Supplementary: A new method for the SI-traceable quantification of element contents in solid samples using LA-ICP-MS

Lena Michaliszyn[1], Tongxiang Ren[2], Anita Röthke[1], Olaf Rienitz[1]

[1] Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany

[2] National Institute of Metrology (NIM), No.18 Bei San Huan Dong Lu, Beijing 100029, P.R. China

Correspondence should be addressed to L. Michaliszyn. (email: lena.michaliszyn@ptb.de) or O. Rienitz (email: olaf.rienitz@ptb.de)

This supplemental material presents:

1 Derivation of the equation summarizing the novel quantification approach using LA-ICP-MS
2 Picture of the y-piece connector used
3 Graphics of average intensities for the calculation of analyte mass fractions
   3.1 Pb in NIST SRM 610
   3.2 Pb in NIST SRM 612
   3.3 Rb in NIST SRM 610
   3.4 Rb in NIST SRM 612

1 Derivation of the equation summarizing the novel quantification approach using LA-ICP-MS

In general this method is based on the fact that the measured intensity of an isotope of the chosen analyte $I({}^{j}\mathrm{A})$ is proportional to the flow of particles $\dot{N}$ (with the constant of proportionality k):

$$I({}^{j}\mathrm{A}) = k \times \dot{N}({}^{j}\mathrm{A}) \tag{S.1}$$

Using the following equation, the flow of particles can be expressed, as shown in equation (S.5), as a function of the isotope abundance of the measured isotope $x({}^{j}\mathrm{A})$, the mass fraction of the analyte element $w(\mathrm{A})$, the mass flow $\dot{m}$, the Avogadro constant N_A as well as the molar mass of this element $M(\mathrm{A})$.

$$n({}^{j}\mathrm{A}) = \frac{m({}^{j}\mathrm{A})}{M({}^{j}\mathrm{A})} = \frac{N({}^{j}\mathrm{A})}{N_\mathrm{A}} \;\rightarrow\; N({}^{j}\mathrm{A}) = n({}^{j}\mathrm{A}) \times N_\mathrm{A} \tag{S.2}$$

$$N({}^{j}\mathrm{A}) = x({}^{j}\mathrm{A}) \times n(\mathrm{A}) \times N_\mathrm{A} = x({}^{j}\mathrm{A}) \times \frac{m(\mathrm{A})}{M(\mathrm{A})} \times N_\mathrm{A} = x({}^{j}\mathrm{A}) \times w(\mathrm{A}) \times \frac{m}{M(\mathrm{A})} \times N_\mathrm{A} \tag{S.3}$$

$$w(\mathrm{A}) = \frac{m(\mathrm{A})}{m} \;\rightarrow\; m(\mathrm{A}) = w(\mathrm{A}) \times m \tag{S.4}$$

$$\dot{N}({}^{j}\mathrm{A}) = \frac{\mathrm{d}N({}^{j}\mathrm{A})}{\mathrm{d}t} \approx \frac{x({}^{j}\mathrm{A}) \times w(\mathrm{A}) \times m \times N_\mathrm{A}}{M(\mathrm{A}) \times t} = \frac{x({}^{j}\mathrm{A}) \times w(\mathrm{A}) \times \dot{m} \times N_\mathrm{A}}{M(\mathrm{A})} \tag{S.5}$$

In the present work the ablated material and a standard solution belonging to a concentration series (in this work i = 0, 1, 2, ... 5) were introduced simultaneously into the plasma. For this reason, the measured intensity is the sum of the intensities resulting from the ablated sample $I_\mathrm{x}({}^{j}\mathrm{A})$ and the simultaneously nebulized solution $I_{\mathrm{z},i}({}^{j}\mathrm{A})$.

$$I({}^{j}\mathrm{A}) = I_\mathrm{x}({}^{j}\mathrm{A}) + I_{\mathrm{z},i}({}^{j}\mathrm{A}) \tag{S.6}$$

Using equation (S.5) the intensity is given as it is shown in equation (S.7).

$$I({}^{j}\mathrm{A}) = \frac{dN({}^{j}\mathrm{A})}{dt} \approx k \times \frac{N({}^{j}\mathrm{A})}{t} = k \times \frac{x({}^{j}\mathrm{A}) \times w(\mathrm{A}) \times \dot{m} \times N_\mathrm{A}}{M(\mathrm{A})} \tag{S.7}$$

This equation can be applied to $I_\mathrm{x}({}^{j}\mathrm{A})$ as well as to $I_{\mathrm{z},i}({}^{j}\mathrm{A})$. Afterwards both terms can be inserted in (S.6) from which (S.10) follows.

$$I_{\mathrm{x}}({}^{j}\mathrm{A}) = k' \times \dot{N}_{\mathrm{x}}({}^{j}\mathrm{A}) = k' \times \frac{x_{\mathrm{x}}({}^{j}A) \times w_{\mathrm{x}}(\mathrm{A}) \times \dot{m}_{\mathrm{x}} \times N_{\mathrm{A}}}{M_{\mathrm{x}}(\mathrm{A})} \tag{S.8}$$

$$I_{\mathrm{z},i}({}^{j}\mathrm{A}) = k'' \times \dot{N}_{\mathrm{z},i}({}^{j}\mathrm{A}) = k'' \times \frac{x_{\mathrm{z}}({}^{j}A) \times w_{\mathrm{z},i}(\mathrm{A}) \times \dot{m}_{\mathrm{z}} \times N_{\mathrm{A}}}{M_{\mathrm{z}}(\mathrm{A})} \tag{S.9}$$

$$I({}^{j}\mathrm{A}) = k' \times \frac{x_{\mathrm{x}}({}^{j}A) \times w_{\mathrm{x}}(\mathrm{A}) \times \dot{m}_{\mathrm{x}} \times N_{\mathrm{A}}}{M_{\mathrm{x}}(\mathrm{A})} + k'' \times \frac{x_{\mathrm{z}}({}^{j}A) \times w_{\mathrm{z},i}(\mathrm{A}) \times \dot{m}_{\mathrm{z}} \times N_{\mathrm{A}}}{M_{\mathrm{z}}(\mathrm{A})} \tag{S.10}$$

By sorting the parameters within the equation and by measuring a certain number of solutions, a linear equation can be formulated.

$$\begin{aligned} I({}^{j}\mathrm{A}) &= \frac{k' \times x_{\mathrm{x}}({}^{j}\mathrm{A}) \times \dot{m}_{\mathrm{x}} \times N_{\mathrm{A}}}{M_{\mathrm{x}}(\mathrm{A})} \times w_{\mathrm{x}}(\mathrm{A}) + \frac{k'' \times x_{\mathrm{z}}({}^{j}\mathrm{A}) \times \dot{m}_{\mathrm{z}} \times N_{\mathrm{A}}}{M_{\mathrm{z}}(\mathrm{A})} \times w_{\mathrm{z},i}(\mathrm{A}) \\ y &= \qquad a_0 \qquad + \qquad a_1 \qquad \times \quad \mathrm{x} \end{aligned} \tag{S.11}$$

$$a_0({}^{j}\mathrm{A}) = \frac{k' \times x_{\mathrm{x}}({}^{j}\mathrm{A}) \times N_{\mathrm{A}}}{M_{\mathrm{x}}(\mathrm{A})} \times \dot{m}_{\mathrm{x}} \times w_{\mathrm{x}}(\mathrm{A}) \tag{S.12}$$

$$a_1({}^{j}\mathrm{A}) = \frac{k'' \times x({}^{j}\mathrm{A}) \times N_{\mathrm{A}}}{M_{\mathrm{z}}(\mathrm{A})} \times \dot{m}_{\mathrm{z}} \tag{S.13}$$

$$\frac{a_0({}^{j}\mathrm{A})}{a_1({}^{j}\mathrm{A})} = \frac{\dfrac{k' \times x_{\mathrm{x}}({}^{j}\mathrm{A}) \times N_{\mathrm{A}}}{M_{\mathrm{x}}(\mathrm{A})} \times \dot{m}_{\mathrm{x}}}{\dfrac{k'' \times x_{\mathrm{z}}({}^{j}\mathrm{A}) \times N_{\mathrm{A}}}{M_{\mathrm{z}}(\mathrm{A})} \times \dot{m}_{\mathrm{z}}} \times w_{\mathrm{x}}(\mathrm{A}) = \frac{\dot{m}_{\mathrm{x}}}{\dot{m}_{\mathrm{z}}} \times w_{\mathrm{x}}(\mathrm{A}) \tag{S.14}$$

$$w_{\mathrm{x}}(\mathrm{A}) = \frac{a_0({}^{j}\mathrm{A})}{a_1({}^{j}\mathrm{A})} \times \frac{\dot{m}_{\mathrm{z}}}{\dot{m}_{\mathrm{x}}} \tag{S.15}$$

(S.14) points out that, assuming the same isotopic pattern in the solid sample and the standard solution, the isotope abundance as well as the molar mass can be cancelled, so an exact knowledge of them is not necessary. Providing the same plasma conditions for the measurement of the solid sample and the solution, the constants of proportionality are equal and can be eliminated. This is the reason for using the same solvent for all solutions and adding some solution into the plasma during the entire measurement sequence.

The mass flow rates are still unknown. Therefore, a measurement of a reference element R with well-known content is required. For this reason, the same equation can be set up and rearranged to the ratio of the unknown mass flows.

$$\frac{a_0(^j\mathrm{R})}{a_1(^j\mathrm{R})}=\frac{\dot{m}_\mathrm{x}}{\dot{m}_\mathrm{z}}\times w_\mathrm{x}(\mathrm{R}) \rightarrow \frac{\dot{m}_\mathrm{z}}{\dot{m}_\mathrm{x}}=\frac{a_1(^j\mathrm{R})}{a_0(^j\mathrm{R})}\times w_\mathrm{x}(\mathrm{R}) \tag{S.16}$$

Substituting (S.16) into (S.15) yields an expression for the mass fraction of the analyte in which all quantities are known or can be determined experimentally.

$$w_\mathrm{x}(\mathrm{A})=\frac{a_0(^j\mathrm{A})}{a_1(^j\mathrm{A})}\times\frac{a_1(^j\mathrm{R})}{a_0(^j\mathrm{R})}\times w_\mathrm{x}(\mathrm{R}) \tag{S.17}$$

In the case of different isotopic patterns in the solid sample and the solution of the respective element A or R the general form of this equation has to be used.

$$\begin{aligned}&\frac{a_0(^j\mathrm{A})}{a_1(^j\mathrm{A})}=\frac{x_\mathrm{x}(^j\mathrm{A})}{M_\mathrm{x}(\mathrm{A})}\times\frac{M_\mathrm{z}(\mathrm{A})}{x_\mathrm{z}(^j\mathrm{A})}\times\frac{\dot{m}_\mathrm{x}}{\dot{m}_\mathrm{z}}\times w_\mathrm{x}(\mathrm{A})\\ &\rightarrow w_\mathrm{x}(\mathrm{A})=\frac{a_0(^j\mathrm{A})}{a_1(^j\mathrm{A})}\times\frac{x_\mathrm{z}(^j\mathrm{A})}{x_\mathrm{x}(^j\mathrm{A})}\times\frac{M_\mathrm{x}(\mathrm{A})}{M_\mathrm{z}(\mathrm{A})}\times\frac{\dot{m}_\mathrm{z}}{\dot{m}_\mathrm{x}}\end{aligned} \tag{S.18}$$

$$\begin{aligned}&\frac{a_0(^j\mathrm{R})}{a_1(^j\mathrm{R})}=\frac{x_\mathrm{x}(^j\mathrm{R})}{M_\mathrm{x}(\mathrm{R})}\times\frac{M_\mathrm{z}(\mathrm{R})}{x_\mathrm{z}(^j\mathrm{R})}\times\frac{\dot{m}_\mathrm{x}}{\dot{m}_\mathrm{z}}\times w_\mathrm{x}(\mathrm{R})\\ &\rightarrow \frac{\dot{m}_\mathrm{z}}{\dot{m}_\mathrm{x}}=\frac{a_1(^j\mathrm{R})}{a_0(^j\mathrm{R})}\times\frac{x_\mathrm{x}(^j\mathrm{R})}{x_\mathrm{z}(^j\mathrm{R})}\times\frac{M_\mathrm{z}(\mathrm{R})}{M_\mathrm{x}(\mathrm{R})}\times w_\mathrm{x}(\mathrm{R})\end{aligned} \tag{S.19}$$

$$w_\mathrm{x}(\mathrm{A})=\frac{a_0(^j\mathrm{A})}{a_1(^j\mathrm{A})}\times\frac{x_\mathrm{z}(^j\mathrm{A})}{x_\mathrm{x}(^j\mathrm{A})}\times\frac{M_\mathrm{x}(\mathrm{A})}{M_\mathrm{z}(\mathrm{A})}\times\frac{a_1(^j\mathrm{R})}{a_0(^j\mathrm{R})}\times\frac{x_\mathrm{x}(^j\mathrm{R})}{x_\mathrm{z}(^j\mathrm{R})}\times\frac{M_\mathrm{z}(\mathrm{R})}{M_\mathrm{x}(\mathrm{R})}\times w_\mathrm{x}(\mathrm{R}) \tag{S.20}$$

2 Picture of the y-piece connector used

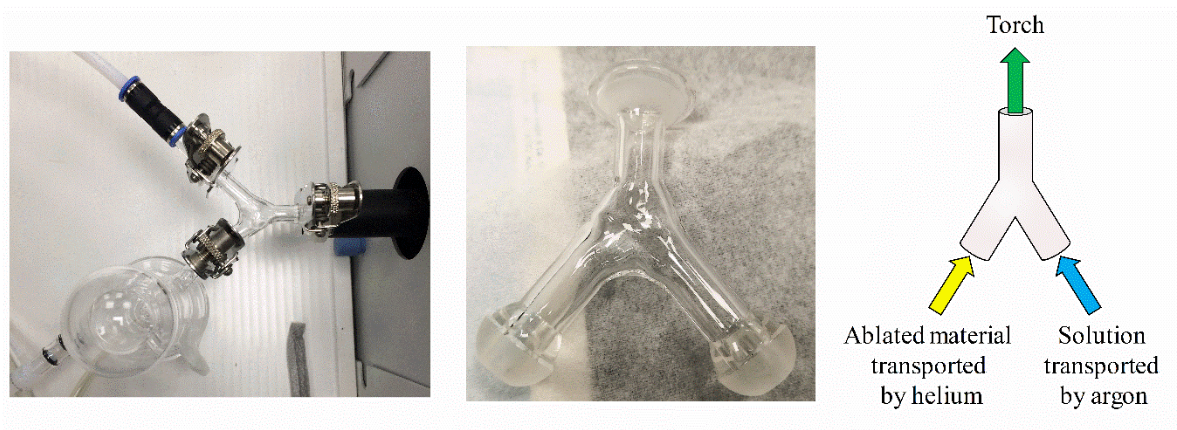


Figure S- 1: Picture of the y-piece connector used (DURAN® borosilicate glass 3.3) to connect the tube of the laser ablation and a spray chamber. Due to the geometry of the connector it is possible to introduce the ablated material and a solution into the plasma simultaneously.

3 Graphics of average intensities for the calculation of the analyte mass fractions

3.1 Pb in NIST SRM 610

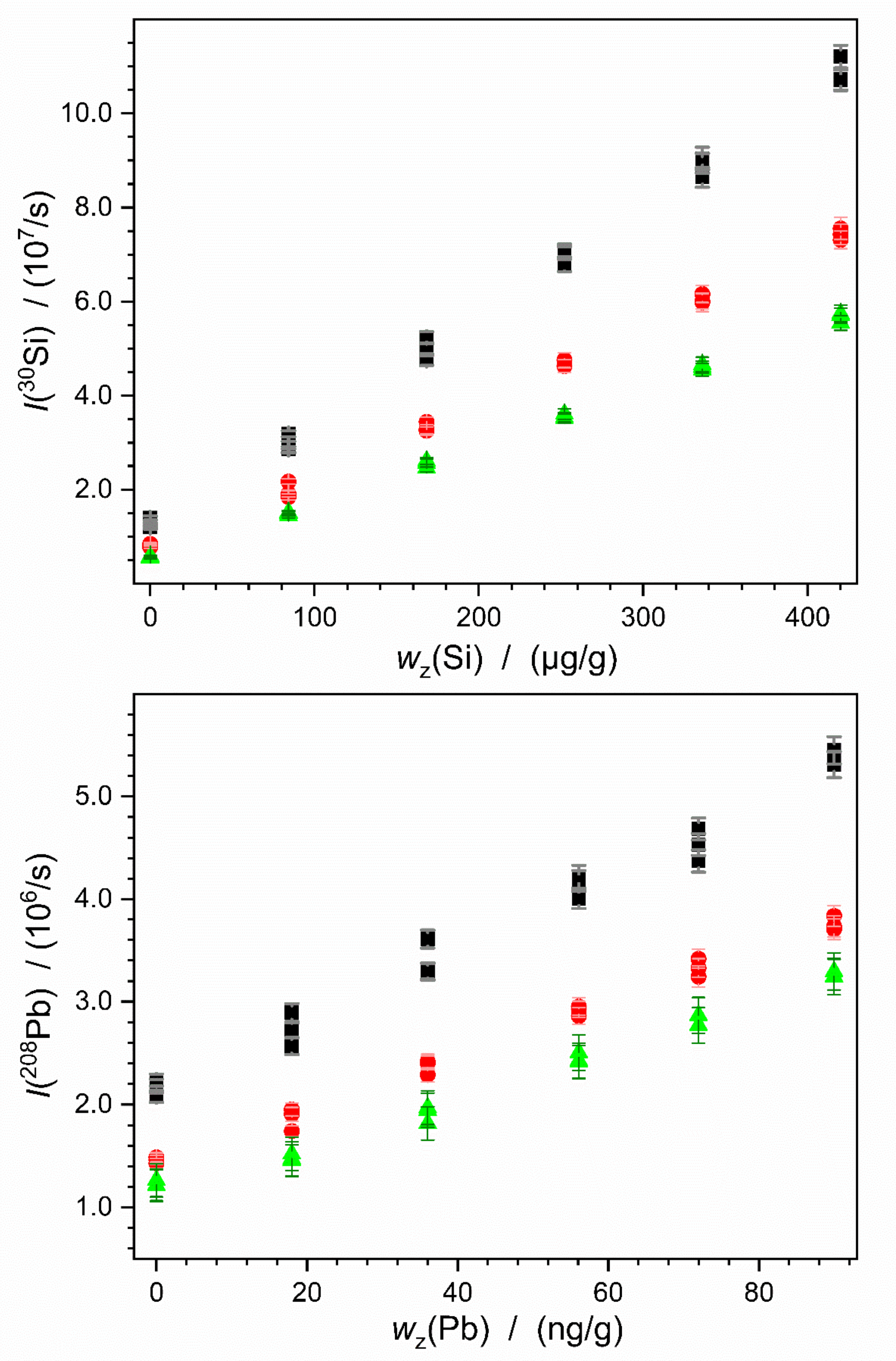
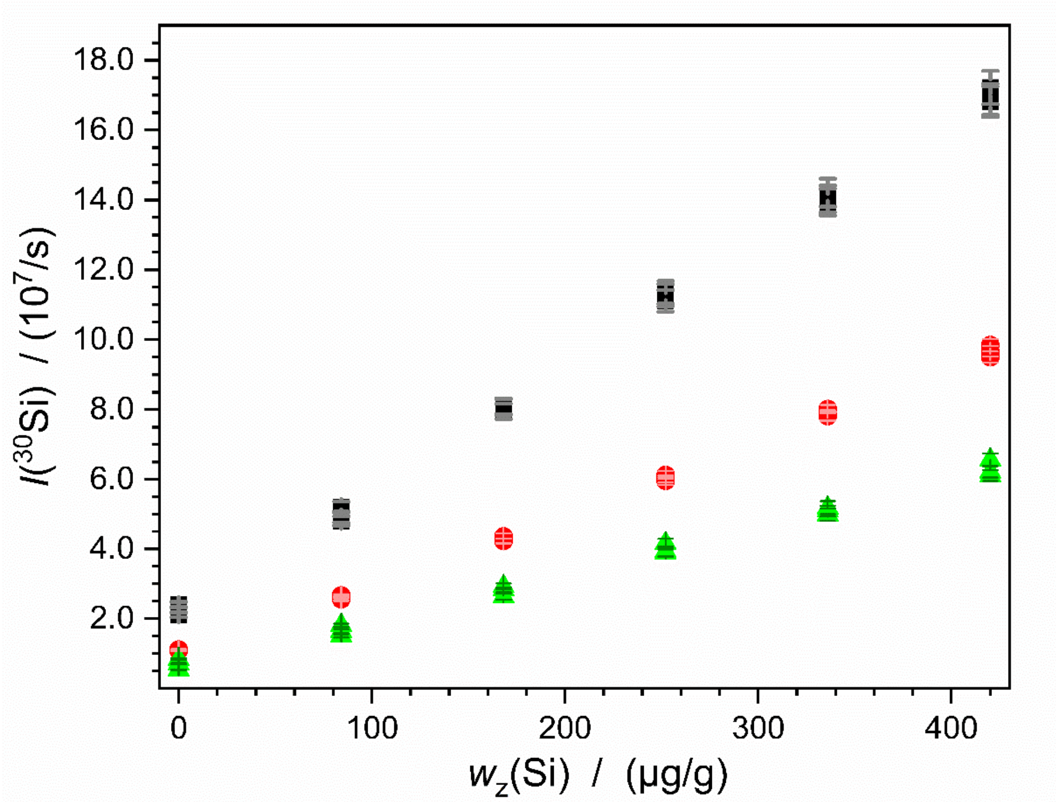


Figure S- 2: Mean intensity of ^{30}Si (upper figure) and ^{208}Pb (lower figure) as a result of the measurement with NIST SRM 610. One data point represents the average values of one laser ablation spot in addition with one solution. The error bars denote the experimental standard uncertainty. The first sequence is represented by the black squares, the second sequence by the red circles and the last measurement sequence by the green triangles.

3.2 Pb in NIST SRM 612



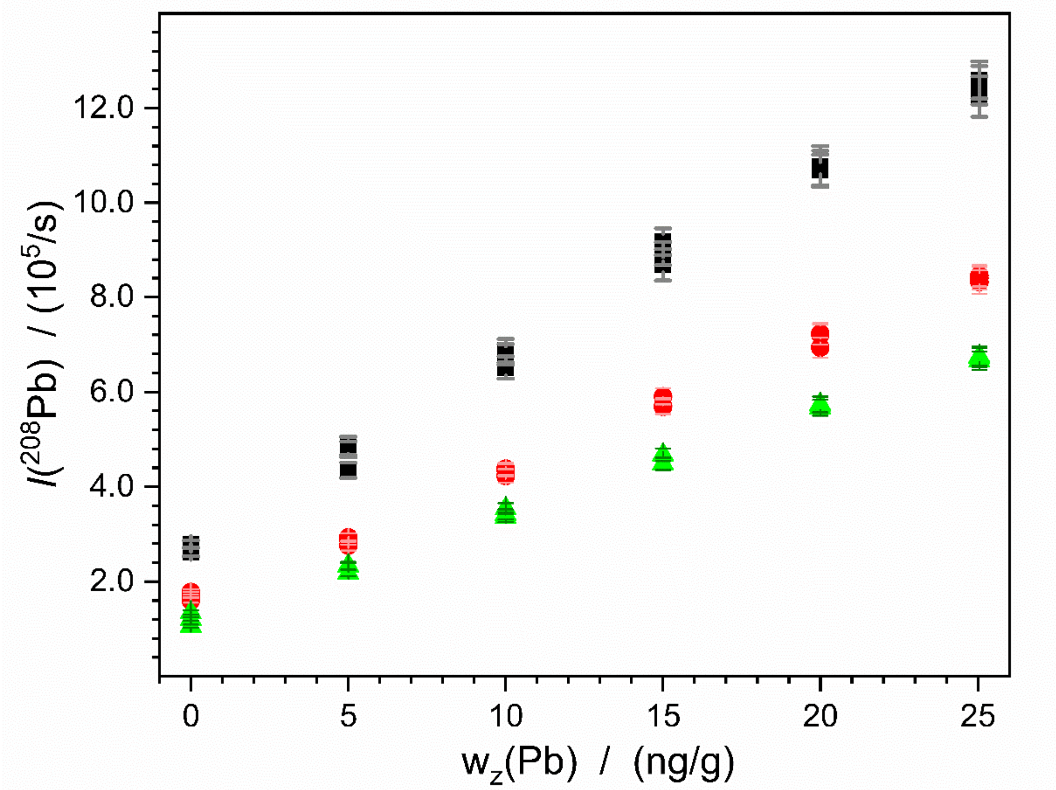


Figure S- 3: Mean intensity of ^{30}Si (upper figure) and ^{208}Pb (lower figure) as a result of the measurement with NIST SRM 612. One data point represents the average values of one laser ablation spot in addition with one solution. The error bars denote the experimental standard uncertainty. The first sequence is represented by the black squares, the second sequence by the red circles and the last measurement sequence by the green triangles.

3.3 Rb in NIST SRM 610

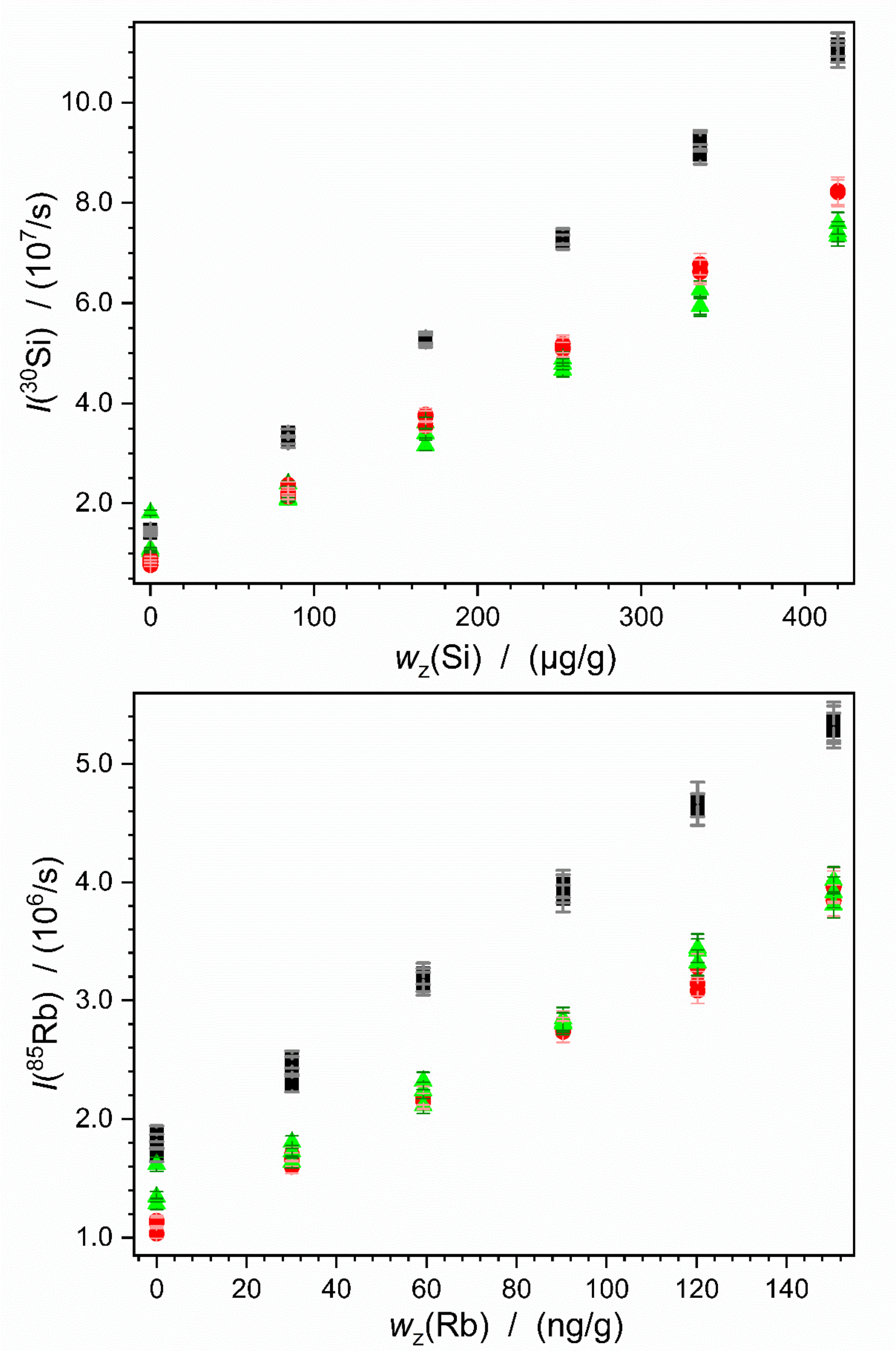


Figure S- 4: Mean intensity of ^{30}Si (upper figure) and ^{85}Rb (lower figure) as a result of the measurement with NIST SRM 610. One data point represents the average values of one laser ablation spot in addition with one solution. The error bars denote the experimental standard uncertainty. The first sequence is represented by the black squares, the second sequence by the red circles and the last measurement sequence by the green triangles.

3.4 Rb in NIST SRM 612

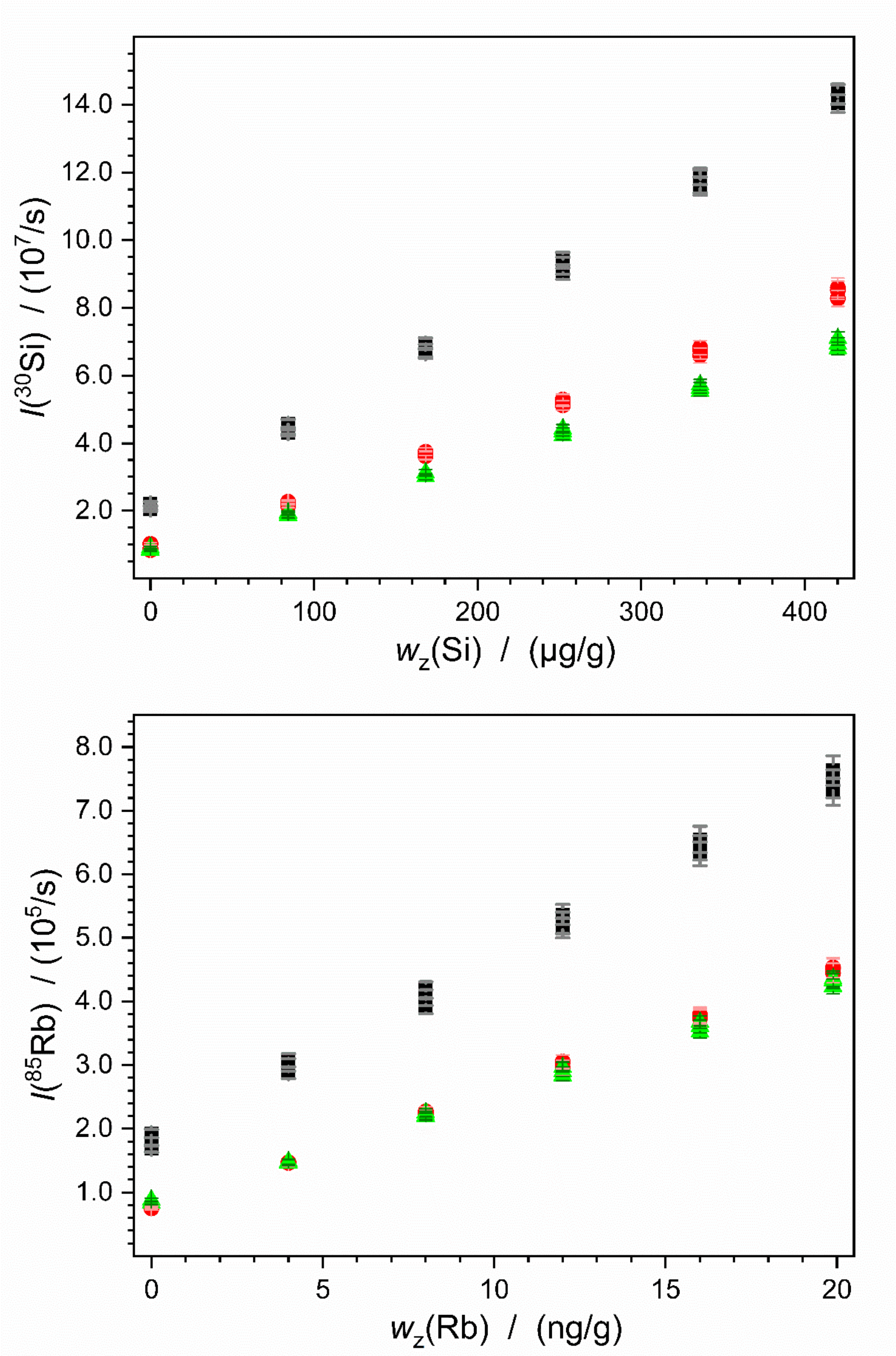


Figure S- 5: Mean intensity of ^{30}Si (upper figure) and ^{85}Rb (lower figure) as a result of the measurement with NIST SRM 612. One data point represents the average values of one laser ablation spot in addition with one solution. The error bars denote the experimental standard uncertainty. The first sequence is represented by the black squares, the second sequence by the red circles and the last measurement sequence by the green triangles.