

Role of Aerosol Water Vapour Loading in Inductively Coupled Plasma Mass Spectrometry*

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The influence of aerosol water loading has been shown to be of great significance in inductively coupled plasma mass spectrometry (ICP-MS). The resultant spectra from both singly charged M^+ , oxide MO^+ and doubly charged M^{2+} species have a strong dependence on the water loading in the plasma. Similarly the levels of polyatomic species, whether derived directly or indirectly from water components (O^+ , H^+) are also significantly improved when loadings are lowered. At low water loadings, the mean ion energies are reduced to low but reasonably constant levels (ca. 4 eV) for a wide range of elements facilitating more predictable plasmas and minimising mass dependent ion focusing.

Keywords: Water loading; inductively coupled plasma source mass spectrometry; cooled spray chamber

To a first approximation the argon inductively coupled plasma (ICP) is an ideal source for mass spectrometry (MS). Mainly singly charged monoatomic ions (M^+) are produced for most elements in the Periodic Table. Sensitivity is very high, typically $>10^6$ counts per second can be expected for solutions of $1 \mu\text{g ml}^{-1}$ for most elements. This combined with background levels of about 10 counts per second yields detection limits at the pg ml^{-1} level. Although the isotopic spectra are very simple, some spectral interferences are observed. Isobaric overlaps between isotopes of the same nominal mass can be found, but, in general, alternative isotopes are available for analytical use. Interferences from other species may also be observed at low levels.^{1,2} These are due to oxide and hydroxide species (MO^+ and MOH^+) and also, less significantly, doubly charged species (M^{2+}) are observed for elements whose second ionisation potentials are below 17 eV. Comprehensive lists of possible polyatomic species have been documented by Gray³ and also by Tan and Horlick.⁴

One of the advantages of the ICP is its ability to accept samples from a variety of sources provided that the sample can be converted into an aerosol for transport into the plasma. Solution nebulisation is the most common technique employed, but alternative techniques where sample vapour is generated by laser ablation,⁵ electrothermal vaporisation,⁶ chemical vapour generation,⁷ arc discharges⁸ or even as solid suspensions⁹ have been employed in ICP-MS.

The ICP, whether used for atomic or mass spectrometry, has a limited tolerance of water vapour.¹⁰ This has been documented with reference to atomic spectrometry, where it has been postulated that undissociated water vapour at (3000–4000 K) represents a considerable thermal buffer in the plasma injector.^{11,12} In ICP-MS the situation is more complex. Ions are principally extracted from an atmospheric plasma (where ionisation temperature T_i may be ca. 7500 K) into a low pressure (ca. 2 mbar) interfacial region situated before a quadrupole mass filter maintained at 10^{-6} mbar. It has been postulated that many of the less desirable spectral features are derived from events occurring within this low pressure interface region.^{1,13,14} Hence, the nature of the plasma and its relationship with this interface would be expected to have a substantial influence on the resulting mass spectrum.¹⁵ This paper describes how many spectral features in ICP-MS can also be influenced by the solvent water loading in the plasma and that the mechanisms may be traced to reactions within the interface.

Experimental

The work described herein was performed on a standard commercially available ICP-MS instrument (VG Plasma-Quad, VG Isotopes, Winsford, UK). The ICP consisted of a two-turn asymmetrically grounded load coil and Fassel-type torch with power derived from a 2.0 kW, 27 MHz RF generator (Henry Radio, USA). A glass, water-cooled, Scott-type spray chamber was used and the wall temperature of this was controlled to $\pm 0.1^\circ\text{C}$ from a Nesslab RTE 9DD recirculator. This allowed the spray-chamber temperature to be varied from -20 to 100°C if required. The nebuliser used was a Babington type¹⁶ which typically operated at 0.750 l min^{-1} with a back pressure of 30 p.s.i. The interface consisted of a nickel sampler (Nicone) with a 1.0-mm orifice, and a nickel skimmer (Nicone, mini-type) with a 0.75-mm orifice. The sampler-skimmer spacing was 4.5 mm. Typical multi-element conditions used were: 1.3-kW power, 12 l min^{-1} coolant and 0.5 l min^{-1} auxiliary flows. The plasma was sampled 10 mm from the load coil. The ion lenses were tuned on 100 ng ml^{-1} ^{115}In , ^{59}Co and ^{208}Pb to give a uniform response across the mass range. Under these conditions instrument response was typically 2×10^6 counts s^{-1} per $\mu\text{g ml}^{-1}$. Solutions were introduced via an eight roller peristaltic pump (Ismatek CH) at a rate of 0.9 ml min^{-1} .

Results and Discussion

The effect of aerosol water loading on the spectral characteristics observed in ICP-MS were measured by incrementally adjusting the spray chamber temperature from 0 to 30°C , the latter temperature being typical of the instrument cabinet temperature in the vicinity of the ICP. This temperature variation raises the vapour pressure of the water in the spray chamber by almost six times (Fig. 1). Using the continuous measurement technique described by Maessen *et al.*¹² the water loading in the plasma changed from 0.075 mg s^{-1} at 0°C to 0.392 mg s^{-1} at 30°C under the conditions used, an increase of over five times. The spectral features observed to be dependent on aerosol loading were: (i) M^+ signal intensity; (ii) MO^+ and M^{2+} levels; (iii) polyatomic ion levels; (iv) residual sampler material contribution; and (v) ion kinetic energy.

M^+ Signal Intensity

On cooling the spray chamber from 30 to 0°C , the ion sensitivity increases dramatically. From Fig. 2, it can be seen that for high mass elements the increase is of the order of 2–3 whereas for low mass elements the increase can be as much as 6–7 times.

* Presented at the 1987 Winter Conference on Plasma and Laser Spectrochemistry, Lyon, France, 12th–16th January, 1987.

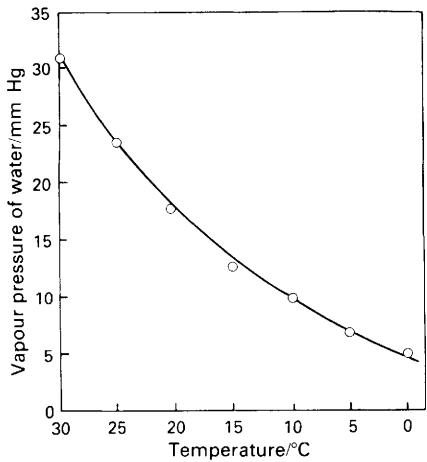


Fig. 1. Variation in water vapour pressure with temperatures at atmospheric pressure¹⁷

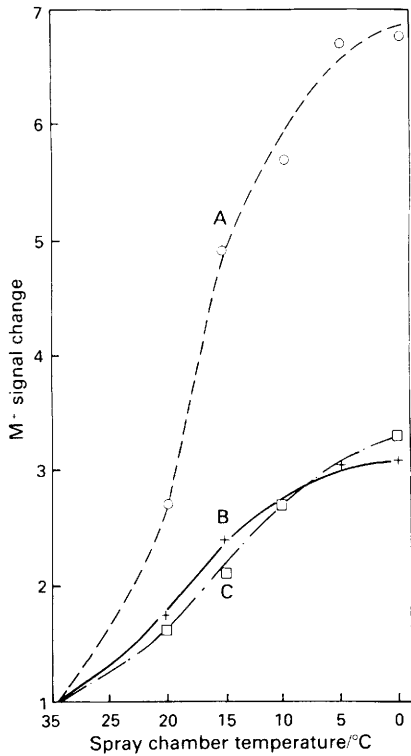


Fig. 2. Change in M^+ (relative to 30 °C) response with spray chamber temperature: A, ^9Be , ^{24}Mg and ^{27}Al ; B, ^{59}Co , ^{115}In , ^{138}Ba and ^{208}Pb ; C, ^{232}Th and ^{238}U . 100 ng ml⁻¹ of each solution; results are averages of five runs

Table 1. Dependence of experimentally measured oxide level on M–O bond energy¹⁷ under typical operating conditions

Oxide level, %	Element	Bond energy/kJ mol ⁻¹
1.0–2.0	Th, U, Ce, La	750–850
0.5–1.0	Ta, Hf, W, Nb, Zr, Pr, Si	670–750
0.1–0.5	Ti, V, Y, Mo, Ru, Ba, Al, rare earths	460–670
0.01–0.1	Ca, Sr, platinumoids	<460
<0.01	Pb, Rb, Cs, Co, Fe, Cr, Ni, Cu, Zn	<460

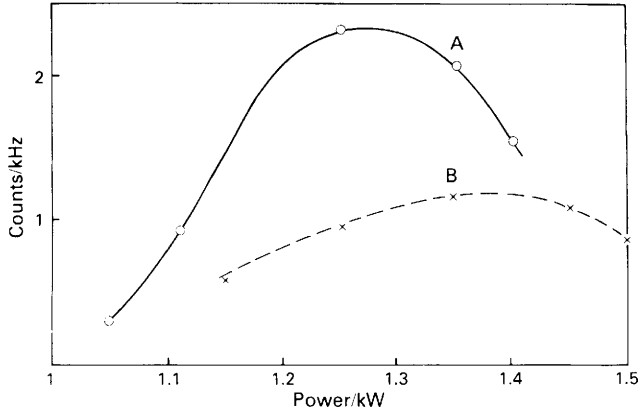


Fig. 3. Power optimisation responses for ^{140}Ce at 0 °C (A) and 30 °C (B) spray chamber temperature

Once partially desolvated, the plasma is probably considerably hotter, extra energy being available which previously was required to dissociate residual water vapour. At below 8 °C there seems little increase indicating that little residual water vapour is then removed. Temperature optimisation curves for $^{140}\text{Ce}^+$ shown in Fig. 3 indicate that at lower water loadings, 100 W less power is required to obtain the maximum signal. However, at 30 °C the increased power still does not return the $^{140}\text{Ce}^+$ signal to the same level as that obtained in the same system with the chamber operated at 0 °C. A sharp maximum is obtained for 0 °C at 1250 W whereas a less well defined maximum at 1350–1400 W was observed for 30 °C.

MO⁺ Levels

Under typical multi-element operating conditions, the levels of MO⁺ are low.¹ The oxide levels predictably depend on the M–O bond strength as can be seen in Table 1 with elements such as Ce, Th and U exhibiting the highest levels. These oxide levels can be reduced by reducing the carrier gas flow^{18,19}; however, this results in a reduction in sensitivity and for the experiments detailed in this work, typical multi-element operating conditions were used, optimised to give an even ion response across the mass range.

Oxide species have been postulated to be formed via recombination reactions in the extraction process. It is unlikely¹ that such oxides would be present in the plasma or in the boundary layer to any significant extent. This, however, may not be so when the oxygen population is increased at high water loadings. From Fig. 4 it can be seen that the oxide levels fall by a factor of approximately two for the most refractory species when chamber temperature is reduced from 30 to 0 °C. Typically MO⁺/M⁺ levels for Th and U fall from about 4.5 to 2.0% whilst that for Ce falls by a similar level from 2.3 to 1.1%. In a dry plasma, typical of that observed in laser ablation work, the oxide levels are reduced by a further order of magnitude, as observed for WO⁺ and UO⁺ in Table 2.²⁰ In such a system the only oxygen present will be that due to either impurities in the argon gas, entrainment of atmospheric oxygen or ingress of oxygen from the boundary layer.

M²⁺ Doubly Charged Levels

The doubly charged ion response is potentially much less of an analytical problem than are oxides. Elements such as barium with a low second ionisation potential (<10 eV) will give M²⁺/M⁺ ratios of ca. 2%. This is lower than can be expected from the Saha equation alone. Whilst thermal ionisation within the plasma is expected to be the dominant process, additional collisional ionisation occurring in the plasma

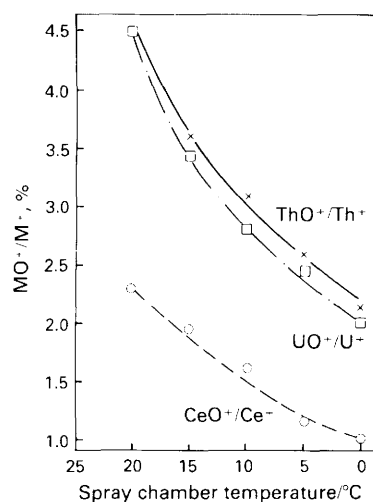


Fig. 4. Effect of spray chamber temperature on oxide levels of U, Ce and Th

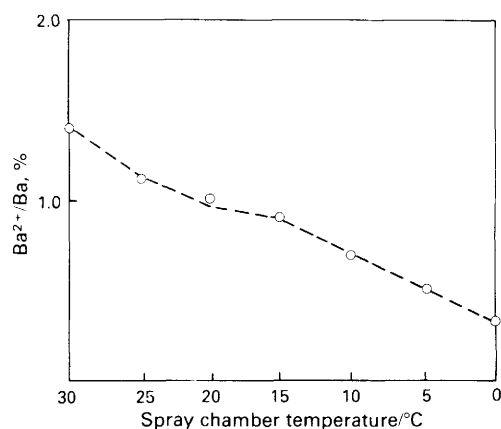


Fig. 5. Effect of spray chamber temperature on the $\text{Ba}^{2+}/\text{Ba}^{+}$ ratio

expanding beyond the orifice involving the ions in the tail of ion energy distribution^{1,14} has been postulated. Fig. 5 shows how the water loading can reduce this to below 1% indicating perhaps a contribution from water to the ionisation process.

Polyatomic Ion Species

Although the spectra in ICP-MS are intrinsically very simple consisting primarily of singly charged species with some low levels of oxide and doubly charged species, some generic polyatomic ion species are observed at low mass (<80 u) which are associated with argon and solvent species. Species such as ArO^{+} and ArN^{+} may be formed by ion-molecule condensation reactions on the surfaces within the expansion chamber and careful attention to sampling design¹³ can reduce these cluster ions. However, reduction in water loading is also critical in obtaining a cleaner background spectrum. Fig. 6 indicates the dependence of ArO^{+} on solvent loading where it can be reduced to ca. 20 ng ml^{-1} equivalent when measured using ^{59}Co as an internal standard. Dimeric species such as Ar_2^{+} are also observed in the background spectrum and Gray³ has shown how these species may be formed within the shock wave in the expansion region. It is not directly obvious how a reduction in water loading could be directly related to dimer formation; it is, however, possible to postulate three-body collision processes in which oxygen may have a dominant role.²¹ Certainly from Fig. 7 it can be seen that there is a strong dependence of Ar_2^{+} species on water loading and improvements up to an order of magnitude can be evidenced at low water loading levels.

Table 2. Comparison of oxide levels in desolvated (spray chamber temperature 0°C) plasma and dry plasma

$\text{MO}^{+}/\text{M}^{+}$	Desolvated plasma	Dry plasma
$\text{UO}^{+}/\text{U}^{+}$	2.05	0.32
$\text{WO}^{+}/\text{W}^{+}$	0.8	0.06

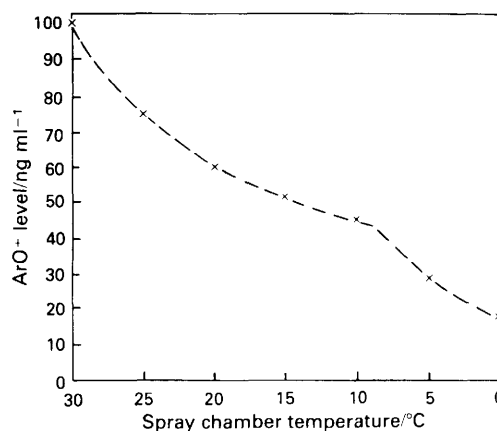


Fig. 6. Effect of spray chamber temperature on polyatomic ion ArO^{+} level at mass 56. ArO^{+} level measured in ng ml^{-1} relative to ^{59}Co at 10 ng ml^{-1}

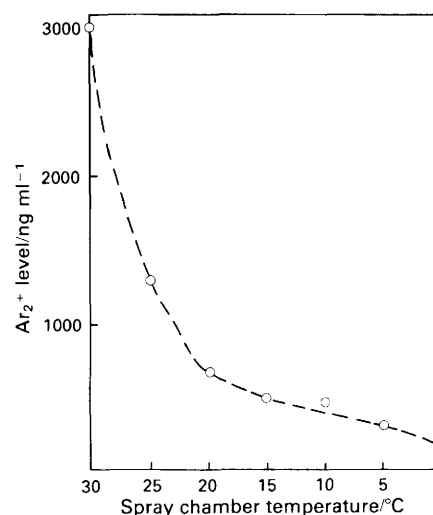


Fig. 7. Effect of spray chamber temperature on Ar_2^{+} at mass 80. Ar_2^{+} level expressed in ng ml^{-1} relative to ^{59}Co at 10 ng ml^{-1}

Residual Sampler Contribution

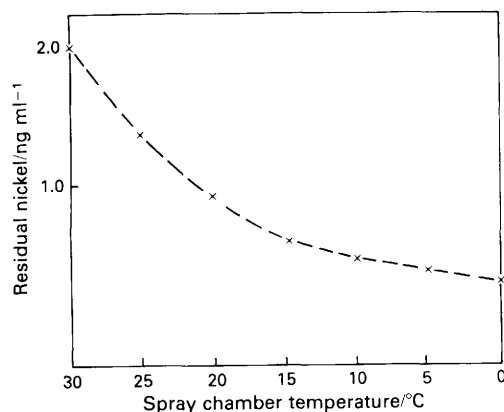
In early prototype ICP-MS instruments, a residual discharge (termed the pinch effect)²² resulted in some material from the sample cone being observed in the spectrum. In current commercial instruments, load coil grounding configurations are used which minimise this effect.^{15,23} Under certain circumstances, some small amounts of orifice material can still be observed. Erosion may also however be attributable to chemical attack and lowering water loadings certainly reduces this to $<0.5 \text{ ng ml}^{-1}$ on the instrument used in this work as shown in Fig. 8. Hence the lifetimes of the sampling orifice have been found to be increased to the order of 4–5 months with rigorous use.

Ion Kinetic Energies

The reduction in M^{2+} with water loadings is indicative that on the instrumentation used here, the ion kinetic energies may also be similarly reduced. Mean ion kinetic energies,

Table 3. Influence of spray chamber temperature (water) on mean ion kinetic energy

Spray chamber temperature	Mean ion kinetic energy/eV			
	²⁷ Al	⁵⁹ Co	¹¹⁵ In	²⁰⁸ Pb
30 °C	12	12	10	12
0 °C	3	4	4	5
Dry plasma	—	4	—	—

**Fig. 8.** Influence of spray chamber temperature on level of residual nickel from sampler system

measured by applying a retarding potential to the d.c. quadrupole rod bias, are seen to fall from 10–12 eV across the mass range, to 4–5 eV at the lower water loadings, as shown in Table 3. These latter values are similar to those obtained in a dry plasma²⁰ and are consistent with observations made by other workers.¹⁴ Although the absolute magnitude of the energies is subject to some error (± 1 –2 eV) the qualitative trend is quite clear, *i.e.*, low, but non-mass dependent values of ion energies are produced at reduced water loadings. This trend is in contrast to work reported by Fulford and Douglas²⁴ who, with their system, reported values which varied from 2 to 9 eV across the mass range.

The dependence of ion energies with water loading may be seen as contradictory to observations made by Olivares and Houk,²⁵ who, using a prototype instrument, observed ion energies of 4–5 eV both with and without aerosol loading. However, in their system an ultrasonic nebuliser with desolvator was employed, this being experimentally analogous to the cooled spray chamber arrangement used here. Bearing this in mind, the actual value for ion energies obtained appear to be encouragingly similar in both works despite the different operating conditions.

Conclusions

The advantages of operating the ICP ion source with low and constant aerosol water loadings or in fact with dry aerosol are many fold. The background spectrum from polyatomic ions is reduced, resulting in potentially improved detection for problematic elements such as Fe and Se. Oxide levels are similarly reduced and ion sensitivity is much improved, consistent with the plasma being more efficient at ion

production when the water, which acts as a thermal buffer, is reduced.

Ion-energy measurements indicate that low ion energies (*ca.* 5 eV) can be obtained with low water loadings using this particular interface and that these are constant across the mass range. This is a particularly attractive situation as it minimises mass discriminatory ion focusing effects and allows for simpler ion focusing.

The idea of totally desolvating the aerosol, however, does not at this stage appear a practical proposition for real analysis. However, operating the spray chamber at 10 °C with low solvent flows does provide a very practical alternative. It may be that future work can be directed towards improving aerosol transport to the ICP particularly with regard to the gas to liquid ratios in the aerosol.

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Paper J7/22

Received February 17th, 1987

Accepted May 21st, 1987