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Matrix effects in MC-ICP-MS: an isotopic case study for Pb

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MC-ICP-MS are sensitive instruments that can provide precise and accurate measurement of isotopic ratios for a plethora of elements when samples go through careful chemical treatment and the instrument is properly calibrated and operated. However, the measured ratios are always biased from their "true" value due to fractionation caused by processes inherent to the technique. Traditional correction methods (*e.g.* normalisation laws, standard-sample-bracketing [SSB]) can usually account for this instrumental bias. Yet, other sources of fractionation may arise when altering the composition of the solution (*e.g.* matrix effects).

We undertook a systematic study of both self-induced matrix effects (SIME) and matrix effects for the measurement of Pb isotopic ratios using both matrix-free solutions and USGS standards (NBS981, JB-3, BCR-2 and G-3). We also investigated a range of Pb/Tl ratios for all materials to assess the accuracy of the Tl correction for different matrices and compositions. We used a Nu Plasma II and a Plasma 3 (Nu Instruments, UK) for the analyses.

For the Nu Plasma II experiments, the isotopic offsets of ratios with larger relative mass differences ((x–y)/y, where $^{x}M/^{y}M$) were greater than those with a lower difference, and a linear correlation was observed ($R^2 > 0.99$) between them. Conversely, the Plasma 3 measurements showed no correlation between the ratios and the relative mass differences, demonstrating a greater stability for the Plasma 3 interface. The adding of matrix did not alter this behaviour and the Pb isotopic ratios were stable over a wide range of sample concentrations (± 50 % that of the bracketing standard) and $^{208}Pb/^{205}Tl$ ratios (1.5 – 4.5). Lastly, we tested two different routines of column chemistry (1 vs 2 column passes), and both yielded precise Pb ratios over the investigated Pb/Tl ranges.

With these results, we provide a comprehensive set of analytical guidelines for Pb isotopic analyses by MC-ICP-MS using different front interfaces (Nu Plasma II and Plasma 3). We also propose that the matching requirements of sample and standard, as well as the Pb/Tl ratios, may vary for different instruments, and need to be more closely matched for the Nu Plasma II than the Plasma 3.