Supplementary Information

Multi-collector Inductively Coupled Plasma Mass Spectrometry: New Developments and Basic Concepts for High-precision Measurements of Mass-dependent Isotope Signatures
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CHIMIA **2022**, *76*, 18-25

Appendix A: Data reduction example for Ti isotope with the double spike technique

Following Rudges et al. [36], the best double spike for Ti isotope analyses is a mix between ^{47}Ti-^{49}Ti. Furthermore, ^{46}Ca and ^{48}Ca interfere with ^{46}Ti and ^{48}Ti, and ^{50}Ti is subjected to interferences of ^{50}Cr and ^{50}V. As we need four of the five Ti isotopes for the double spike reduction, including the two spiked isotopes, the best solution is to use ^{46}Ti, ^{47}Ti, ^{48}Ti and ^{49}Ti, but to avoid ^{50}Ti. This however requires that ^{44}Ca is analyzed together with the Ti isotopes, which allows to correct for Ca interferences on ^{46}Ti and ^{48}Ti.

The first step is to employ a background correction. The background in solution MC-ICP-MS is estimated by measuring the same acid solution that is used for the sample introduction. The obtained average intensities on the different isotopes ($\overline{^{j}\text{Ti}_{\text{background}}}$ and $\overline{^{44}\text{Ca}_{\text{background}}}$) is then subtracted individually from each cycle of the sample (*j* stands for Ti with masses 46, 47, 48 and 49) and the (*) indicates a background corrected isotope:

$$^{j}\text{Ti}^{*}_{\text{sample}} = {}^{j}\text{Ti}_{\text{sample}} - \overline{^{j}\text{Ti}_{\text{background}}} \qquad \text{and} \qquad {}^{44}\text{Ca}^{*}_{\text{sample}} = {}^{44}\text{Ca}_{\text{sample}} - \overline{^{44}\text{Ca}_{\text{background}}} \qquad (A.1)$$

In the second step, one estimates the average instrumental mass bias $\bar{\beta}$ based on the average measured intensities of ^{46}Ti, ^{47}Ti, ^{48}Ti and ^{49}Ti using the double spike equation (j stands for Ti with masses 46, 48 and 49):

$$\overline{^{j/47}\text{Ti}^{*}_{\text{Sample}}} = \left[\lambda \cdot {}^{j/47}Ti_{Spike} + (1 - \lambda) \cdot {}^{j/47}Ti_{Standard} \cdot (m_i/m_{47})^{\bar{\alpha}} \right] \cdot (m_i/m_{47})^{\bar{\beta}} \qquad (A.2)$$

The obtained instrumental mass fractionation factor $\bar{\beta}$ is then used to calculate the abundance of ^{46}Ca and ^{48}Ca in the sample for each measured cycle, assuming that the Ca isotopes in the solution are present in natural abundance ($^{j/44}\text{Ca}_{\text{Natural}}$; i.e. ^{46}Ca/^{44}Ca = 0.00192 and ^{48}Ca/^{44}Ca = 0.08965):

$$^{j}\text{Ca}^{*}_{\text{Sample}} = {}^{44}\text{Ca}^{*}_{\text{Sample}} \cdot {}^{j/44}\text{Ca}_{\text{Natural}} \cdot (m_i/m_{44})^{\bar{\beta}} \qquad (A.3)$$

These values are then subtracted from the measured and background corrected intensities of ^{46}Ti and ^{48}Ti, for each cycle individually, with (**) indicating that an isotope is blank and interference corrected:

$$^{j}\text{Ti}^{**}_{\text{Sample}} = {}^{j}\text{Ti}^{*}_{\text{Sample}} - {}^{j}\text{Ca}^{*}_{\text{Sample}} \qquad (A.4)$$

The background and interreference corrected values for ^{46}Ti and ^{48}Ti are then used in equation (6), which can be solved for each cycle:

$$^{46/47}\text{Ti}^{**}_{\text{Sample}} = \left[\lambda \cdot {}^{46/47}\text{Ti}_{\text{Spike}} + (1\text{-}\lambda) \cdot {}^{46/47}\text{Ti}_{\text{Reference Material}} \cdot (m_{46}/m_{47})^{\alpha} \right] \cdot (m_{46}/m_{47})^{\beta}$$
$$^{48/47}\text{Ti}^{**}_{\text{Sample}} = \left[\lambda \cdot {}^{48/47}\text{Ti}_{\text{Spike}} + (1\text{-}\lambda) \cdot {}^{48/47}\text{Ti}_{\text{Reference Material}} \cdot (m_{48}/m_{47})^{\alpha} \right] \cdot (m_{48}/m_{47})^{\beta} \qquad (A.5)$$
$$^{49/47}\text{Ti}^{*}_{\text{Sample}} = \left[\lambda \cdot {}^{49/47}\text{Ti}_{\text{Spike}} + (1\text{-}\lambda) \cdot {}^{49/47}\text{Ti}_{\text{Reference Material}} \cdot (m_{49}/m_{47})^{\alpha} \right] \cdot (m_{49}/m_{47})^{\beta}$$

The solutions for α in equation (A.5) allow to calculate the $^{49}Ti/^{47}Ti$ ratios and thus the $\delta^{49/47}Ti$ value for each measured cycle:

$$^{49/47}Ti_{Sample} = {}^{49/47}Ti_{Reference\ Material} \cdot (m_{49}/m_{47})^\alpha \qquad (A.6)$$

$$\delta^{49/47}Ti_{Sample}\ (‰) = \left(\frac{^{49/47}Ti_{Sample}}{^{49/47}Ti_{Reference\ Material}} - 1 \right) \cdot 1000 \qquad (A.7)$$

In equation (A.7) it is assumed that the reference material equals the one for Ti isotope nomenclature. Afterwards, an outlier rejection (e.g. the Chauvenet criterion) is applied to all analyzed cycles and the $\delta^{49/47}Ti$ of the sample is defined as the average of all cycles that passed the outlier test. The same data reduction procedure is used for samples and reference material. As a last step, an offset correction is employed that corrects the $\delta^{49/47}Ti$ value of the sample for the difference between the measured $\delta^{49/47}Ti$ value of the bracketing reference material and the defined value. If the value of the reference material is defined as 0‰ (i.e. it is also the reference material in equation (1)) the offset correction translates to:

$$\delta^{49/47}Ti_{Sample}^{offset} = \delta^{49/47}Ti_{Sample} - (0.5 \cdot \delta^{49/47}Ti_{STD1} + 0.5 \cdot \delta^{49/47}Ti_{STD2}) \qquad (A.8),$$

with $\delta^{49/47}Ti_{Sample}^{offset}$ being the final composition of the sample after offset correction. The 2SE of all cycles after outlier rejection for a Ti isotope analyzes with the double spike technique is normally around ± 0.02‰. More importantly however, the intermediate measurement precision (2SD) of repeated measurements of secondary standards that have a similar complex matrix as a sample and that were treated identically to a sample (i.e. including ion-exchange chemistry) is often below ±0.035‰.

Appendix B: Relation of λ to the proportion of double spike in a sample-double spike mixture

The proportion of double spike (p) in a sample-double spike mixture is related to λ following equation (9) in Rudge et al. [36]:

$$p = \left(1 + \frac{1-\lambda}{\lambda} \cdot \left(\frac{1 + \sum_k R_{Sample}^{i/j}}{1 + \sum_k R_{Spike}^{i/j}} \right) \right)^{-1} \qquad (B.1).$$

In this equation, the sum is calculated over all isotope ratios, not only the three ratios used in the double spike equation. For example, applied to Ti isotopes and using the ratios from equation (A.5) it reads:

$$p = \left(1 + \frac{1-\lambda}{\lambda} \cdot \left(\frac{1 + \sum \left[R_{Sample}^{46/47} + R_{Sample}^{48/47} + R_{Sample}^{49/47} + R_{Sample}^{50/47} \right]}{1 + \sum \left[R_{Spike}^{46/47} + R_{Spike}^{48/47} + R_{Spike}^{49/47} + R_{Spike}^{50/47} \right]} \right) \right)^{-1} \qquad (B.2).$$