Mass discrimination in MC-ICP-MS: example from Cu-Zn isotopes

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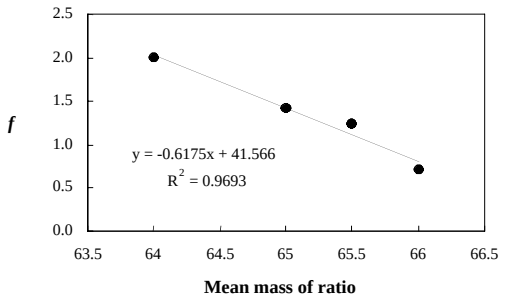
Cu and Zn isotopes in NIST976 and SpexPure Cu and Zn standard have been measured using a VG Axiom MC-ICP-MS, to investigate the mass discrimination, its stability and its dependency on sample matrices.

Based on the measurement of NIST976, a precision between 70-90 ppm can be achieved for $^{65}Cu/^{63}Cu$ ratio within an analytical session over 15 hours. This would translate into 0.09 per mil in $\delta^{65}Cu$, significantly smaller than recently reported $\delta^{65}Cu$ variations in natural samples. Thus, "sample-standard bracketing" for mass bias correction may be adequate, provided that samples are matrix matched with the standard .

NIST976 solutions spiked with various amounts of SpexPure Zn were used to measure Cu and Zn isotopes. It was found that the mass discrimination factor *f* was not constant across the Cu and Zn mass region. However, there appeared to be a correlation between *f* and mass (Fig. 1).



Similar correlation between *f* and mass has also been reported recently for Nd, Hf, and Pb-Tl isotope ratios. The correlation between *f* and Cu, Zn isotopes is independent of Zn concentration, and remains stable within an analytical session. Furthermore, data obtained from various models of MC-ICP-MS indicate that such correlations seem to be common to all currently available instruments.

These results suggest that mass bias correction by assuming equal *f* (e.g., $^{146}Nd/^{142}Nd$ for Nd isotopes, $^{205}Tl/^{203}Tl$ for Pb isotopes, and $^{68}Zn/^{64}Zn$ for $^{65}Cu/^{63}Cu$) does not fully account for the true mass bias in MC-ICP-MS. The correlation between *f* and mass can be used to further correct for mass bias, and may result in improved precision and accuracy of isotope ratio measurement in MC-ICP-MS.

References

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Factors influencing the vertical Pb distribution in a shooting range soil

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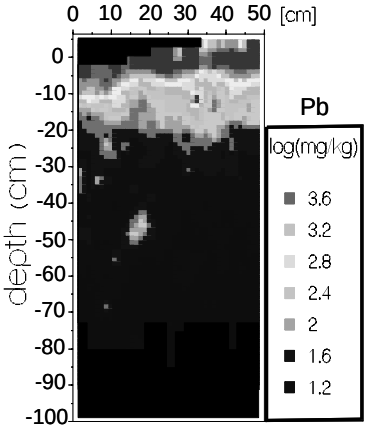
Soils in the vicinity of shooting ranges are often highly contaminated with Pb from bullets. Although metallic Pb(0) corrodes to secondary minerals with very low solubility, and dissolved Pb^{2+} is strongly sorbed by soil components, prior studies have found elevated Pb concentrations in the subsoil. A possible explanation is the transport of dissolved Pb or Pb bound to mobile colloids along preferential flow paths (PFP), i.e., bypassing the major part of reactive surfaces. To verify this mechanism, we investigated the cm-scale variation of Pb concentrations in a soil profile in relation to PFP.

A shooting range in Losone (Ticino, CH) was selected because of severe Pb contamination, strongly acidic soil (pH 3-4), and its proximity to a nature preservation area. PFP were identified by irrigating an undisturbed soil in the forest 50 m behind the stop butt with a reactive dye tracer (brilliant blue) and a conservative bromide tracer. We sampled a 50 x 100 cm^2 depth profile with 2.5-cm resolution, and measured element concentrations by X-ray fluorescence (XRF), and dye tracer concentration with a color meter. For selected samples, Pb speciation was investigated by selective sequential extractions and X-ray absorption fine structure spectroscopy (XAFS).



We found that the Pb concentration rapidly declined from >10,000 mg/kg in the upper 5 cm to background levels of 30 mg/kg at 40 cm depth. However, in one spot at about 50 cm depth (see figure below), elevated Pb concentrations of 300 mg/kg were found. This Pb spot coincided with elevated concentrations of Br and dye, suggesting transport of Pb along PFP. The distribution of Sb and Cu, two other metals deposited with gun pellets, followed a similar pattern. Thus, despite the low pH, Pb was strongly retained in the topsoil, and only a small fraction migrated down the profile. XAFS showed that Pb^{2+} was predominately bound to carboxylate groups by forming an inner-sphere sorption complex. Nevertheless, about 50% of total Pb occurred as mobile species (extractable by NH_4NO_3 and acetate).