

# **The triple isotope calibration approach – a new calibration approach for obtaining absolute isotope ratios of multi-isotopic elements**

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The calibration of isotope ratio measurements is an ongoing challenge since instrumental isotope fractionation (IIF) has been detected in mass spectrometry (MS). There is a variety of approaches which either bypass IIF such as delta measurements or refer to reference materials (RMs) and thus shifting the problem of calibration to somebody else: the RM producer. For certifying isotope RMs with absolute isotope ratios only a few approaches are available, namely the isotope mixture approach, the double spike approach, the mass bias regression model and total evaporation in TIMS. All of them require either enriched isotopes, isotope RMs of another element or an RM for correcting residual error. As the enriched isotopes required for the isotope mixture and the double spike approach need to be fully characterized beforehand, all mentioned calibration approaches require a standard.

Here, a new and standard-free calibration approach for obtaining absolute isotope ratios of multi-isotopic elements has been developed [1]. The underlying principle is that each MS suffers from IIF and thus yields a specific isotope fractionation line in a three-isotope diagram. When applying a second MS featuring a different ionization mechanism, we obtain a second isotope fractionation line with a different slope in the same three-isotope diagram. In both cases the absolute isotope ratios range somewhere on the isotope fractionation line. Consequentially, the intersect of both lines yield the absolute isotope ratios of the measured sample. This theory has been tested by measuring Cd and Pb isotope ratios of suitable isotope RMs with a TIMS and an ICP-MS, both equipped with multi-collector array. During the measurements the ionization conditions were changed such that different extent of the isotope fractionation has been achieved. With the resulting data set the theory described above could be verified. The obtained absolute isotope ratios were metrologically compatible with the certified isotope ratios. The remaining average bias of -5 ‰ can be reduced with further improvements. The calibration approach is universal and can be applied to any multi-isotopic element and it is not limited by the type of the mass spectrometer.

[1] Vogl J (2020), *Analytical and Bioanalytical Chemistry* 413, 821-826