Mass discrimination during MC-ICPMS isotopic ratio measurements: investigation by means of synthetic isotopic mixtures and application to the calibration of new IRMM zinc candidate CRMs

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A long known way of anchoring isotope ratio values to the SI system is by means of gravimetrically prepared isotopic mixtures combined with, in most cases, thermal ionisation mass spectrometry (TIMS). Multi-collector double focusing inductively coupled plasma (MC-ICP) – MS can now also be used but, as illustrated here with a series of Zn measurements, important issues regarding mass discrimination effects must be addressed specifically. In our study variations in time of mass discrimination effects are propagated as an uncertainty component. Mass discrimination for the ratios involving low abundance isotopes in the mixtures is evaluated from the linear proportionality observed for the other ratios between ε (mass discrimination = $(m_1/m_2)^{\varepsilon}$ model) and the average mass of the isotopes. Linear proportionality between mass discrimination and the logarithm of the isotope ratio values for $n(^{67}Zn)/n(^{64}Zn)$ and $n(^{68}Zn)/n(^{64}Zn)$ in the mixtures is used iteratively to evaluate mass discrimination for the same ratios in the isotopically enriched materials. Eventually, ratios in natural-like materials are calibrated by external bracketing using the isotopic mixtures.

The relative expanded uncertainty (k = 2) estimated for these ratio values in the mixtures and the natural zinc samples was in the range of 0.034 - 0.048%. The agreement between our results and those obtained with a single detector TIMS and with another MC-ICP-MS further validated this work.

Ar(Zn) = 65.37778 (22) found for IRMM-3702 – also proposed as 'Delta 0' for delta-scale isotopic measurements – differs significantly from the current IUPAC value by Chang et al.[1]. Measurement of the Zn isotope ratios in the material used by Chang et al. [1] have revealed large systematic differences (1.73% to 5.6%) that suggest unrecognized measurement biases in their results.

References

[1] Chang T-L. ; Zhao M-T. ; Li W-J. Wang; J. Qian Q-Y., (2001) *IJMS* **208**, 113-118.