

Electronic Supplementary Material: Combining standard addition and isotope dilution in order to improve SI traceable LA-ICP-MS measurements

Lena Michaliszyn,^{*a} Axel Pramann,^a Anita Röthke^a and Olaf Rienitz^a

^a Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany.

This supplement material presents:

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1 Detailed derivation of equations for the calculation of the mass fraction of a non-matrix element in a solid sample using LA-ID-ICP-MS

The method is based on the correlation between the measured intensity of the isotope ($I(^j\text{E})$) and the flow of analyte ions (N). This flow can be expressed by the isotope abundance of the measured isotope ($x(^j\text{E})$), the mass fraction of the analyte element in the sample ($w(\text{E})$), the mass flow of the sample (\dot{m}) and the Avogadro constant (N_A), and the molar mass of the element of interest ($M(\text{E})$), see eq. (1).

$$I(^j\text{E}) = k(^j\text{E}) \times \frac{x(^j\text{E}) \times w(\text{E}) \times \dot{m} \times N_A}{M(\text{E})} \quad (1)$$

Because of mass discrimination, the measured intensities must be corrected by a so-called K -factor. K is determined by measuring a material of known (or certified) isotopic composition. The isotope dilution measurement is mainly based on the isotope ratio of the monitor isotope (^2E) to the reference isotope (^1E). Therefore, the ratio of interest is $R_2 = x(^2\text{E})/x(^1\text{E})$. The ratio R denotes usually R_2 . The measured intensity is, for this work, the sum of the intensities from the ablated sample material (x) and the simultaneously introduced blend solution (bz), which was prepared beforehand from the standard (z) and spike (y) solutions. Because of the use of several solutions are used, the index i specifies the solution (bz) used.

$$K_i = \frac{R_i^{\text{true}}}{R_i^{\text{meas}}} \quad (2)$$

$$R_{\text{bxz},i}(\text{E}) = K_{i,2} \times \frac{I_{\text{bxz},i}(^2\text{E})}{I_{\text{bxz},i}(^1\text{E})} = K_i \times \frac{I_x(^2\text{E}) + I_{y,i}(^2\text{E}) + I_{z,i}(^2\text{E})}{I_x(^1\text{E}) + I_{y,i}(^1\text{E}) + I_{z,i}(^1\text{E})} \quad (3)$$

Provided the mass flow is constant over time, eq. (1) can be inserted into eq. (3) for each intensity. If the same conditions are present throughout, the whole measurement the proportionality factors ($k(^j\text{E})$) can be reduced to the mass bias correction factor K . The introduced solution contains z and y, so the mass flows of them are equal. The mass fractions of the solution are expressed by the masses, the mass fractions of the stock solutions used, and the mass of the final measurement solution (eq. (4b)).

$$R_{\text{bxz},i}(\text{E}) = \frac{\frac{x_x(^2\text{E}) \times w_x(\text{E}) \times \dot{m}_x}{M_x(\text{E})} + \frac{x_y(^2\text{E}) \times w_{y,i}(\text{E}) \times \dot{m}_y}{M_y(\text{E})} + \frac{x_z(^2\text{E}) \times w_{z,i}(\text{E}) \times \dot{m}_z}{M_z(\text{E})}}{\frac{x_x(^1\text{E}) \times w_x(\text{E}) \times \dot{m}_x}{M_x(\text{E})} + \frac{x_y(^1\text{E}) \times w_{y,i}(\text{E}) \times \dot{m}_y}{M_y(\text{E})} + \frac{x_z(^1\text{E}) \times w_{z,i}(\text{E}) \times \dot{m}_z}{M_z(\text{E})}} \quad (4a)$$

$$\text{with } K_{i,2} = \frac{k(^1\text{E})}{k(^2\text{E})} \text{ and } \dot{m}_y = \dot{m}_z = \dot{m}_{yz} \wedge w_{y,i} = \frac{m_{y,i}}{m_{\text{bz},i}} \times w_y \wedge w_{z,i} = \frac{m_{z,i}}{m_{\text{bz},i}} \times w_z \quad (4b)$$

In the following steps eq. (4a) with the side conditions eq. (4b), will be rearranged in the form of an equation of a linear regression (eq. (8)).

$$\begin{aligned} R_{\text{bxz},i}(\text{E}) \times \frac{x_x(^1\text{E}) \times w_x(\text{E}) \times \dot{m}_x}{M_x(\text{E})} + R_{\text{bxz},i}(\text{E}) \times \frac{x_y(^1\text{E}) \times \frac{m_{y,i}}{m_{\text{bz},i}} \times w_y(\text{E}) \times \dot{m}_{yz}}{M_y(\text{E})} + R_{\text{bxz},i}(\text{E}) \times \frac{x_z(^1\text{E}) \times \frac{m_{z,i}}{m_{\text{bz},i}} \times w_z(\text{E}) \times \dot{m}_{yz}}{M_z(\text{E})} \\ = \frac{x_x(^2\text{E}) \times w_x(\text{E}) \times \dot{m}_x}{M_x(\text{E})} + \frac{x_y(^2\text{E}) \times \frac{m_{y,i}}{m_{\text{bz},i}} \times w_y(\text{E}) \times \dot{m}_{yz}}{M_y(\text{E})} + \frac{x_z(^2\text{E}) \times \frac{m_{z,i}}{m_{\text{bz},i}} \times w_z(\text{E}) \times \dot{m}_{yz}}{M_z(\text{E})} \quad (5) \end{aligned}$$

$$\begin{aligned}
& (x_x ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E}) - x_x ({}^2\text{E})) \times \frac{w_x(\text{E}) \times \dot{m}_x}{M_x(\text{E})} + (x_y ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E}) - x_y ({}^2\text{E})) \times \frac{m_{y,i}}{m_{\text{bz},i}} \times \frac{w_y(\text{E}) \times \dot{m}_{yz}}{M_y(\text{E})} \\
& + (x_z ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E}) - x_z ({}^2\text{E})) \times \frac{m_{z,i}}{m_{\text{bz},i}} \times \frac{w_z(\text{E}) \times \dot{m}_{yz}}{M_z(\text{E})} = 0
\end{aligned} \tag{6}$$

$$\begin{aligned}
& (x_y ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E}) - x_y ({}^2\text{E})) \times \frac{m_{y,i}}{m_{\text{bz},i}} \times \frac{w_y(\text{E}) \times \dot{m}_{yz}}{M_y(\text{E})} \\
& = - (x_z ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E}) - x_z ({}^2\text{E})) \times \frac{m_{z,i}}{m_{\text{bz},i}} \times \frac{w_z(\text{E}) \times \dot{m}_{yz}}{M_z(\text{E})} - (x_x ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E}) - x_x ({}^2\text{E})) \times \frac{w_x(\text{E}) \times \dot{m}_x}{M_x(\text{E})}
\end{aligned} \tag{7}$$

$$\underbrace{\frac{x_y ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E}) - x_y ({}^j\text{E})}{x_x ({}^2\text{E}) - x_x ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E})} \times \frac{m_{y,i}}{m_{\text{bz},i}}}_{y_i} = \underbrace{\frac{w_z(\text{E})}{w_y(\text{E})} \times \frac{M_y(\text{E})}{M_z(\text{E})}}_{a_1} \times \underbrace{\frac{x_z ({}^2\text{E}) - x_z ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E})}{x_x ({}^2\text{E}) - x_x ({}^1\text{E}) \times R_{\text{bxz},i}(\text{E})} \times \frac{m_{z,i}}{m_{\text{bz},i}}}_{x_i} + \underbrace{\frac{w_x(\text{E})}{w_y(\text{E})} \times \frac{M_y(\text{E})}{M_x(\text{E})} \times \frac{\dot{m}_x}{\dot{m}_{yz}}}_{a_0} \tag{8}$$

The goal of the method is to determine the mass fraction of the element in the solid sample ($w_x(\text{E})$). To obtain an equation for this, the slope (a_0) is divided by the y-intercept (a_1). Because of the unknown mass flows \dot{m}_{yz} and \dot{m}_x , eq. (9) is rearranged for this quotient as well.

$$\frac{a_0(\text{E})}{a_1(\text{E})} = \frac{w_x(\text{E})}{w_y(\text{E})} \times \frac{M_y(\text{E})}{M_x(\text{E})} \times \frac{\dot{m}_x}{\dot{m}_{yz}} \times \frac{w_y(\text{E})}{w_z(\text{E})} \times \frac{M_z(\text{E})}{M_y(\text{E})} = \frac{w_x(\text{E})}{w_z(\text{E})} \times \frac{M_z(\text{E})}{M_x(\text{E})} \times \frac{\dot{m}_x}{\dot{m}_{yz}} \tag{9}$$

$$w_x(\text{E}) = w_z(\text{E}) \times \frac{a_0(\text{E})}{a_1(\text{E})} \times \frac{\dot{m}_{yz}}{\dot{m}_x} \times \frac{M_x(\text{E})}{M_z(\text{E})} \wedge \frac{\dot{m}_{yz}}{\dot{m}_x} = \frac{a_1}{a_0} \times \frac{w_x(\text{E})}{w_z(\text{E})} \times \frac{M_z(\text{E})}{M_x(\text{E})} \tag{10}$$

At this point, an equation to calculate the measurand of interest is obtained (eq. (10)). However, the molar masses of the element in the solid sample and the reference material must be known or determined. Therefore, another substitution is performed. The isotope abundances in eq. (8) will be replaced with the isotope ratios according to the definitions in eq. (11). Because of the total number of isotopes (N) of the considered element, the index j is used to define the isotopes.

$$x_x ({}^j\text{E}) = \frac{R_{x,j}(\text{E})}{\sum_{j=1}^N R_{x,j}(\text{E})} \wedge x_y ({}^j\text{E}) = \frac{R_{y,j}(\text{E})}{\sum_{j=1}^N R_{y,j}(\text{E})} \wedge x_z ({}^j\text{E}) = \frac{R_{z,j}(\text{E})}{\sum_{j=1}^N R_{z,j}(\text{E})} \tag{11}$$

Again, a linear equation results (eq. (13)) and the expression for the mass fraction is deviated by dividing the slope by the y-intercept (eqs. (14) and (15a)).

$$\begin{aligned}
& \frac{R_{\text{bxz},i}(\text{E}) - R_y(\text{E})}{R_x(\text{E}) - R_{\text{bxz},i}(\text{E})} \times \frac{\sum_{j=1}^N R_{x,j}(\text{E})}{\sum_{j=1}^N R_{y,j}(\text{E})} \times \frac{m_{y,i}}{m_{\text{bz},i}} \\
& = \frac{w_z(\text{E})}{w_y(\text{E})} \times \frac{M_y(\text{E})}{M_z(\text{E})} \times \frac{R_z(\text{E}) - R_{\text{bxz},i}(\text{E})}{R_x(\text{E}) - R_{\text{bxz},i}(\text{E})} \times \frac{\sum_{j=1}^N R_{x,j}(\text{E})}{\sum_{j=1}^N R_{z,j}(\text{E})} \times \frac{m_{z,i}}{m_{\text{bz},i}} + \frac{w_x(\text{E})}{w_y(\text{E})} \times \frac{M_y(\text{E})}{M_x(\text{E})} \times \frac{\dot{m}_x}{\dot{m}_{yz}} \tag{12}
\end{aligned}$$

$$\begin{aligned}
& \underbrace{\frac{R_{\text{bxz},i}(\text{E}) - R_y(\text{E})}{R_x(\text{E}) - R_{\text{bxz},i}(\text{E})} \times \frac{m_{y,i}}{m_{\text{bz},i}}}_{y_i} \\
&= \underbrace{\frac{w_z(\text{E})}{w_y(\text{E})} \times \frac{M_y(\text{E})}{M_z(\text{E})} \times \frac{\sum_{j=1}^N R_{y,j}(\text{E})}{\sum_{j=1}^N R_{z,j}(\text{E})}}_{a_1} \times \underbrace{\frac{R_z(\text{E}) - R_{\text{bxz},i}(\text{E})}{R_x(\text{E}) - R_{\text{bxz},i}(\text{E})} \times \frac{m_{z,i}}{m_{\text{bz},i}}}_{x_i} + \underbrace{\frac{w_x(\text{E})}{w_y(\text{E})} \times \frac{M_y(\text{E})}{M_x(\text{E})} \times \frac{\dot{m}_x}{\dot{m}_{yz}} \times \frac{\sum_{j=1}^N R_{y,j}(\text{E})}{\sum_{j=1}^N R_{x,j}(\text{E})}}_{a_0} \quad (13)
\end{aligned}$$

$$\frac{a_0(\text{E})}{a_1(\text{E})} = \frac{w_x(\text{E})}{w_y(\text{E})} \times \frac{M_y(\text{E})}{M_x(\text{E})} \times \frac{\dot{m}_x}{\dot{m}_{yz}} \times \frac{\sum_{j=1}^N R_{y,j}(\text{E})}{\sum_{j=1}^N R_{x,j}(\text{E})} \times \frac{w_y(\text{E})}{w_z(\text{E})} \times \frac{M_z(\text{E})}{M_y(\text{E})} \times \frac{\sum_{j=1}^N R_{z,j}(\text{E})}{\sum_{j=1}^N R_{y,j}(\text{E})} = \frac{w_x(\text{E})}{w_z(\text{E})} \times \frac{M_z(\text{E})}{M_x(\text{E})} \times \frac{\dot{m}_x}{\dot{m}_{yz}} \times \frac{\sum_{j=1}^N R_{z,j}(\text{E})}{\sum_{j=1}^N R_{x,j}(\text{E})} \quad (14)$$

$$w_x(\text{E}) = w_z(\text{E}) \times \frac{a_0(\text{E})}{a_1(\text{E})} \times \frac{\dot{m}_{yz}}{\dot{m}_x} \times \frac{M_x(\text{E})}{M_z(\text{E})} \times \frac{\sum_{j=1}^N R_{x,j}(\text{E})}{\sum_{j=1}^N R_{z,j}(\text{E})} \quad (15a)$$

$$\frac{\dot{m}_{yz}}{\dot{m}_x} = \frac{a_1(\text{E})}{a_0(\text{E})} \times \frac{w_x(\text{E})}{w_z(\text{E})} \times \frac{M_z(\text{E})}{M_x(\text{E})} \times \frac{\sum_{j=1}^N R_{z,j}(\text{E})}{\sum_{j=1}^N R_{x,j}(\text{E})} \quad (15b)$$

These equations still contain the unknown mass flows. At this point, the general element E is replaced by the analyte element A and the reference element R, respectively. Here, it is important to choose a reference element contained in the same sample, as the analyte element with an known mass fraction. Equation (14) is rearranged to get an expression for $w_x(\text{A})$ (eq. (16a)) as well as an equation for \dot{m}_{yz}/\dot{m}_x (eq. (16b)).

$$w_x(\text{A}) = w_z(\text{A}) \times \frac{a_1(\text{A})}{a_0(\text{A})} \times \frac{\dot{m}_{yz}}{\dot{m}_x} \times \frac{M_x(\text{A})}{M_z(\text{A})} \times \frac{\sum_{j=1}^N R_{x,j}(\text{A})}{\sum_{j=1}^N R_{z,j}(\text{A})} \quad (16a)$$

$$\frac{\dot{m}_{yz}}{\dot{m}_x} = \frac{a_1(\text{R})}{a_0(\text{R})} \times \frac{w_x(\text{R})}{w_z(\text{R})} \times \frac{M_z(\text{R})}{M_x(\text{R})} \times \frac{\sum_{j=1}^N R_{z,j}(\text{R})}{\sum_{j=1}^N R_{x,j}(\text{R})} \quad (16b)$$

After replacing the mass flow ratio with eq. (16b), a final equation is obtained which allows $w_x(\text{A})$ to be calculated directly after a LA-ID-ICP-MS measurement. The equation is simplified for the same isotopic pattern in the solid sample x and the solution z.

$$w_x(\text{A}) = w_z(\text{A}) \times \frac{w_x(\text{R})}{w_z(\text{R})} \times \frac{a_0(\text{A})}{a_1(\text{A})} \times \frac{a_1(\text{R})}{a_0(\text{R})} \times \frac{M_x(\text{A})}{M_z(\text{A})} \times \frac{M_z(\text{R})}{M_x(\text{R})} \times \frac{\sum_{j=1}^N R_{x,j}(\text{A})}{\sum_{j=1}^N R_{z,j}(\text{A})} \times \frac{\sum_{j=1}^N R_{z,j}(\text{R})}{\sum_{j=1}^N R_{x,j}(\text{R})} \quad (17)$$

2 Pre-calculation for the solution preparation

For isotope dilution, the ratios in the blends should generally be close to unity or to a defined value. Therefore, it was necessary to pre-calculate the masses of the standard (z) and the spike (y) stock solutions, which need to be mixed and topped up with the solvent to reach the target mass fractions and ratios. For the new LA-ID-ICP-MS approach, this must be done as well. However, the measured ratio is a combination of the solution mixture (bz), which contains z and y, and the ablated material of the solid sample (x). Thus, in the first step, the intensities of the ablated material and a solution for comparison must be recorded. With these results, the equivalent mass fraction (w_{eq}) of the sample can be calculated. This value represents the value if the solid sample were a solution.

$$R_{bxz,i}(E) = \frac{x_x(^2E) \times w_{eq}(E) \times \frac{\dot{m}_x}{M_x(E)} + x_{bz,i}(^2E) \times w_{bz,i}(E) \times \frac{\dot{m}_{yz}}{M_{bz,i}(E)}}{x_x(^1E) \times w_{eq}(E) \times \frac{\dot{m}_x}{M_x(E)} + x_{bz,i}(^1E) \times w_{bz,i}(E) \times \frac{\dot{m}_{yz}}{M_{bz,i}(E)}} \quad (18)$$

Provided that the mass flow of the solution (\dot{m}_{yz}) and the ablated material (\dot{m}_x) are the same, they should cancel each other out. This is a huge advantage, because it is not necessary to determine or estimate the mass flow.

$$R_{bxz,i}(E) = \frac{x_x(^2E) \times w_{eq}(E) \times \frac{\dot{m}_{yz}}{M_x(E)} + x_{bz,i}(^2E) \times w_{bz,i}(E) \times \frac{\dot{m}_{yz}}{M_{bz,i}(E)}}{x_x(^1E) \times w_{eq}(E) \times \frac{\dot{m}_{yz}}{M_x(E)} + x_{bz,i}(^1E) \times w_{bz,i}(E) \times \frac{\dot{m}_{yz}}{M_{bz,i}(E)}} = \frac{\dot{m}_{yz} \times \left(\frac{x_x(^2E) \times w_{eq}(E)}{M_x(E)} + \frac{x_{bz,i}(^2E) \times w_{bz,i}(E)}{M_{bz,i}(E)} \right)}{\dot{m}_{yz} \times \left(\frac{x_x(^1E) \times w_{eq}(E)}{M_x(E)} + \frac{x_{bz,i}(^1E) \times w_{bz,i}(E)}{M_{bz,i}(E)} \right)} \quad (19)$$

$$R_{bxz,i}(E) = \frac{\frac{x_x(^2E) \times w_{eq}(E)}{M_x(E)} + \frac{x_{bz,i}(^2E) \times w_{bz,i}(E)}{M_{bz,i}(E)}}{\frac{x_x(^1E) \times w_{eq}(E)}{M_x(E)} + \frac{x_{bz,i}(^1E) \times w_{bz,i}(E)}{M_{bz,i}(E)}} \quad (20)$$

The parameters in eq. (20) can be rearranged and sorted by the first blend (bz) and the solid sample. The result is given in eq. (23).

$$R_{bxz,i}(E) \times \frac{x_x(^1E) \times w_{eq}(E)}{M_x(E)} + R_{bxz,i}(E) \times \frac{x_{bz,i}(^1E) \times w_{bz,i}(E)}{M_{bz,i}(E)} = \frac{x_x(^2E) \times w_{eq}(E)}{M_x(E)} + \frac{x_{bz,i}(^2E) \times w_{bz,i}(E)}{M_{bz,i}(E)} \quad (21)$$

$$R_{bxz,i}(E) \times \frac{x_{bz,i}(^1E) \times w_{bz,i}(E)}{M_{bz,i}(E)} - \frac{x_{bz,i}(^2E) \times w_{bz,i}(E)}{M_{bz,i}(E)} = \frac{x_x(^2E) \times w_{eq}(E)}{M_x(E)} - R_{bxz,i}(E) \times \frac{x_x(^1E) \times w_{eq}(E)}{M_x(E)} \quad (22)$$

$$\frac{w_{bz,i}}{M_{bz,i}} \times (R_{bxz,i}(E) \times x_{bz,i}(^1E) - x_{bz,i}(^2E)) = \frac{w_{eq}(E)}{M_x(E)} \times (x_x(^2E) - R_{bxz,i}(E) \times x_x(^1E)) \quad (23)$$

The isotope abundance in the first blend ($x_{bz,i}(^1E)$, j = number of selected isotope and N = total number of isotopes) and the molar mass ($M_{bz,i}$) can be replaced with the single components of the solution.

$$x_{bz,i}(^jE) = \frac{n_z(^jE) + n_y(^jE)}{n_{z,i}(E) + n_{y,i}(E)} = \frac{x_z(^jE) \times \frac{m_{z,i} \times w_z(E)}{M_z(E)} + x_{y,j}(E) \times \frac{m_{y,i} \times w_y(E)}{M_y(E)}}{\frac{m_{z,i} \times w_z(E)}{M_z(E)} + \frac{m_{y,i} \times w_y(E)}{M_y(E)}} \quad (24)$$

$$M_{bz,i}(E) = \sum_{j=1}^N (x_{bz,i}(jE) \times M_j(E)) = \frac{\frac{m_{z,i} \times w_z(E)}{M_z(E)} \times \sum_{j=1}^N (x_z(jE) \times M_j(E)) + \frac{m_{y,i} \times w_y(E)}{M_y(E)} \times \sum_{j=1}^N (x_{y,j}(E) \times M_j(E))}{\frac{m_{z,i} \times w_z(E)}{M_z(E)} + \frac{m_{y,i} \times w_y(E)}{M_y(E)}(E)} \quad (25)$$

The molar masses of the standard (z) and spike (y) stock solutions as well as their amounts of substance can be cancelled out.

$$w_{bz,i}(E) \times \frac{\frac{m_{z,i} \times w_z(E)}{M_z(E)} + \frac{m_{y,i} \times w_y(E)}{M_y(E)}}{\frac{m_{z,i} \times w_z(E)}{M_z(E)} \times \left(\underbrace{\sum_{j=1}^N (x_z(jE) \times M_j(E))}_{=M_z(E)} \right) + \frac{m_{y,i} \times w_y(E)}{M_y(E)} \times \left(\underbrace{\sum_{j=1}^N (x_{y,j}(E) \times M_j(E))}_{=M_y(E)} \right)} \times \left(R_{bxz,i}(E) \times \frac{x_{z,1}(E) \times \frac{m_{z,i} \times w_z(E)}{M_z(E)} + x_{y,1}(E) \times \frac{m_{y,i} \times w_y(E)}{M_y(E)}}{\frac{m_{z,i} \times w_z(E)}{M_z(E)} + \frac{m_{y,i} \times w_y(E)}{M_y(E)}} - \frac{x_{z,2}(E) \times \frac{m_{z,i} \times w_z(E)}{M_z(E)} + x_{y,2}(E) \times \frac{m_{y,i} \times w_y(E)}{M_y(E)}}{\frac{m_{z,i} \times w_z(E)}{M_z(E)} + \frac{m_{y,i} \times w_y(E)}{M_y(E)}} \right) = \frac{w_{eq}}{M_x} \times (x_x(2E) - R_{bxz,i}(E) \times x_x(1E)) \quad (26)$$

In the following steps, the equation is rearranged further.

$$w_{bz,i}(E) \times \frac{R_{bxz,i}(E) \times \left(x_{z,1}(E) \times \frac{m_{z,i} \times w_z(E)}{M_z(E)} + x_{y,1}(E) \times \frac{m_{y,i} \times w_y(E)}{M_y(E)} \right) - x_{z,2}(E) \times \frac{m_{z,i} \times w_z(E)}{M_z(E)} - x_{y,2}(E) \times \frac{m_{y,i} \times w_y(E)}{M_y(E)}}{\underbrace{m_{z,i} \times w_z(E) + m_{y,i} \times w_y(E)}_{=w_{bz,i}(E) \times m_{bz,i}}} = \frac{w_{eq}(E)}{M_x(E)} \times (x_{x,2}(E) - R_{bxz,i}(E) \times x_{x,1}(E)) \quad (27)$$

$$\frac{\frac{m_{z,i} \times w_z(E)}{M_z(E)} \times (R_{bxz,i}(E) \times x_{z,1}(E) - x_{z,2}(E)) + \frac{m_{y,i} \times w_y(E)}{M_y(E)} \times (R_{bxz,i}(E) \times x_{y,1}(E) - x_{y,2}(E))}{m_{bz,i}} = \frac{w_{eq}(E)}{M_x(E)} \times (x_{x,2}(E) - R_{bxz,i}(E) \times x_{x,1}(E)) \quad (28)$$

After factoring the amount of substance out, the mass of the pre-blend is moved to the other side of the equal sign.

$$\begin{aligned} \frac{m_{z,i} \times w_z(\mathbf{E})}{M_z(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{z,1}(\mathbf{E}) - x_{z,2}(\mathbf{E})) + \frac{m_{y,i} \times w_y(\mathbf{E})}{M_y(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{y,1}(\mathbf{E}) - x_{y,2}(\mathbf{E})) \\ = \frac{w_{\text{eq}}(\mathbf{E})}{M_x(\mathbf{E})} \times (x_{x,2}(\mathbf{E}) - R_{\text{bxz},i}(\mathbf{E}) \times x_{x,1}(\mathbf{E})) \times m_{\text{bz},i} \end{aligned} \quad (29)$$

Afterwards, the rearranged definition of $m_{\text{bz},i} \times w_{\text{bz},i}(\mathbf{E})$ (eq. (30)) is used to substitute $m_{y,i} \times w_y$ in eq. (29).

$$m_{\text{bz},i} \times w_{\text{bz},i}(\mathbf{E}) = m_{z,i} \times w_z(\mathbf{E}) + m_{y,i} \times w_y(\mathbf{E}) \rightarrow m_{y,i} \times w_y(\mathbf{E}) = m_{\text{bz},i} \times w_{\text{bz},i}(\mathbf{E}) - m_{z,i} \times w_z(\mathbf{E}) \quad (30)$$

$$\begin{aligned} \frac{m_{z,i} \times w_z(\mathbf{E})}{M_z(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{z,1}(\mathbf{E}) - x_{z,2}(\mathbf{E})) + \frac{m_{\text{bz},i} \times w_{\text{bz},i}(\mathbf{E}) - m_{z,i} \times w_z(\mathbf{E})}{M_y(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{y,1}(\mathbf{E}) - x_{y,2}(\mathbf{E})) \\ = \frac{w_{\text{eq}}(\mathbf{E})}{M_x(\mathbf{E})} \times (x_{x,2}(\mathbf{E}) - R_{\text{bxz},i}(\mathbf{E}) \times x_{x,1}(\mathbf{E})) \times m_{\text{bz},i} \end{aligned} \quad (31)$$

The new fraction is split into two fractions with a common denominator.

$$\begin{aligned} \frac{m_{z,i} \times w_z(\mathbf{E})}{M_z(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{z,1}(\mathbf{E}) - x_{z,2}(\mathbf{E})) + \frac{m_{\text{bz},i} \times w_{\text{bz},i}(\mathbf{E})}{M_y(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{y,1}(\mathbf{E}) - x_{y,2}(\mathbf{E})) \\ - \frac{m_{z,i} \times w_z}{M_y} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{y,1}(\mathbf{E}) - x_{y,2}(\mathbf{E})) = \frac{w_{\text{eq}}(\mathbf{E})}{M_x(\mathbf{E})} \times (x_{x,2}(\mathbf{E}) - R_{\text{bxz},i}(\mathbf{E}) \times x_{x,1}(\mathbf{E})) \times m_{\text{bz},i} \end{aligned} \quad (32)$$

All terms with the standard in the numerator are then sorted to the left side and all other terms to the right side of the equals sign.

$$\begin{aligned} \frac{m_{z,i} \times w_z(\mathbf{E})}{M_z(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{z,1}(\mathbf{E}) - x_{z,2}(\mathbf{E})) - \frac{m_{z,i} \times w_z(\mathbf{E})}{M_y(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{y,1}(\mathbf{E}) - x_{y,2}(\mathbf{E})) \\ = \frac{w_{\text{eq}}(\mathbf{E})}{M_x(\mathbf{E})} \times (x_{x,2}(\mathbf{E}) - R_{\text{bxz},i}(\mathbf{E}) \times x_{x,1}(\mathbf{E})) \times m_{\text{bz},i} - \frac{m_{\text{bz},i} \times w_{\text{bz},i}(\mathbf{E})}{M_y(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{y,1}(\mathbf{E}) - x_{y,2}(\mathbf{E})) \end{aligned} \quad (33)$$

The measurand of interest is the mass of the standard stock solution (m_z). To obtain an equation which allows the calculation of this measurand, it is necessary to factor it out.

$$\begin{aligned} m_{z,i} \times \left[\frac{w_z(\mathbf{E})}{M_z(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{z,1}(\mathbf{E}) - x_{z,2}(\mathbf{E})) - \frac{w_z(\mathbf{E})}{M_y(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{y,1}(\mathbf{E}) - x_{y,2}(\mathbf{E})) \right] \\ = \frac{w_{\text{eq}}(\mathbf{E})}{M_x(\mathbf{E})} \times (x_{x,2}(\mathbf{E}) - R_{\text{bxz},i}(\mathbf{E}) \times x_{x,1}(\mathbf{E})) \times m_{\text{bz},i} - \frac{m_{\text{bz},i} \times w_{\text{bz},i}(\mathbf{E})}{M_y(\mathbf{E})} \times (R_{\text{bxz},i}(\mathbf{E}) \times x_{y,1}(\mathbf{E}) - x_{y,2}(\mathbf{E})) \end{aligned} \quad (34)$$

$$m_{z,i} = \frac{\frac{w_{\text{eq}}(\text{E})}{M_x(\text{E})} \times (x_{x,2}(\text{E}) - R_{\text{bxz},i}(\text{E}) \times x_{x,1}(\text{E})) \times m_{\text{bz},i} - \frac{m_{\text{bz},i} \times w_{\text{bz},i}(\text{E})}{M_y(\text{E})} \times (R_{\text{bxz},i}(\text{E}) \times x_{y,1}(\text{E}) - x_{y,2}(\text{E}))}{\frac{w_z(\text{E})}{M_z(\text{E})} \times (R_{\text{bxz},i}(\text{E}) \times x_{z,1}(\text{E}) - x_{z,2}(\text{E})) - \frac{w_z(\text{E})}{M_y(\text{E})} \times (R_{\text{bxz},i}(\text{E}) \times x_{y,1}(\text{E}) - x_{y,2}(\text{E}))} \quad (35)$$

In addition, to m_z the mass of the spike stock solution is required. With the calculated standard mass (eq. (35)) and the definition in eq. (30), m_y can be calculated in accordance with eq. (36).

$$m_{y,i} = \frac{m_{\text{bz},i} \times w_{\text{bz},i} - m_{z,i} \times w_z(\text{E})}{w_y(\text{E})} \quad (36)$$

For both calculations, the mass ($m_{\text{bz},i}$) as well as the mass fraction ($w_{\text{bz},i}$) of the final solution and the isotope ratio ($R_{\text{bxz},i}(\text{E})$) must be defined by the user in accordance with the requirements of ICP-MS and the laser ablation used.

3 Isotope ratio of boron

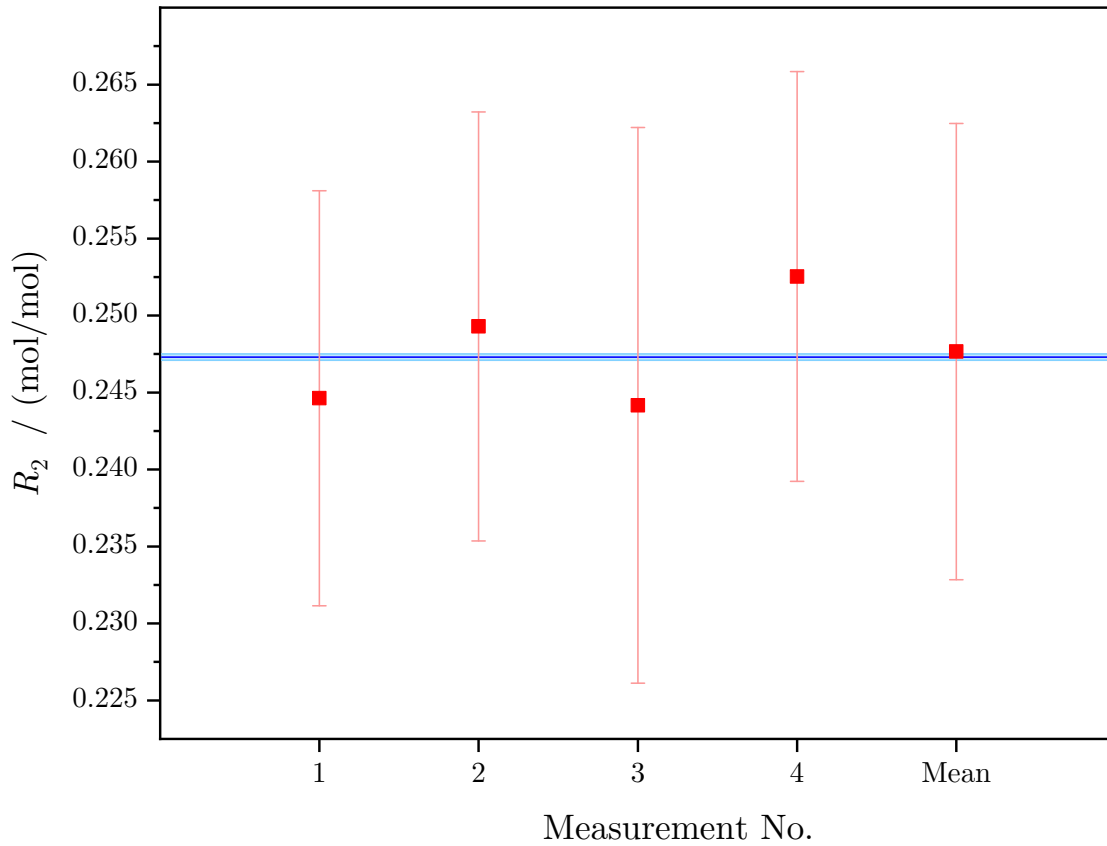
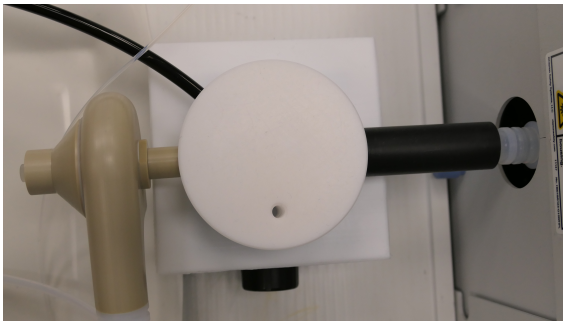


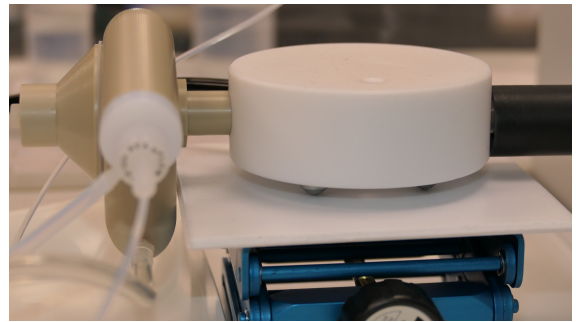
Fig. 1 Comparison of measured and corrected isotope ratio by LA of NIST SRM 612 (■) to the certified ratio of NIST SRM 951 (-) with $U_{k=2}$.

4 The y-piece

The pictures in this section show the custom built PTFE y-piece made. It was used for the LA-ID-ICP-MS measurements, while the LA-ICP-MS measurements were performed using a y-piece made of DURAN® borosilicate glass. During the measurement, the setup was improved by using ball casters on a PTFE surface (fig. 2) instead of a stand (fig. 3). With the ball casters, the setup was more flexible and was able to follow the movement of the torch box.



(a) Top view



(b) Right-hand side

Fig. 2 Custom-built PTFE y-piece. The y-piece rests on three ball casters which, in turn, rest on a PTFE surface for better flexibility when the torch box is moved.



(a) Left-hand side with top view



(b) Top view

Fig. 3 Custom-built PTFE y-piece. Because of its high operating weight, it is mounted on a stand.