

## A systematic characterisation of concentration mismatch effects in MC-ICP-MS

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MC-ICP-MS can produce sensitive, precise and accurate isotopic ratio measurements for a wide range of elements. However, the measured ratios are always biased from their “true” value. This bias is due to fractionation caused by processes inherent to the technique, such as desolvation, vapourisation and ionisation in the ICP, and extraction and transportation. Altering the composition of the solution (pH, type of acid, matrix, etc) causes changes in mass bias that cannot always be corrected by traditional methods (*e.g.* normalisation laws, standard-sample-bracketing [SSB]). Self Induced Matrix Effects (SIME) occur when such fractionation is related to differences in the concentration of a solution, even matrix-free. We undertook a systematic study of SIME for several isotopic systems (Li, Mg, Fe, Zn, Sr, Nd, Hf, Pb) using matrix-free solutions, by varying the concentration of the samples within  $\pm 50$  % relative to the bracketing standard.

SIME was observed for all studied elements when using dry plasma, and the isotopic offsets of ratios with larger relative mass differences ( $(x-y)/y$ , where  $^xM/^yM$ ) were greater than those with a lower difference. For Nd and Pb ratios, there is a linear correlation ( $R^2 > 0.99$ ) between the isotopic offsets and the relative mass difference between the isotopes. However, other systems do not show such a correlation.

Opposite trends (preferential transmission of lighter vs heavier isotopes) were observed when using a high-sensitivity skimmer rather than the standard dry plasma one. This indicates the presence of a non-linear mass bias component to SIME that cannot be solely explained by the ‘zone-model’ mechanism<sup>1</sup> proposed for it. Other parameters investigated are the total ion load in the plasma and the natural abundance of the isotopes, which were found to play a key role, especially for ratios with a low-abundance isotope.

With these results, we can describe the behaviour of SIME-fractionation for elements of different masses and chemical properties, and provide a comprehensive set of analytical guidelines for isotopic analyses by MC-ICP-MS. We also propose that the matching requirements of sample and standard may vary for different ratios within an isotopic system. Thus, concentration-matching should be performed according to the ratio with the most restrictive requirements.

[1] Malinovsky *et al.* (2003), *J Anal Atom Spectrom* 18, 687-69