Multi-element Analysis of Complex Samples Using Collision/Reaction Cell ICP-MS, Without Element-Specific Conditions, Cluster Ions or Analyte Loss

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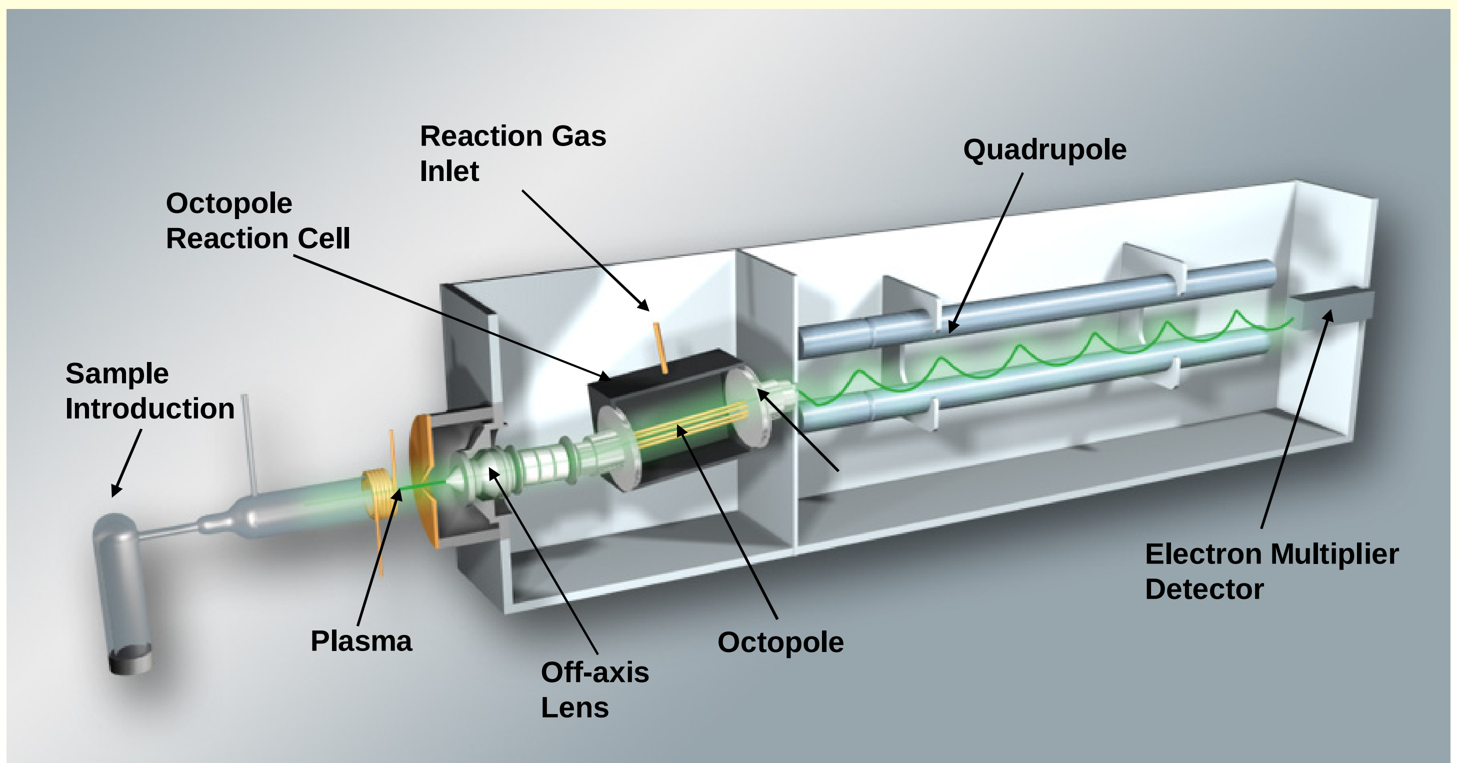
Introduction to ICP-MS

Conventional ICP-MS is a proven technique, used routinely for a wide range of applications where metals are measured at trace or minor concentrations (ng/L to mg/L concentrations). The very high temperature of the Argon ICP used in most ICP-MS instruments provides efficient matrix decomposition and good ionisation for most analytes, with relatively few problematic interferences. In complex samples, however, some interferences can occur at levels which contribute to analyte signals, resulting in errors in reported concentration results.

The optimisation of the plasma and sample introduction parameters to minimise the appearance of matrix polyatomic species (minimising the CeO^+/Ce^+ ratio) is well-known. However the combination of high matrix and low analyte levels requires an additional means of further reducing the level of these polyatomic species in the mass spectrum, to allow accurate determinations without reliance on complex interference correction equations. A relatively recent development in ICP-MS has utilised collision/reaction cell technology to allow the interferences to be filtered from the ion beam, after extraction into the vacuum system. The Agilent 7500c collision/reaction cell ICP-MS system is illustrated schematically below.



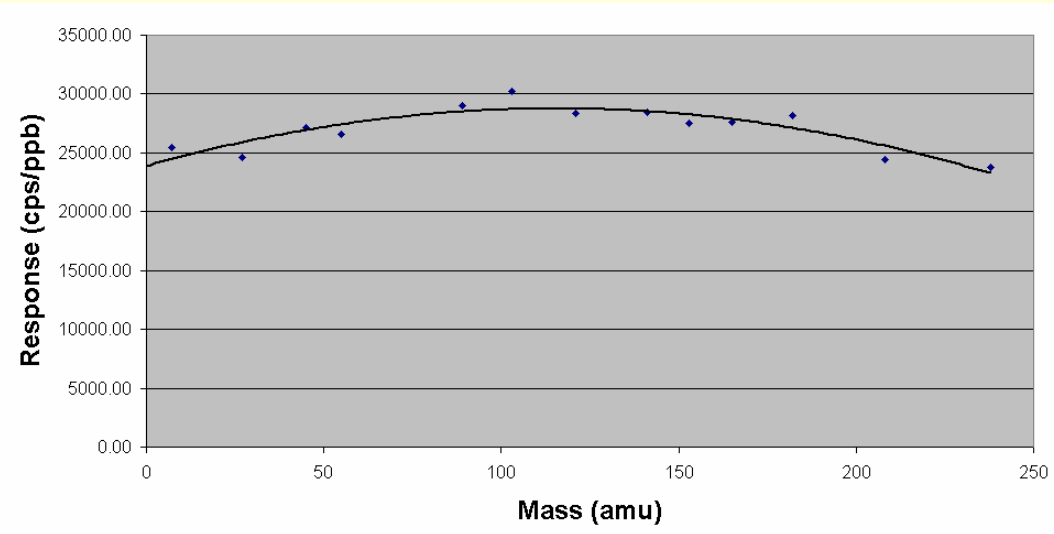
7500c Octopole Reaction Cell Schematic

Semi-Quantitative Analysis with Cell-Based ICP-MS

The use of semi-quantitative analysis has long been recognised as a powerful and flexible approach to sample analysis by ICP-MS. The technique, which can be considered as a non-specific calibration routine, relies on the fact that the response per unit concentration for a given analyte isotope will be predictable, based on its mass, isotopic abundance and degree of ionisation (calculated from the SAHA equation). This predictability of response means that one element may be used to provide a calibration for a different element, provided appropriate corrections are made for the mass, abundance and ionisation. In commercial ICP-MS systems, a "mass/response" curve is derived from the analysis of a multi-element standard and interpolation is used to calculate response factors for the elements not present in the standard. Analysis of unknown samples can then be carried out, with accurate results being produced for many elements, based on a calibration that contained only a few.

When collision-reaction cell systems are used, this predictability of the relative response between different analytes must be maintained, in order for accurate semi-quantitative results to be produced. In the absence of a well-defined mass response curve, every element to be determined would have to be present in the calibration standard, giving a single-point calibration for each element, rather than a true semi-quantitative calibration. Given the two main limitations of highly reactive gases, the unpredictable formation of cluster ions and the loss of analytes by reaction with the cell gas, simple and accurate semi-quantitative analysis is only possible when a low reactivity cell gas is used. The use of semiquantitative analysis with inert He as a cell gas is illustrated below.

Semi-Quantitative Mass Response, using the Agilent 7500 ICP-MS



Agilent 7500 Mass Response in Standard Mode

Semi-Quantitative Mass Response

In normal routine operation, the mass response curve is derived from the analysis of a standard containing a limited number of elements. The greater the number of elements in the calibration standard, the more accurate the semi-quantitative results, as the interpolation between reference elements spans a smaller mass range.

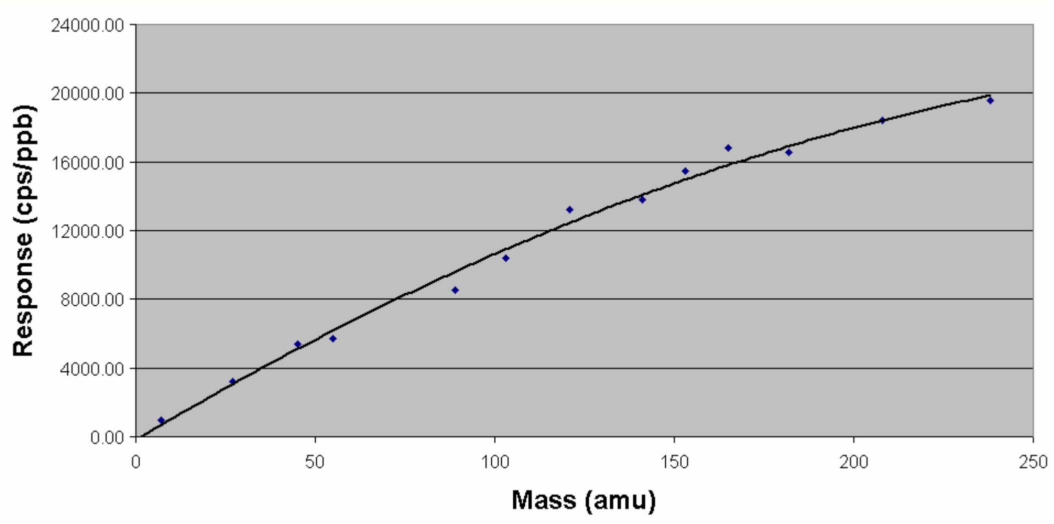
For this illustration, the elements Li, Al, Sc, Mn, Y, Rh, Sb, Pr, Eu, Ho, W, Pb and U were used as reference elements, in order to indicate the response across the mass range

Comparison of Mass Response Curves

The mass response curves above and right show the effect of adding helium cell gas at 5mL per minute.

Transmission of light elements was reduced due to scattering from the cell gas. However, due to the fact that an inert cell gas was used, the response curve was not disrupted by the formation of cluster ions or the unpredictable loss of analyte ions due to reaction with the cell gas.

The maintenance of a reliable mass response curve meant that accurate semi-quantitative results could be produced, using only a limited number of elements in the semi-quantitative calibration standard.

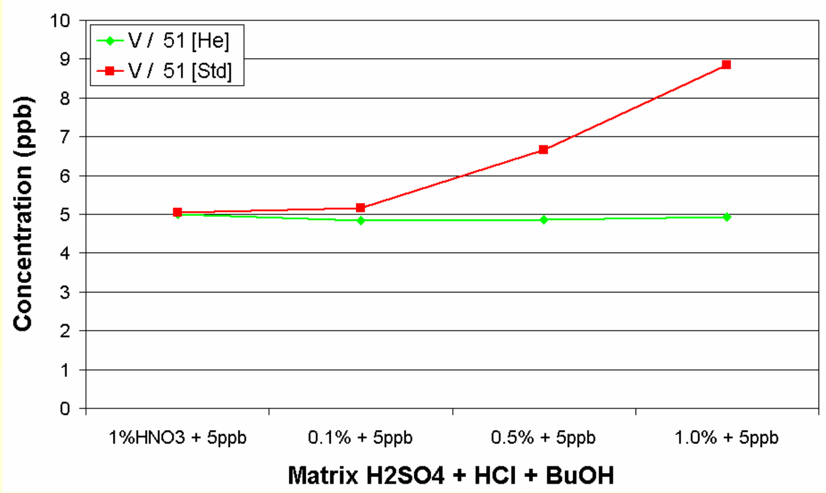


Agilent 7500 Mass Response in Helium Mode

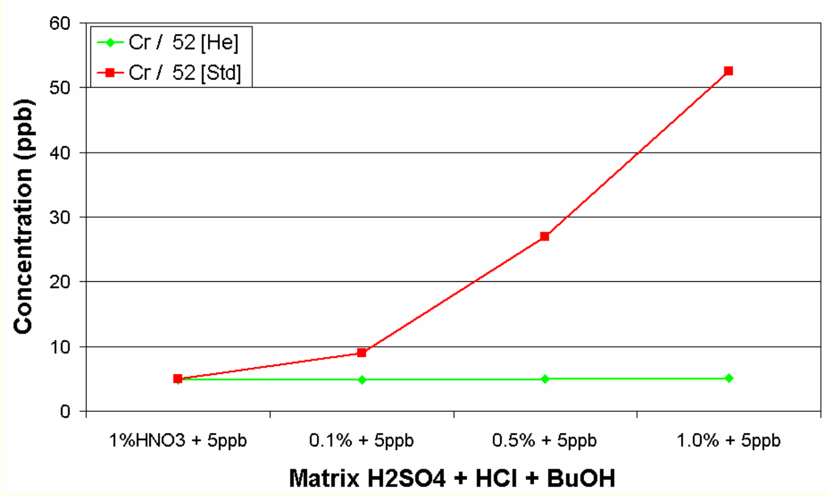
Interference Removal in a Variable Matrix

Interference removal using collision/reaction processes occurs by 3 principal methods: Collision Induced Dissociation (CID), Reaction and Energy Discrimination (ED). CID occurs for only a limited number of species, while reaction is most suitable for efficient removal of a small number of species, as it is highly dependent on the reactivity of the analyte, the target interference and other competing reaction partners. This makes reaction of limited use in complex and unknown matrices. ED can be used against almost any interference, requires no knowledge of the sample or the reactivity of analyte/interference and is independent of sample matrix. This is illustrated below for 5ppb spike recoveries for multiple elements in a range of sample matrices containing up to 1% of HCl, H_2SO_4 and Butanol.

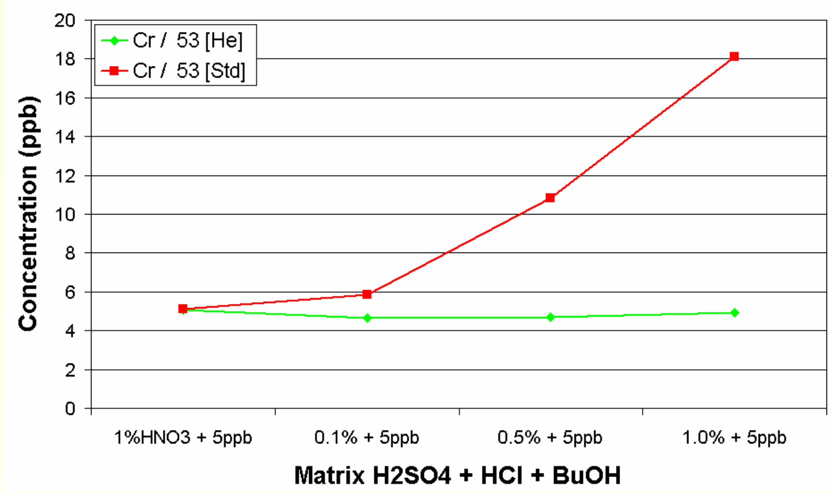
Removal of ClO^+ overlap on ^{51}V in a Variable Matrix



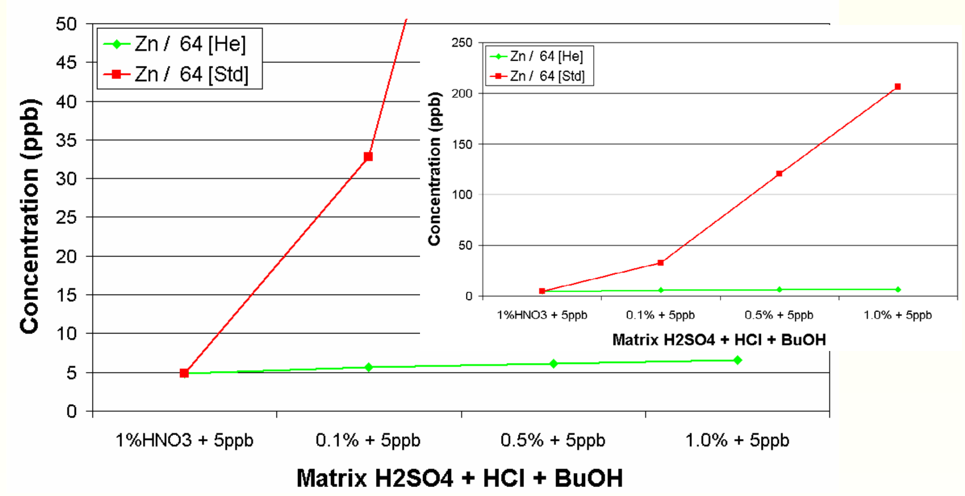
Removal of ArC^+ overlap on ^{52}Cr in a Variable Matrix



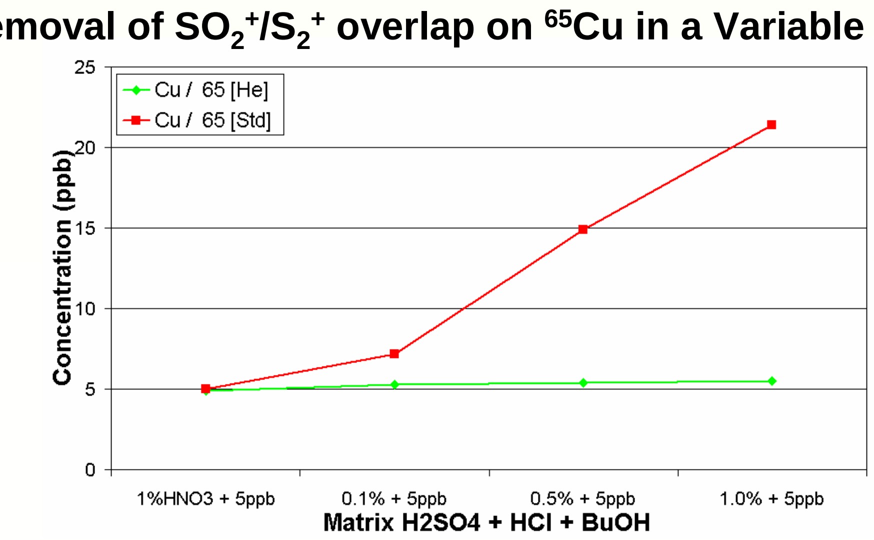
Removal of ClO^+ overlap on ^{53}Cr in a Variable Matrix



Removal of SO_2^+/S_2^+ overlap on ^{64}Zn in a Variable Matrix



Removal of SO_2^+/S_2^+ overlap on ^{65}Cu in a Variable Matrix



The plots shown above illustrate the removal of multiple interfering species from multiple analyte isotopes, using a single set of cell conditions and a light, inert cell gas (He) to promote efficient energy discrimination. High efficiency of energy discrimination is only possible if the ion energy is well controlled, which is achieved using the ShieldTorch System on the Agilent 7500c.

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