analogous to the Mg II/Mg I ratio in ICP optical emission spectrometry (OES), whereby a Mg II/Mg I ratio of 10 constitutes robust conditions. While minimizing the oxide ratio usually corresponds to robust conditions, there is no specific target value that is widely accepted as indicating robust conditions. Furthermore, tuning for low oxide ratios does not necessarily guarantee minimal matrix effects, as they really address polyatomic interferences. From experiments, conducted in parallel for both MS and OES, there were some element pairs of similar mass and very different ionization potential that were exploited for such a purpose, the rationale being that, if these elements were ionized to the same extent, then that could be indicative of a robust plasma. The Be II/Li I intensity ratio was directly related to the Mg II/Mg I ratio in OES. Moreover, the ${}^9\text{Be}^+/\text{Li}^+$ ratio was inversely related to the CeO^+/Ce^+ and LaO^+/La^+ oxide ratios in MS. The effects of different matrices (i.e. 0.01–0.1 M Na) were also investigated and compared to a conventional argon plasma optimized for maximum sensitivity. The suppression effect of these matrices was significantly reduced, if not eliminated in the case of 0.01 M Na, when the ${}^9\text{Be}^+/\text{Li}^+$ ratio was around 0.30 on the Varian 820 MS instrument. Moreover, a very similar ratio (0.28) increased robustness to the same extent on a completely different ICP-MS instrument (PerkinElmer NEXION). Much greater robustness was achieved using a mixed-gas plasma with nitrogen in the outer gas and either nitrogen or hydrogen as a sheathing gas, as the ${}^9\text{Be}^+/\text{Li}^+$ ratio was then around 1.70. To the best of our knowledge, this is the first report on using a simple analyte intensity ratio, ${}^9\text{Be}^+/\text{Li}^+$, to gauge plasma robustness.

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1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is an established ultra-trace analysis technique featuring multi-elemental detection capability with high sensitivity and over a wide linear dynamic range [1]. However, it is plagued by non-spectroscopic interferences (also called matrix effects) originating from different sources, such as electrostatic effects during aerosol generation and processing within the sample introduction system [2–4], which can result in analyte signal enhancement or suppression, and space charge effects downstream of the skimmer and in the ion optics region [5], which lead to mass-dependent analyte signal suppression. Because the latter, which are often prevalent, depend on the absolute amount of matrix, they can be mitigated by sample dilution if analyte levels are well above the determination limit. In all other cases, more time-consuming calibration strategies than a simple external calibration have to be used, such as internal standardization, standard addition, and isotope dilution, which involve spiking each sample with internal standard, analyte

standard or enriched nuclide. This spiking step not only takes time but increases the risk of contamination [6,7].

Several studies have thus been carried out in an attempt to find robust conditions eliminating matrix effects. For instance, optimising instrumental conditions in the presence of the matrix may enable analysis by external calibration [8], but such conditions are only applicable to the matrix in question. Another approach involved an instrument modification that is not easily made by ICP-MS users, where electrons generated by a heated filament inside the extraction lens reduced space charge effects as they moved through the ion path towards the skimmer [9]. Spatial profiling of ion distributions in the plasma showed that there was a sampling position beyond which analyte signal suppression turned into enhancement and that this position depended on the matrix, condition of the sampler and skimmer cones, etc. [10]. Mixed-gas plasmas resulting from the addition of nitrogen to the outer plasma gas, with or without concurrent addition of nitrogen or hydrogen as a sheath around the nebulizer gas, effectively mitigate matrix effects but, usually, at the expense of sensitivity [11–14].

From ICP optical emission spectrometry (OES), high radio frequency (R.F.) power, low nebulizer gas flow rate and low sample uptake rate, and/or a wider bore injector produce robust plasma conditions, under

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which the matrix composition of the sample has little effect on analyte intensity. Robust plasmas provide improved sample desolvation, vaporization, atomization and ionization through greater energy transfer from the bulk plasma to the central channel [15,16]. In ICP-OES, robust plasma conditions can be characterized by monitoring the Mg II (280.270 nm)/Mg I (285.213 nm), ionic to atomic line emission ratio. In general, a Mg II/Mg I ratio of 10 or greater constitutes robust plasma conditions [17,18]. There is no equivalent measure of robustness in ICP-MS, where robust plasma conditions are generally reflected by significantly reduced oxide fractions, minimal matrix effects and greater ionization of elements with a high first ionization potential (such as As or Zn). This robustness is usually achieved with a concurrent considerable loss in sensitivity.

Early ICP-MS literature showed that the ionization temperature (T_{ion}) in the central channel of the plasma can be estimated by taking the simple intensity ratio of singly charged ions from two elements of different ionization energy (IE) and similar mass. The intensity ratio of Cd^+/I^+ was used in solving the Saha equation, at a given electron number density, to determine T_{ion} for diagnostic purposes in both Ar and Ar–N₂ plasmas [19–21]. These studies showed that T_{ion} in the central channel of the plasma was increased with an increase in R.F. power and a decrease in carrier gas flow rate, both of which correspond to requirements for robust plasma conditions [16].

The goal of this work was to attempt to identify an equivalent to the Mg II/Mg I ratio in OES for MS by considering some element pairs of similar mass and very different ionization potentials. If the plasma conditions were such that elements of significantly different first ionization potentials were ionized to the same extent, then that could be indicative of a robust plasma. The establishment of a plasma robustness indicator in ICP-MS would be very significant as it would serve as an empirical benchmark, allowing for the direct comparison of plasma robustness between different instruments. It would also facilitate instrument optimisation by operators with basic knowledge of ICP-MS.

2. Experimental

2.1. Instrumentation

The ICP-MS research was conducted on a Varian 820MS (Mulgrave, Victoria, Australia) quadrupole-based instrument equipped with a MicroMist concentric nebulizer (Glass Expansion, MA, USA) fitted into a Peltier-cooled Scott double-pass spray chamber maintained at 0 °C. The generation of mixed-gas plasmas was described previously [13, 14]. Briefly, the gas plumbing was modified so that ultra-high purity N₂ could be added through the additional gas inlet of the instrument into the outer plasma gas. As well, ultra-high purity H₂ or N₂ was added to the central channel using the manufacturer-fitted sheathing device between the spray chamber and the torch. Mass flow controllers (Model 1259C-01000SV, MKS Instruments Inc., Andover, MA, USA)

were used to set the outer N₂ flow rate and H₂ or N₂ sheathing gas flow rate. The plasma operating conditions and measurement parameters are summarized in Table 1.

Measurements were also done on a lateral view ARCOS ICP-OES instrument (SPECTRO Analytical Instruments, Kleve, Germany) fitted with a multimode sample introduction system (MSIS) in nebulisation mode with a Mira Mist parallel path nebulizer (both from Burgener Research Inc., Mississauga, Canada). The plasma operating conditions and measurement parameters are summarized in Table 2.

2.2. Reagents

Commercially available 1000 mg/L single element standard solutions (SCP Science, Quebec, Canada), doubly deionized water (DDW) (Arium Pro UV/DI System, Sartorius Stedim Biotech, Goettingen, Germany), sub-boiled HNO₃ (ACS grade; Fisher Scientific, Ottawa, Canada) and NaNO₃ salt (BDH AnalaR, Toronto, Canada) were used to prepare blanks and 10 µg/L multi-elemental standard solutions in ultrapure 2% (v/v) HNO₃, with and without 0.01 M Na or 0.1 M Na. A DST-1000 sub-boiling distillation system (Savillex, Minnetonka, USA) was used to purify HNO₃.

2.3. Optimization

Before carrying out multivariate optimization of plasma operating conditions in ICP-MS, the plasma torch position was adjusted horizontally and vertically (under computer-control) to ensure that the plasma was centered on the sampler. Then, conditions were varied over the ranges of 18.0–20.0 L/min plasma gas flow rate, 1.8–2.0 L/min auxiliary gas flow rate, 0–0.10 L/min Ar sheath gas flow rate, 0.5–1.1 L/min nebulizer gas flow rate, 5–9 mm sampling depth and 1.30–1.50 kW R.F. power to maximize either sensitivity for a 5 µg/L multi-element solution containing Be, Ba, Ce, Mg, In, Pb and Th, while maintaining acceptable levels of oxide and doubly-charged ion ratios, or robustness by maximizing the ⁹Be⁺/⁷Li⁺ ratio for multi-element standard solutions in 0.01 M Na.

The multivariate optimisation of a mixed-gas plasma with N₂ in the outer gas and as a sheath was described previously [13]. In the case of the mixed-gas plasma with N₂ in the outer gas and H₂ as a sheath [14], a general full factorial experimental design was first used to fix the sampling depth, R.F. power and ion optics voltages at their optimum values. A multivariate optimization of the N₂ flow rate in the plasma gas, H₂ sheath gas flow rate and Ar nebulizer gas flow rate was then carried out using a central composite response surface experimental design (Table 3), again to maximize the relative signal intensity (with/without Na), with a value of 1 signifying the eradication of matrix effects. In all cases, experiments were repeated over several months to ensure the reproducibility of the results.

Table 1
Operating conditions for Varian 820MS ICP-MS instrument.

Parameter	Ar plasma at maximum sensitivity	Robust Ar plasma	Ar–N ₂ –N ₂ plasma [13]	Ar–N ₂ –H ₂ plasma
Ar plasma gas flow rate (L/min)	18.0			
Ar auxiliary gas flow rate (L/min)	1.80			
N ₂ gas flow rate (mL/min)	–	–	20	462
Sheath gas flow rate (mL/min)	20 (Ar)	20 (Ar)	90 (N ₂)	4 (H ₂)
Ar nebulizer gas flow rate (L/min)	1.00	0.80	0.80	0.80
R.F. power (kW)	1.40	1.50	1.50	1.45
Sampling depth (mm)	5.00			
Sample uptake rate (µL/min)	300			
Scanning mode	Peak hopping			
Dwell time (µs)	10,000			

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