

# Scale Conversion and Uncertainty Calculations in Isotope Delta Measurements

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Isotope ratio applications are on the increase and a major part of which are delta measurements, because they are easier to perform than the determination of absolute isotope ratios while offering lower measurement uncertainties. Delta measurements use artefact-based scales and therefore scale conversions are required due to the lack of the scale defining standards. Such scale conversions often form the basis for comparing data being generated in numerous projects and therefore need to be as accurate as possible. In practice, users are tempted to apply linear approximations, which are not sufficiently exact, because delta values are defined by nonlinear relationships. The bias of such approximations often is beyond typical measurement uncertainties and its extent can hardly be predicted. Therefore, exact calculations are advised. Here, the exact equations and the bias of the approximations are presented, and calculations are illustrated by real-world examples. Measurement uncertainty is indispensable in this context and therefore, its calculation is described as well for determining delta values but also for scale conversions. Approaches for obtaining a single delta measurement and for repeated measurements are presented. For the latter case, a new approach for calculating the measurement uncertainty is presented, which considers covariances between the isotope ratios.

Keywords: delta isotope standard, delta scale, in-house calibration solution, isotope ratios, isotope reference material, measurement uncertainty, scale conversion.

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Isotope ratios are increasingly used in all disciplines of science ranging from archaeology to zoology for providing insights into natural processes, the provenance of a specimen or the residence history and migration paths of animals and human beings (Font *et al.* 2007, Vautour *et al.* 2015, He *et al.* 2019, Vogl *et al.* 2019). Absolute isotope ratios or isotope amount ratios would be the perfect tool for these investigations. However, the measurement of absolute isotope ratios is hindered, because the required reference materials offering sufficiently small measurement uncertainties for resolving natural isotopic variations are barely available (Vogl and Pritzkow 2010). Absolute isotope ratio measurements without suitable reference materials are extremely demanding. Therefore, delta scale measurements were introduced in the past and have been used predominantly since then. The major advantage here is that the measured sample isotope ratio is compared with the measured standard isotope ratio by calculating the relative

difference of both. Usually, it is expressed in ‰ (=  $10^{-3}$ ). This way, factors correcting for instrumental isotope fractionation cancel and therefore will not affect the result(s). When symmetric standard-sample bracketing additionally is applied, drifts are minimised. Typically, matrix and intensity matching are applied as well as adjusting the acid concentration and the signal intensity of the matrix separated sample and the standard to  $\pm 10\%$  or better. Then, the impact of the matrix and of an incomplete background correction are minimised. When properly applied, this approach can lead to a precision of better than  $0.01\%$  and expanded measurement uncertainties in the range of  $0.05\%$  to  $0.1\%$  (Vogl *et al.* 2020). Important here is the definition of a delta scale and the availability of an internationally agreed-upon delta isotope standard, which anchors the delta scale. The preferred anchor point of delta scales by analysts is the origin, because then calculations are straightforward. When the anchor point is not the origin, or

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when a second isotope standard with  $\delta \neq 0$  is applied, it can be regarded as a virtual, second delta scale and the measured delta value has to be transferred to the origin, the primary delta scale. This is the case, for example when an in-house isotope standard (calibration solution) is used for the standard-sample bracketing. With the increase of isotope ratio applications and the expansion to elements that have not been focussed upon before, frequently individual delta scales are set up in parallel by independent research groups. To allow the comparison of delta values obtained on different scales, both standards need to be measured against one another and the delta values obtained on the samples need to be converted. As delta scales are relative scales, no simple addition or subtraction of delta values yields the correct result and is allowed in this context. To improve comparability in delta measurements, especially for metal isotopes and those elements typically measured by ICP-MS, and to foster the use of in-house isotope standards (calibration solutions), thus allowing an availability for longer or infinite periods, the necessary equations will be deduced and presented in this work.

Measurement uncertainty has the same level of importance as the correct scale conversion, because measurement results can only be compared when they are traceable to the same source/reference/unit. Traceability in turn requires a measurement uncertainty for each calibration within the analytical procedure. Precision data, especially repeatability, are not sufficient to enable comparability, as they underestimate or even neglect contributions from other sources such as the calibration standard, the sample dissolution, the matrix separation or incomplete correction of instrumental isotope fractionation especially in laser ablation applications. All these contributions are considered when setting up a complete uncertainty budget. Admittedly, this might seem complicated when realising it for the first time, but with continuous application it will become routine.

In isotope delta measurements of H, C, N, O and S guidelines and applications for obtaining measurement uncertainties according to current international guidelines (JCGM 2008) are already available (Gröning 2011, Chen *et al.* 2013, Dunn *et al.* 2015, 2019, Meija and Chartrand 2018). In the certification of metal and metalloid isotope delta reference materials this is the case as well (Vogl and Rosner 2012, Vogl *et al.* 2020). In isotope delta measurements of metal isotopes and other elements being accessible by ICP-MS, however, measurement uncertainty according to current international guidelines often is lacking. To support the users in setting up corresponding uncertainty budgets, we present two models for calculating the measurement uncertainty in delta measurements. The first

model focuses on a single measurement and includes all possible sources of uncertainty contributions. It is an enhancement of a previously published approach (Rosner *et al.* 2011). The second model is a completely new approach that focuses on the repeated measurement of a sample within one measurement sequence, and which considers correlations between the parameters. This model is mainly intended for calibrating in-house isotope standards, but it may as well be applied to repeated sample measurements, provided uncertainty contributions for sample preparation and matrix separation are added.

## Scale conversion

As pointed out above (isotope) delta values are relative isotope ratios, which are related to an internationally accepted isotope delta standard, preferably an isotope reference material. The delta scale itself is defined by its origin, which predominantly is realised by the isotope standard. A delta value is defined as the difference of a measured isotope ratio of a sample  $r_{\text{smp}}^{i/i}$ , and the measured isotope ratio of the reference  $r_{\text{ref}}^{i/i}$ , divided by the measured isotope ratio of the reference,  $r_{\text{ref}}^{i/i}$  (Equation (1)):

$$\delta_{\text{smp/ref}}^{i/i}(E) = \frac{r_{\text{smp}}^{i/i} - r_{\text{ref}}^{i/i}}{r_{\text{ref}}^{i/i}} = \frac{r_{\text{smp}}^{i/i}}{r_{\text{ref}}^{i/i}} - 1 \quad (1)$$

The measured isotope ratio  $r^{i/i}$  denotes actually the ratio of the measured intensities (e. g. ion current  $I$  in A, counting rate  $dN/dt$  in  $s^{-1}$  or voltage  $U$  in V) observed on the masses of the two isotopes  ${}^iE$  and  ${}^iE$  of the element  $E$ , with typically  $M_i > M_j$ . For example (in case of currents):

$$\begin{aligned} r_{\text{smp}}^{26/24} &= \frac{I_{\text{smp}}({}^{26}\text{Mg})}{I_{\text{smp}}({}^{24}\text{Mg})} \wedge r_{\text{ref}}^{26/24} \\ &= \frac{I_{\text{ref}}({}^{26}\text{Mg})}{I_{\text{ref}}({}^{24}\text{Mg})} \wedge \delta_{\text{smp/ref}}^{26/24}(\text{Mg}) = \frac{\frac{I_{\text{smp}}({}^{26}\text{Mg})}{I_{\text{smp}}({}^{24}\text{Mg})}}{\frac{I_{\text{ref}}({}^{26}\text{Mg})}{I_{\text{ref}}({}^{24}\text{Mg})}} - 1 \quad (2) \end{aligned}$$

For all equations and all calculations throughout this paper it has to be noted that delta values are used according to Equation (1). This means 0.001 is used instead of 1‰. After all calculations are performed, the delta value is expressed in ‰, % etc. Consequently, all delta values provided in ‰ have to be divided by 1000 before performing the calculations (or any other corresponding factor in case another unit was applied).

Based on Equation (1) the delta scale is defined as well. The reference represents the origin,  $\delta = 0$ , of the scale and

any other point is defined by Equation (1). In some cases, a second anchor point is defined for the delta scale. This is the case when the original reference that defines the scale is exhausted, or when a virtual origin has been defined. In fact, in both cases a second scale has been defined, because Equation (1) clearly states, that whatever reference is being applied it defines the origin,  $\delta = 0$ , of the currently applied delta scale. In such cases a scale conversion is required, when the delta values shall be expressed on the original delta scale. The same applies when an in-house isotope standard is being applied as a bracketing standard to save the original isotope standard (reference). In total we differentiate between three different cases, which will be explained in the following paragraphs on real world examples. The underlying measurements have been performed by MC-ICP-MS by applying the standard-sample bracketing (SSB) approach, within which each sample is bracketed by a preceding and a succeeding standard measurement. As delta scales are not linear, an equation system for the transformations needs to be set up. In this equation system, the sample is labelled with the index  $x$ , while the first (original) isotope standard is labelled  $y$  and the second isotope standard is labelled  $z$ . The deduction of the equation system is presented in the online supporting information.

### Inversion of sample and standard

A sample  $x$  is measured in SSB against the second isotope standard  $z$ , which is used as bracketing standard, and the corresponding delta value  $\delta_{x/z}$  is calculated according to Equation (1). Now, the delta value needs to be expressed as isotope standard  $z$  measured against sample  $x$ ,  $\delta_{z/x}$ . Most frequently this occurs when sample  $x$  is being replaced by the isotope standard  $y$ , which is measured against isotope standard  $z$  yielding the delta value  $\delta_{y/z}$ . This value needs to be converted into the delta value of isotope standard  $z$  against isotope standard  $y$ ,  $\delta_{z/y}$ . In other words the delta value of isotope standard  $y$  on the scale  $z$  is transferred into the delta value of  $z$  on the scale  $y$ . This conversion can be calculated by applying Equation (3):

$$\delta_{z/y} = \frac{-\delta_{y/z}}{\delta_{y/z} + 1} \quad (3)$$

A practical example is the measurement of DSM3, the isotope standard anchoring the magnesium delta scale, i.e., the scale for  $\delta^{25/24}(\text{Mg})$  and  $\delta^{26/24}(\text{Mg})$ , against the new certified isotopic reference material (iCRM) ERM-AE143 (see Figure 1). For simplicity we consider only  $\delta^{26/24}(\text{Mg})$  in this context (because  $\delta^{25/24}(\text{Mg})$  calculations are analogous).

DSM3 represents the original isotope standard  $y$ , which anchors the delta scale for magnesium, while ERM-AE143 represents the second isotope standard  $z$ , which is the new iCRM for magnesium. The delta value  $\delta^{26/24}(\text{Mg})$  of DSM3 measured against ERM-AE143,  $\delta_{y/z}$  is 3.295‰ with a combined uncertainty of  $u_c = 0.013\%$  (Vogl *et al.* 2020). After applying Equation (3) we obtain the delta value  $\delta^{26/24}(\text{Mg})$  of ERM-AE143 measured against DSM3,  $\delta_{z/y}$ , which is -3.284‰, again with a combined uncertainty of  $u_c = 0.013\%$ . This demonstrates that simply inverting the algebraic sign would lead to a delta value that, in this case, is wrong by -0.011‰. This deviation is of the same magnitude as the combined uncertainty and therefore cannot be neglected.

### Second scale anchor

The delta scale is established with  $\delta_{y/y} = 0$ . In case the original isotope standard  $y$  is exhausted, or it has been defined as a virtual origin without representation by any isotope standard, the user requires a (second) standard  $z$  with  $\delta_{z/y} \neq 0$ , assigned by measurement or by definition. The sample  $x$  is measured against isotope standard  $z$  by applying the SSB approach. The so obtained delta value,  $\delta_{x/z}$  needs to be converted to the delta value of sample  $x$  against isotope standard  $y$ ,  $\delta_{x/y}$ , to enable comparability with other delta values obtained on the scale  $y$ . This conversion is realised by Equation (4) (also see Coplen 1994):

$$\delta_{x/y} = \delta_{x/z} \times \delta_{z/y} + \delta_{x/z} + \delta_{z/y} \quad (4)$$

A practical example would be the measurement of the sample IRMM-009 against the new certified isotopic reference material (iCRM) ERM-AE143 (see Figure 2). For simplicity we consider only  $\delta^{26/24}(\text{Mg})$  in this context (because  $\delta^{25/24}(\text{Mg})$  calculations are analogous). DSM3 represents the original isotope standard  $y$ , which anchors the delta scale for magnesium and might be exhausted, while ERM-AE143 represents the second anchor  $z$  or rather the replacement of the original anchor. The delta value  $\delta^{26/24}(\text{Mg})$  of IRMM-009 measured against ERM-AE143,  $\delta_{x/z}$  is -1.656‰ with a combined uncertainty of  $u_c = 0.014\%$  (Vogl *et al.* 2020). After applying Equation (4) using the knowledge of  $\delta_{z/y} = -3.284\%$  (with a combined uncertainty of  $u_c = 0.013\%$ ) of the second or replacement anchor  $z$ , we obtain the delta value  $\delta^{26/24}(\text{Mg})$  of IRMM-009 against DSM3,  $\delta_{x/y}$ , which is -4.934‰ with a combined uncertainty of  $u_c = 0.020\%$ . When the simplification following Equation (7) is used a deviation of -0.0054‰ results, which is already more than a quarter of the combined uncertainty.

## Conversion to another delta scale

In case two or more delta scales with different origins exist for one isotope ratio, a conversion of delta values to any of the delta scales might be necessary to enable comparability of measurement results. Let us assume the delta value of sample x was measured against isotope standard z, yielding  $\delta_{x/z}$  and it should be converted to the delta value of sample x against isotope standard y,  $\delta_{x/y}$ . In the same sequence isotope standard y was measured against standard z, yielding  $\delta_{y/z}$ . Then  $\delta_{x/y}$  can be calculated according to Equation (5) (obtained by inserting Equation (3) into Equation (4)):

$$\delta_{x/y} = \frac{\delta_{x/z} + 1}{\delta_{y/z} + 1} - 1 \quad (5)$$

A special variation of delta scale conversion is the application of an in-house isotope standard, which is a pure solution of the element of interest and it is applied as the bracketing standard to save the running short or (nearly) exhausted first (original) isotope standard. The in-house isotope standard simply represents isotope standard z and the link to isotope standard y is obtained by the measurement of  $\delta_{y/z}$  (y against isotope standard z). In Figure 3 the scale conversion for applying an in-house isotope standard is illustrated for the magnesium delta scale. The applied in-house isotope standard used for the SSB approach was ERM-AE143 and the sample IRMM-009 was measured against this in-house isotope standard. The delta value of DSM3 measured against ERM-AE143, i.e.,  $\delta_{\text{DSM3/ERM-AE143}}^{26/24}(\text{Mg}) = \delta_{y/z}$  is known and published (Vogl *et al.* 2020). With both data the delta value of IRMM-009 against DSM3 (-4.934‰ with a combined uncertainty of  $u_c = 0.020\%$ ) can be calculated by applying Equation (5). When the simplification following Equation (8) is used a deviation of -0.016‰ results, which is already more than three quarters of the combined uncertainty and therefore cannot be neglected.

## Simplification/linear approximation of Equations (3) – (5)

Simple linear operations lead to a bias for the cases presented above. To illustrate the extent of the bias and its dependency on the magnitude of the corresponding delta value(s) we simulated several scenarios using Equations (3) – (5) to be able to compare the correct calculation, the wrongly approximated linear calculation and the bias of the latter for a range of delta values between -100‰ and +100‰. All of the above described three cases, namely the interchanging of sample and isotope standard, the use of a secondary scale anchor and the scale conversion are

covered. The following linear approximations (that are frequently applied in delta calculations) have been used (e.g., Wolfsberg *et al.* 2010, Bao *et al.* 2020):

Approximation for 'inversion' (section "Inversion of sample and isotope standard")

$$-1 \ll \delta_{y/z} \ll 1 \Rightarrow \frac{-\delta_{y/z}}{\delta_{y/z} + 1} \approx -\delta_{y/z} \Rightarrow \delta_{z/y} \approx -\delta_{y/z} \quad (6)$$

Approximation for 'sum' (section "Second scale anchor")

$$\begin{aligned} -1 \ll \delta_{x/z} \times \delta_{z/y} \ll 1 &\Rightarrow \delta_{x/z} \times \delta_{z/y} + \delta_{x/z} + \delta_{z/y} \\ &\approx \delta_{x/z} + \delta_{z/y} \Rightarrow \delta_{x/y} \approx \delta_{x/z} + \delta_{z/y} \end{aligned} \quad (7)$$

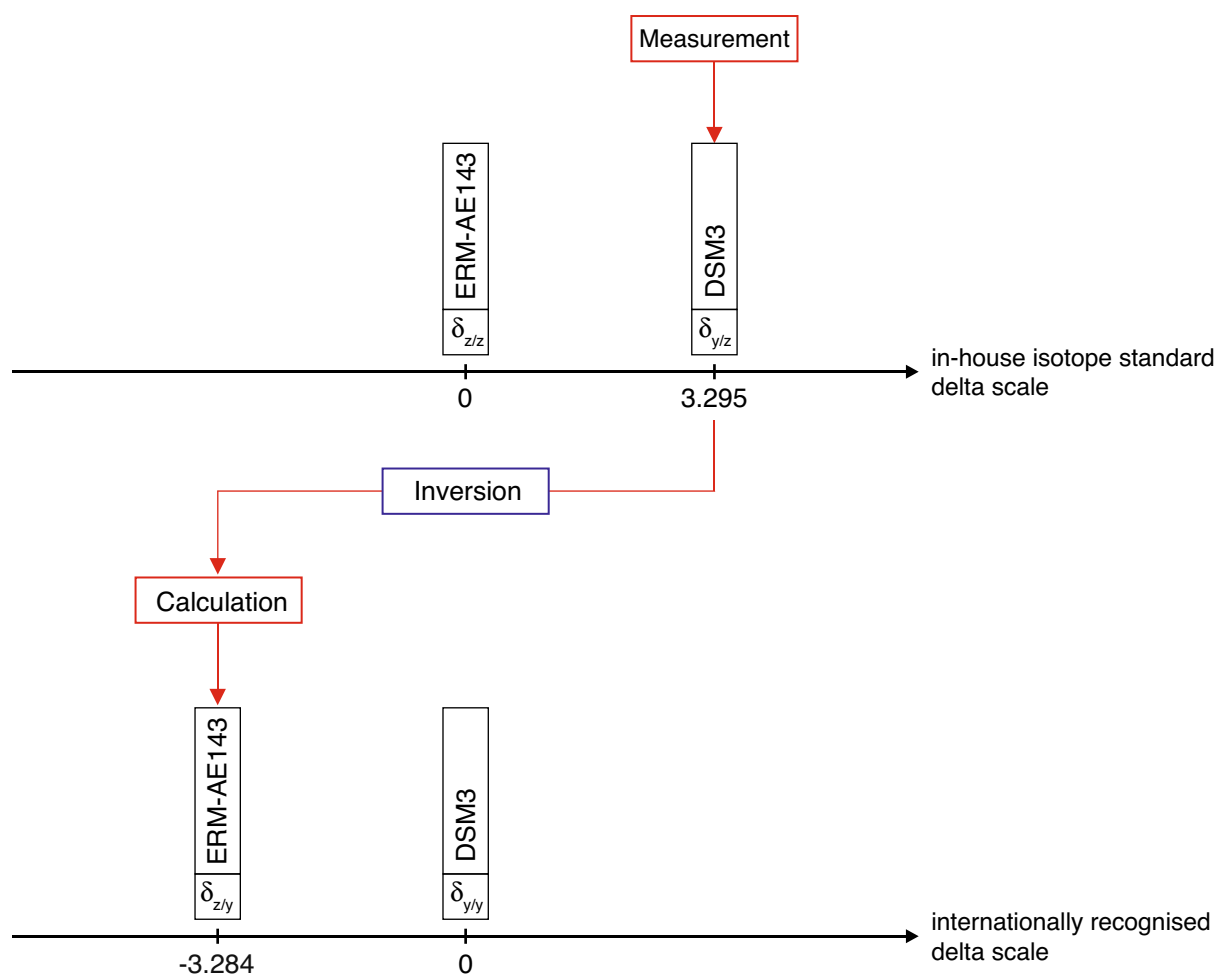
Approximation for 'difference' (section "Conversion to another delta scale")

$$\begin{aligned} -1 \ll \delta_{y/z} \ll 1 &\Rightarrow \frac{\delta_{x/z} + 1}{\delta_{y/z} + 1} - 1 \approx \delta_{x/z} - \delta_{y/z} \\ &\Rightarrow \delta_{x/y} \approx \delta_{x/z} - \delta_{y/z} \end{aligned} \quad (8)$$

In all cases, the absolute deviation  $\Delta_\delta$  of the approximated result  $\delta_{\text{smpl/ref}}^{\text{app}}$  from the exact result  $\delta_{\text{smpl/ref}}$  in ‰ and the relative deviation  $\Delta_{\text{rel}}\delta_{\text{smpl/ref}} = \left( \delta_{\text{smpl/ref}}^{\text{app}} - \delta_{\text{smpl/ref}}^{\text{exc}} \right) / \delta_{\text{smpl/ref}}$  in % were calculated. The calculations are summarised in an Excel® file in the online supporting information. The results are depicted in Figures S1–S9 in Appendix S2 (online supporting information). The results show that the linear approximations can – in rare, but hardly predictable, circumstances – lead to results with a bias smaller than the uncertainty of the exact result. But in the majority of cases the deviations are much larger than uncertainties of the exact results (sometimes even as much as several ‰). Therefore, it always seems to be a wise decision to prefer the exact solutions (Equations 3–5) to the above approximations to be on the safe side. In the age of spreadsheet calculation software this seems to be an acceptable inconvenience. In Table 1 some exemplary comparisons between the exact and simplified solutions are compiled demonstrating the necessity to use the exact equations.

## Measurement uncertainty associated with delta values

Measurement uncertainty is a "Non-negative parameter characterising the dispersion of the quantity values being attributed to a measurand, based on the information used" (JCGM 2012). In other words, the measurement uncertainty sets the limits within which a result is regarded as accurate,

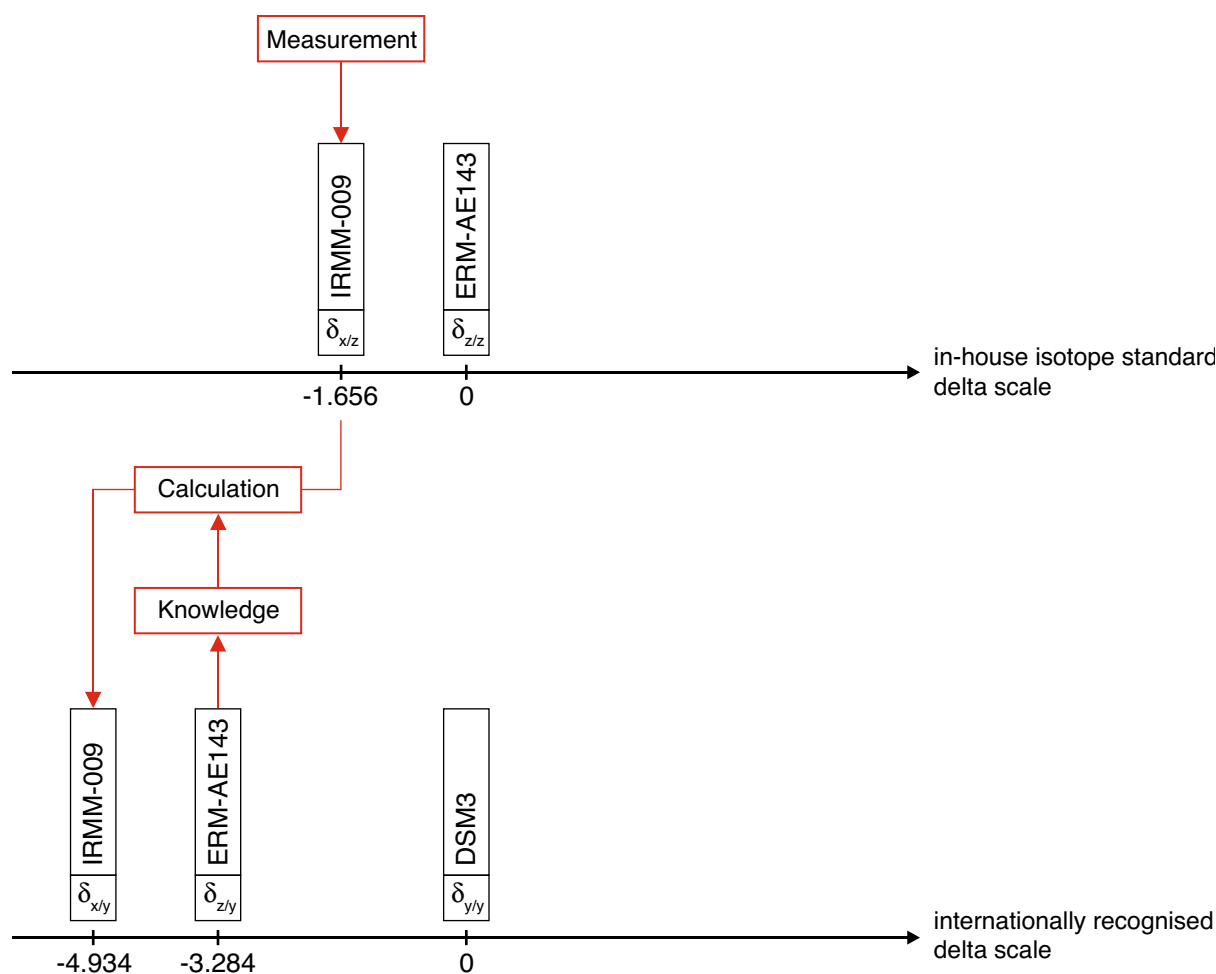


**Figure 1.** Inversion of sample and isotope standard. Conversion of the measured  $\delta_{y/z}$  (scale anchor z) to  $\delta_{z/y}$  (scale anchor y) illustrated for the magnesium delta scale and the application of an in-house isotope standard (z, here ERM-AE143) and the internationally recognised scale anchor (y, here DSM3).

i.e. precise and true. In contrast, a precision value only provides the user with a measure of reproducibility, which is a certain probability, mostly 95%, for a succeeding measurement to fall into the same specified interval. Therefore, measurement uncertainties are mandatory for all delta measurements to enable traceability to the specified delta scale and its scale anchor and to enable comparability among all delta measurements. Although measurement uncertainty meanwhile has been widely accepted and is prescribed in international standards for testing laboratories (ISO 2017) and reference material producers (ISO 2016), it is hardly realised in isotope ratio measurements. Disregarding the manifold reasons for this, a major obstacle is the lack of information and of suitable approaches. To solve this, we provide two approaches for calculating measurement uncertainty in delta measurements together with calculation tools.

### Measurement uncertainty for a single measurement

In research projects within which isotope ratio measurements are applied, samples typically are processed and measured only once. For sets of several tens or hundreds of samples and a sample processing time of several days, the expenditure of time would be too high, if repeated sample processing is applied. Hence, we need an approach for calculating the measurement uncertainty for single delta measurements. The basic approach was developed by Rosner *et al.* (2011) for thermal ionisation mass spectrometry (TIMS) measurements and has been improved and modified for MC-ICP-MS by Geilert *et al.* (2015). The equation for the delta value is expanded by "adding" factors,  $\kappa_i$ , for individual uncertainty contributions, leading to the equation we use for the uncertainty calculation (Equation (9)).



**Figure 2.** Delta scale with anchor points at  $\delta_{y/y} = 0$  and  $\delta_{z/y} \neq 0$ . Conversion of the measured  $\delta_{x/z}$  (scale anchor z) to  $\delta_{x/y}$  (scale anchor y), because the original scale anchor y might be exhausted, illustrated for the magnesium delta scale and the application of an in-house isotope standard (z, here ERM-AE143) and the internationally recognised scale anchor (y, here DSM3) using the knowledge of the  $\delta_{z/y} \neq 0$  acquired prior to the exhaustion of y.

These factors,  $\kappa_i$ , have the value one (in order to leave the actual value untouched) and a specific uncertainty contribution. Additionally, the measured isotope ratio of the isotope standard is replaced by the mean of the isotope ratios of the preceding and succeeding isotope standard, thus reflecting the real measurement procedure.

$$\delta_{\text{sm}/\text{ref}}^{i/j}(\text{E}) = \left[ \frac{r_{\text{sm}}^{i/j} \times \kappa_1 \times \kappa_2 \times \kappa_3 \times \kappa_6 \times \kappa_7}{0.5 \times (r_{\text{ref},1}^{i/j} + r_{\text{ref},2}^{i/j}) \times \kappa_4} \times \kappa_5 \right] - 1 \quad (9)$$

In Equation (9) we added up to seven factors  $\kappa_i$  representing uncertainty contributions from (1) the sample digestion, (2) the analyte-matrix separation, (3) incompletely corrected mass spectrometric background, (4) the heterogeneity of the

bracketing standard, (5) the mass bias drift incompletely compensated for by the bracketing approach, (6) the offset in mass bias due to incomplete matrix matching, and (7) residual interferences. It has to be noted here, that these seven uncertainty contributions do not necessarily apply to all measurement procedures, and in some cases further factors  $\kappa_i$  need to be added, but in most cases these seven factors  $\kappa_i$  reflect the reality of delta measurements carried out by MC-ICP-MS. The associated uncertainties of the factors  $\kappa_i$  are either obtained from data extracted from the measurement sequence, from measurements carried out during method development and/or validation or from expert judgement. Examples on how to obtain these uncertainties are provided in the references (Rosner *et al.* 2011, Geilert *et al.* 2015, Tatzel *et al.* 2019, Vogl *et al.* 2020).

**Table 1.**

Compilation of examples for the absolute and relative deviations ( $\Delta\delta_{\text{smp/ref}}$  and  $\Delta_{\text{rel}} \delta_{\text{smp/ref}}$  resp.) of the simplified solutions (calculated using Equations 6–8) from the exact solutions (according to Equations 3–5)

<b>Inversion of sample x and reference z (section <i>Inversion of sample and isotope standard</i>)</b>					
		<b>Exact solution</b>	<b>Approximation</b>	<b>Abs. bias</b>	<b>Rel. bias</b>
		<b>Eqn. 3</b>	<b>Eqn. 6</b>		
$\delta_{x/z}$ (‰)		$\delta_{z/y}$ (‰)	$\delta_{z/y}$ (‰)	$\Delta\delta_{z/y}$ (‰)	$\Delta_{\text{rel}} \delta_{z/y}$ (%)
-80.00		86.96	80.00	-6.96	-8.0
3.295		-3.284	-3.295	-0.011	0.33
100.0		-90.9	-100.0	-9.1	10
<b>Second scale anchor (section <i>Second scale anchor</i>)</b>					
		<b>Exact solution</b>	<b>Approximation</b>	<b>Abs. bias</b>	<b>Rel. bias</b>
		<b>Eqn. 4</b>	<b>Eqn. 7</b>		
$\delta_{x/z}$ (‰)	$\delta_{z/y}$ (‰)	$\delta_{x/y}$ (‰)	$\delta_{x/y}$ (‰)	$\Delta\delta_{x/y}$ (‰)	$\Delta_{\text{rel}} \delta_{x/y}$ (%)
3.400	-3.284	0.105	0.116	0.011	11
-1.656	-3.284	-4.935	-4.940	-0.005	0.11
-100	-10.0	-109	-110	-1.0	0.92
<b>Conversion to another delta scale (section <i>Conversion to another delta scale</i>)</b>					
		<b>Exact solution</b>	<b>Approximation</b>	<b>Abs. bias</b>	<b>Rel. bias</b>
		<b>Eqn. 5</b>	<b>Eqn. 8</b>		
$\delta_{x/z}$ (‰)	$\delta_{y/z}$ (‰)	$\delta_{x/y}$ (‰)	$\delta_{x/y}$ (‰)	$\Delta\delta_{x/y}$ (‰)	$\Delta_{\text{rel}} \delta_{x/y}$ (%)
-100.00	3.295	-102.96	-103.30	-0.34	0.33
-1.656	3.295	-4.935	-4.951	-0.016	0.33
100.00	10.0	89.11	90.00	0.89	1.0

See the paragraph above. In some cases, the relative deviation is likely to reach 11%, which is by far more than the uncertainty associated with the actual result, underpinning the importance of the use of the exact equations. See also the tables in the online supporting information.

The combined standard uncertainty of the delta value can then be calculated either by applying special software such as the GUM Workbench (Metrodata GmbH, Braunschweig, Germany), by using the Kragten approach (Kragten 1994), the NIST uncertainty machine (NIST 2021), or by using the square sum approach via Equation (10):

$$u\left(\delta_{\text{smp/ref}}^{i/j}(E)\right) = \left(\delta_{\text{smp/ref}}^{i/j}(E) + 1\right) \sqrt{\left(\frac{u\left(\frac{r_{\text{smp}}^{i/j}}{r_{\text{smp}}^{i/j}}\right)}{r_{\text{smp}}^{i/j}}\right)^2 + \left(\frac{u\left(\frac{r_{\text{rel},1}^{i/j}}{r_{\text{rel},1}^{i/j} + r_{\text{rel},2}^{i/j}}\right)}{r_{\text{rel},1}^{i/j} + r_{\text{rel},2}^{i/j}}\right)^2 + \left(\frac{u\left(\frac{r_{\text{rel},2}^{i/j}}{r_{\text{rel},1}^{i/j} + r_{\text{rel},2}^{i/j}}\right)}{r_{\text{rel},1}^{i/j} + r_{\text{rel},2}^{i/j}}\right)^2 + \sum_{l=1}^7 \left(\frac{u(\kappa_l)}{\kappa_l}\right)^2} \quad (10)$$

Here it has to be noted that numerical differentiation, which is applied in the Kragten approach and in the "GUM Workbench", can lead to slight biases when applied to non-linear relationships. The Monte-Carlo method considers non-linear relationships and leads to correct results. Therefore, it can be used for validating the application of numerical differentiation, which is the reason why the "GUM Workbench" also contains a Monte-Carlo module.

An Excel template for calculating the measurement uncertainty according to Equation (10) is provided in the online supporting information (see tab MU Single measurement). Note: Measured isotope ratios and their associated uncertainties have to be entered as absolute values. This applies also for the factors  $\kappa_l$ . The value of  $\kappa_l$  is one and for an associated standard uncertainty of 1‰ (assumed value) the value 0.001 has to be entered. The standard uncertainty of a measured isotope ratio typically is the standard deviation of the mean.

The expanded measurement uncertainty can be obtained from the combined standard uncertainty (Equation (10)) by multiplying it with the coverage factor  $k$ , which in most cases is 2 provided the distribution is normal and the degrees of freedom is high (sufficiently large number of measurement points).

A practical example is the measurement of the  $\delta_{\text{smp/LSVEC}}^{7/6}$  in a cathode material of a Li battery and its associated measurement uncertainty (Winckelmann *et al.* 2021). The  ${}^7\text{Li}/{}^6\text{Li}$  isotope ratio measurements were carried out in SSB mode by applying MC-ICP-MS as described in Winckelmann *et al.* (2021). The measured

${}^7\text{Li}/{}^6\text{Li}$  isotope ratios for measurement 1 of sample A1 and the preceding and the succeeding isotope reference material LSVEC1 and LSVEC2 are listed in Table 2 with their associated standard uncertainties expressed as the standard deviation of the mean of each measurement. The individual uncertainty contributions  $\kappa_i$  are listed in Table 2 as well, and were obtained as follows. The uncertainty contribution for sample digestion  $\kappa_1$  was estimated as 0.1‰ (corresponds to 0.0001) based on expert judgement, e.g., here the reproducibility of individually digested samples can be applied. Those for the analyte-matrix separation was assessed as half of the maximum difference between the delta values of a Li ICP standard and of the same Li ICP standard after separation. The separated Li ICP standard was mixed with a simulated matrix prior to the separation. As a combined measure for  $\kappa_1$  and  $\kappa_2$  half of the difference between the measured delta value and the reference or assigned delta value of a suitable reference material or sample can be used. The instrumental blank measured in 2% nitric acid was subtracted from each measurement. Due to fluctuations in the instrumental blank, however, an uncertainty contribution occurs. This contribution  $\kappa_3$  was assessed as the standard deviation of the mean of all blank measurements in the measurement sequence divided by the average signal intensity of all samples. The heterogeneity of the bracketing standard NIST RM 8545 (LSVEC), represented by  $\kappa_4$ , was estimated as 0.1‰ (corresponding to 0.0001) based on expert judgement, e.g., here the typical repeatability of isotope standard measurements can be applied. Even better would be the spread of individually dissolved or diluted aliquots of the bracketing standard. Although a drift in mass bias is compensated by the SSB approach as explained above, a residual uncertainty contribution  $\kappa_5$  remains. This is calculated as the average of the individual drifts between two

succeeding standard measurements divided by two. The influence of unmatched matrix between sample and standard, represented by  $\kappa_6$ , was estimated as 0.15‰ (corresponding to 0.00015) based on expert judgement. More detailed investigations can determine the difference in delta values for an acid mismatch or for an incompletely separated matrix. Contributions due to mass spectrometric interferences (optionally  $\kappa_7$ ) do not apply. By combining the individual uncertainty contributions listed in Table 2 by applying Equation (10) yields a combined standard uncertainty of 0.324‰. The final result for the delta value  $\delta_{\text{A1/LSVEC}}^{7/6}$  in sample A1 is 14.78‰ with an associated expanded measurement uncertainty of 0.65‰ ( $k = 2$ ). This is the value and its associated measurement uncertainty of measurement 1. Combining this with measurements 2 and 3 yields the final delta value of  $\delta_{\text{A1/LSVEC}}^{7/6} = 14.52\text{‰}$  with an associated expanded measurement uncertainty of 0.70‰ ( $k = 2$ ) as published in Winkelmann *et al.* (2021).

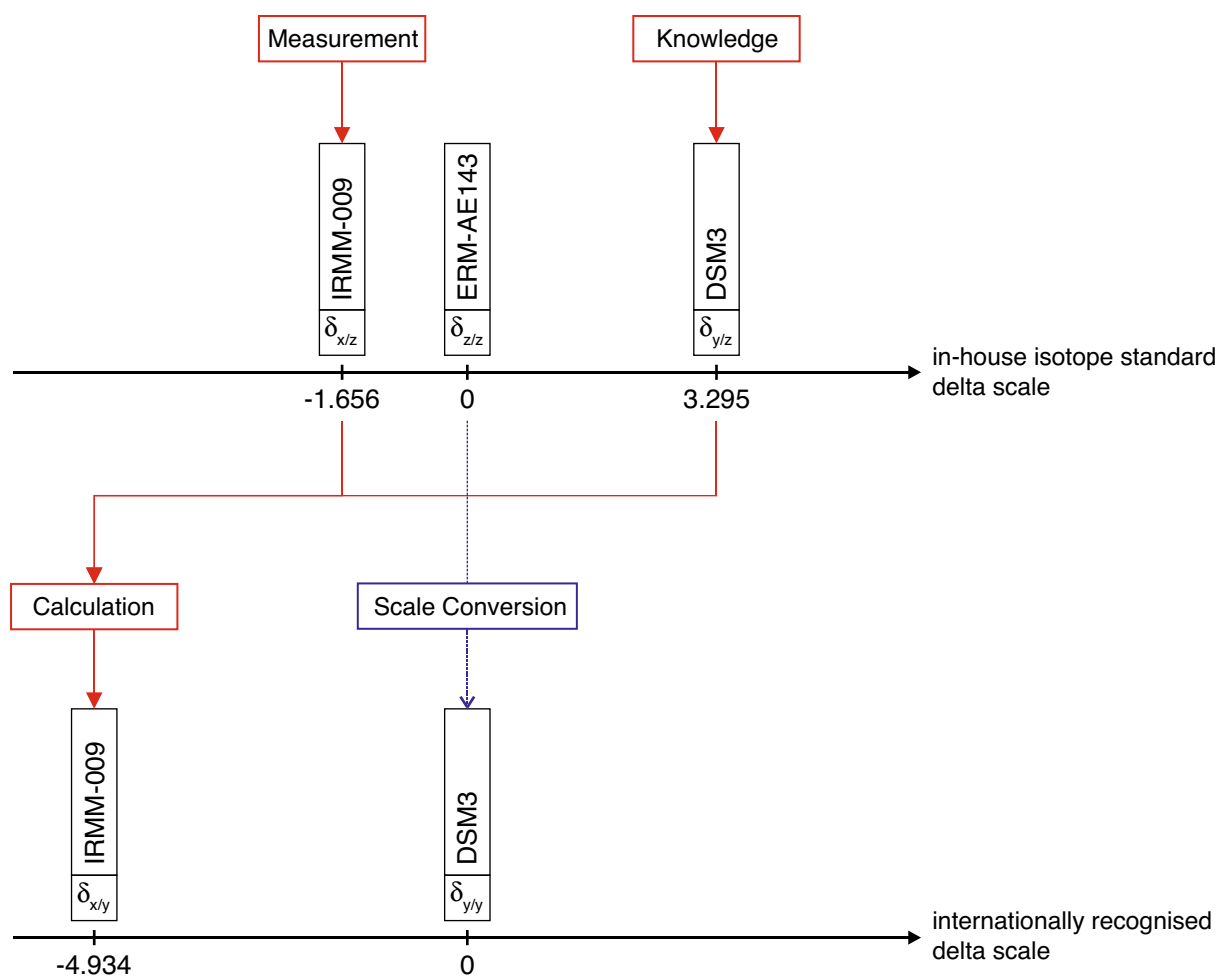
### Measurement uncertainty for repeated measurements

In some applications, however, more reliable data are required for reference measurements or for linking an in-house isotope standard to a delta scale. ‘More reliable data’, however, is a qualitative statement, which can hardly be used in real world applications. Turning it into a quantitative statement results in ‘smaller measurement uncertainties’. Most typically, these are obtained by increasing the number of measurements. In the case of delta measurements this means we measure the respective sample  $N$  times in a measurement sequence by applying the SSB approach. This gives us  $N$  isotope ratios for the sample and  $N + 1$  isotope ratios for the standard. All

**Table 2.** Measured quantity values and their associated standard uncertainties and determined and assessed uncertainty contributions for measurement 1 of  $\delta_{\text{A1/LSVEC}}^{7/6}$  in sample A1 (Winkelmann *et al.* 2021)

Symbol	Quantity	Unit	Value	$u$
$r_{\text{A1}}^{7/6}$	Measured ratio ${}^7\text{Li}/{}^6\text{Li}$ in sample A1	V/V	15.41055	0.00020
$r_{\text{LSVEC1}}^{7/6}$	Measured ratio ${}^7\text{Li}/{}^6\text{Li}$ in standard LSVEC1	V/V	15.18897	0.00023
$r_{\text{LSVEC2}}^{7/6}$	Measured ratio ${}^7\text{Li}/{}^6\text{Li}$ in standard LSVEC2	V/V	15.18323	0.00023
$\kappa_1$	Uncertainty contribution for sample digestion	1	1	0.00010
$\kappa_2$	Uncertainty contribution for analyte-matrix separation	1	1	0.000088
$\kappa_3$	Uncertainty contribution for blank	1	1	0.00022
$\kappa_4$	Uncertainty contribution for standard inhomogeneity	1	1	0.00010
$\kappa_5$	Uncertainty contribution for mass bias drift	1	1	0.000047
$\kappa_6$	Uncertainty contribution for matrix effects on the mass bias	1	1	0.00015
$\delta_{\text{A1/LSVEC}}^{7/6}$ (Li)	Isotope delta value for the ratio ${}^7\text{Li}/{}^6\text{Li}$ in sample A1 vs. LSVEC	‰	14.78	0.32





**Figure 3.** Scale conversion from  $\delta_{x/z}$  (scale anchor z) to  $\delta_{x/y}$  (scale anchor y) illustrated for the magnesium delta scale and the application of an in-house isotope standard (z, here ERM-AE143) and the internationally recognised scale anchor (y, here DSM3).

measured isotope ratios are correlated via the mass spectrometer, its mass bias and the drift thereof. When for example the mass bias drifts, standard and sample isotope ratios are affected the same way. Now, standard and sample are not measured at the same time, which complicates the assessment of the correlation. However, when calculating the average of the preceding and the succeeding standard of each sample measurement, a standard isotope ratio is obtained which in first approximation corresponds to the time of the sample measurement (Figure 4), provided the drift in the corresponding time interval is continuous and approximately homogenous.

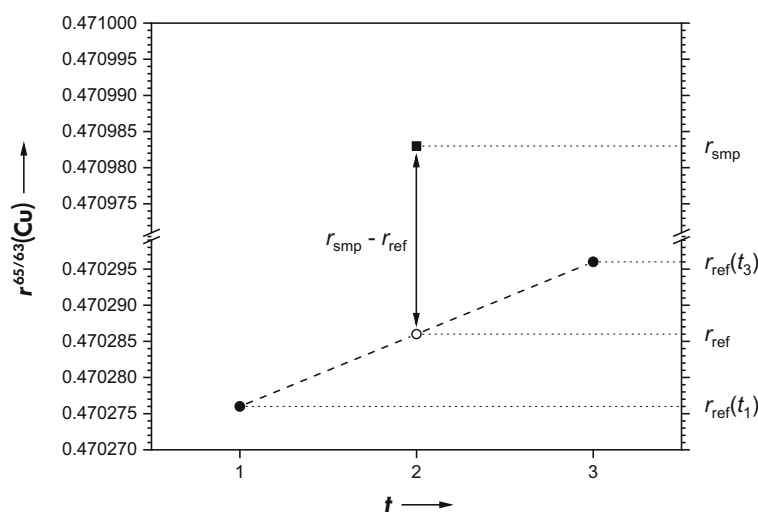
This results in  $N$  pairs of isotope ratios, one of which is the sample isotope ratio and the other one is the averaged standard isotope ratio. When listing these  $N$  pairs of isotope ratios in the order of their measurement time, the empirical covariance  $u(x_i, x_j)$  for the sample and the standard isotope

ratios is calculated according to Equation (11), and the empirical correlation coefficient  $r_{\text{cor}}$  according to Equation (12) (JCGM 2008):

$$u(x_i, x_j) = \frac{\sum_{i=1}^N [(x_{i,i} - \bar{x}_i) \times (x_{i,j} - \bar{x}_j)]}{N \times (N-1)} \quad (11)$$

$$r_{\text{cor}}(x_i, x_j) = \frac{u(x_i, x_j)}{u(x_i) \times u(x_j)} \quad \text{with } -1 \leq r_{\text{cor}} \leq +1 \quad (12)$$

With  $\bar{x}_{\text{smpl}}^{i/j}$  and  $\bar{x}_{\text{refr}}^{i/j}$  the averaged isotope ratios of the sample and the averaged standards, the delta value is calculated according to Equation (1). The associated combined uncertainty is calculated either by applying special software such as the GUM Workbench (Metrodata GmbH, Braunschweig, Germany), by using the Kragten approach (Kragten 1994), the NIST uncertainty machine



**Figure 4. Bracketing of the measurement of an unknown sample ( $r_{smp}$ ) by one measurement each of a standard before  $r_{ref}(t_1)$  and after  $r_{ref}(t_3)$  the sample measurement, as displayed in a diagram of isotope ratios  $r$  versus time  $t$ . The arithmetic mean  $r_{ref} = [r_{ref}(t_1) + r_{ref}(t_3)]/2$  of the measurement values represents the linear interpolation to the time  $t_2$  of the sample measurement. The difference  $r_{smp} - r_{ref}$  is used to calculate the delta value.**

(NIST 2021), or by using the square sum approach via Equation (13).

$$u\left(\delta_{smp/ref}^{i/i}(E)\right) = \left(\delta_{smp/ref}^{i/i}(E) + 1\right) \sqrt{\left(\frac{u\left(r_{smp}^{i/i}\right)}{r_{smp}^{i/i}}\right)^2 + \left(\frac{u\left(r_{ref}^{i/i}\right)}{r_{ref}^{i/i}}\right)^2} - 2 \frac{u\left(r_{smp}^{i/i}, r_{ref}^{i/i}\right)}{r_{smp}^{i/i} r_{ref}^{i/i}} \quad (13)$$

In case a processed sample was analysed several times, the corresponding uncertainty contributions  $\kappa_i$  must be added analogue to Equation (10). Section S.4 demonstrates how Equation (13) was derived.

Here it has to be noted as well that numerical differentiation, which is applied in the Kragten approach and in GUM Workbench, can lead to slight biases when applied to non-linear relationships. The Monte-Carlo method considers non-linear relationships and leads to correct results. Therefore, it can be used for validating the application of numerical differentiation, which is the reason why GUM workbench also contains a Monte-Carlo module.

## Application of an in-house isotope standard

Often the first (original) delta standards, those representing the origin of the delta scale ( $\delta = 0$ ), are in short supply or

even not available. In this case it is reasonable to apply a second standard or an in-house isotope standard. In-house isotope standards, provided they are present in solution form, have the advantage that they are relatively cheap, and their supply most commonly is not limited. The disadvantages are that in-house isotope standards need to be calibrated against the first or second standard and that this calibration adds an additional uncertainty component. The uncertainty related to the calibration, however, can be significantly reduced by performing a sufficiently large number of measurements ( $N > 10$ ).

## Examples and required measurements

As an example we choose those from Figure 3 where the  $\delta^{26/24}(\text{Mg})$  value of sample  $x$ , represented by ERM-AE144 is measured by using an in-house isotope standard  $y$  as bracketing standard, here represented by ERM-AE143. After measurements are completed, the measured delta value  $\delta_{ERM-AE144/ERM-AE143}^{26/24}(\text{Mg})$  needs to be converted to  $\delta_{ERM-AE144/DSM3}^{26/24}(\text{Mg})$  with DSM3 (index  $z$ ) representing the origin of the Mg delta scale. For this we need two measurements/measurement series. First, the measurement of  $\delta_{ERM-AE144/ERM-AE143}^{26/24}(\text{Mg})$  and second the measurement of  $\delta_{DSM3/ERM-AE143}^{26/24}(\text{Mg})$ . Concerning  $\delta_{ERM-AE144/ERM-AE143}^{26/24}(\text{Mg})$  we distinguish in the following calculation example two cases: (a) one individual measurement of  $\delta_{ERM-AE144/ERM-AE143}^{26/24}(\text{Mg})$  (see above) and (b) repeated measurements of  $\delta_{ERM-AE144/ERM-AE143}^{26/24}(\text{Mg})$  within one measurement sequence (see chapter Measurement

**Table 3.**  
Measured quantity values and their associated standard uncertainties and determined and assessed uncertainty contributions the  $\delta_{\text{ERM-AE144/ERM-AE143}}^{26/24}(\text{Mg})$

Symbol	Quantity	Unit	Value	$u$
$r_{\text{ERM-AE144}}^{26/24}$	Measured ratio $^{26}\text{Mg}/^{24}\text{Mg}$ in sample ERM-AE144	V/V	0.1596742	0.0000020
$r_{\text{ERM-AE143\_1}}^{26/24}$	Measured ratio $^{26}\text{Mg}/^{24}\text{Mg}$ in standard ERM-AE143_1	V/V	0.1599442	0.0000016
$r_{\text{ERM-AE143\_2}}^{26/24}$	Measured ratio $^{26}\text{Mg}/^{24}\text{Mg}$ in standard ERM-AE143_2	V/V	0.1599317	0.0000019
$\kappa_1$	Uncertainty contribution for sample digestion	1	1	0
$\kappa_2$	Uncertainty contribution for analyte-matrix separation	1	1	0
$\kappa_3$	Uncertainty contribution for blank	1	1	0.0000077
$\kappa_4$	Uncertainty contribution for standard inhomogeneity	1	1	0.000010
$\kappa_5$	Uncertainty contribution for mass bias drift	1	1	0.0000079
$\kappa_6$	Uncertainty contribution for matrix effects on the mass bias	1	1	0
$\kappa_7$	Uncertainty contribution for mass spectrometric interferences	1	1	0
$\delta_{\text{ERM-AE144/ERM-AE143}}^{26/24}(\text{Mg})$	Isotope delta value for the ratio $^{26}\text{Mg}/^{24}\text{Mg}$ in sample ERM-AE144 vs. ERM-AE143	‰	-1.649	0.025

uncertainty for repeated measurements). The intercalibration of the ERM-AE143 and the DSM3 delta scale has already been carried out and we can take  $\delta_{\text{DSM3/ERM-AE143}}^{26/24}(\text{Mg})$  from the literature (Vogl *et al.* 2020). In case the standard used as in-house isotope standard has not yet been calibrated vs. the primary delta standard these measurements need to be carried out in the readers laboratory (for uncertainty calculation see chapter Measurement uncertainty for repeated measurements and Repeated measurements of  $\delta_{\text{ERM-AE144/ERM-AE143}}^{26/24}(\text{Mg})$ ) or via an intercomparison as described in Vogl *et al.* (2020).

### Single measurement of $\delta_{\text{ERM-AE144/ERM-AE143}}^{26/24}(\text{Mg})$

A single Mg isotope ratio measurement of ERM-AE144 was carried out by MC-ICP-MS as described in Vogl *et al.* (2020) by applying ERM-AE143 as bracketing standard. The measurement results, the associated standard uncertainties, and additional uncertainty contributions  $\kappa_i$  are listed in Table 3. Additional uncertainty contributions for sample digestion,  $\kappa_1$ , analyte-matrix separation,  $\kappa_2$ , matrix effects on the mass bias,  $\kappa_6$ , and mass spectrometric interferences,  $\kappa_7$ , do not apply here, because the sample is a pure Mg solution. Consequentially the uncertainties of  $\kappa_1$ ,  $\kappa_2$ ,  $\kappa_6$ , and  $\kappa_7$  were set to zero. The uncertainty contribution for blank,  $\kappa_3$ , was obtained as set out in the section *Measurement uncertainty for a single measurement*, the uncertainty contribution for standard inhomogeneity,  $\kappa_4$ , was obtained from the certification report ( $u_{\text{lb}}$ , Vogl *et al.* 2018) and the uncertainty contribution for mass bias drift,  $\kappa_5$ , was obtained by dividing the overall drift within the SSB measurement sequence by the number of measured samples. By applying Equation (1) and Equation (10), the

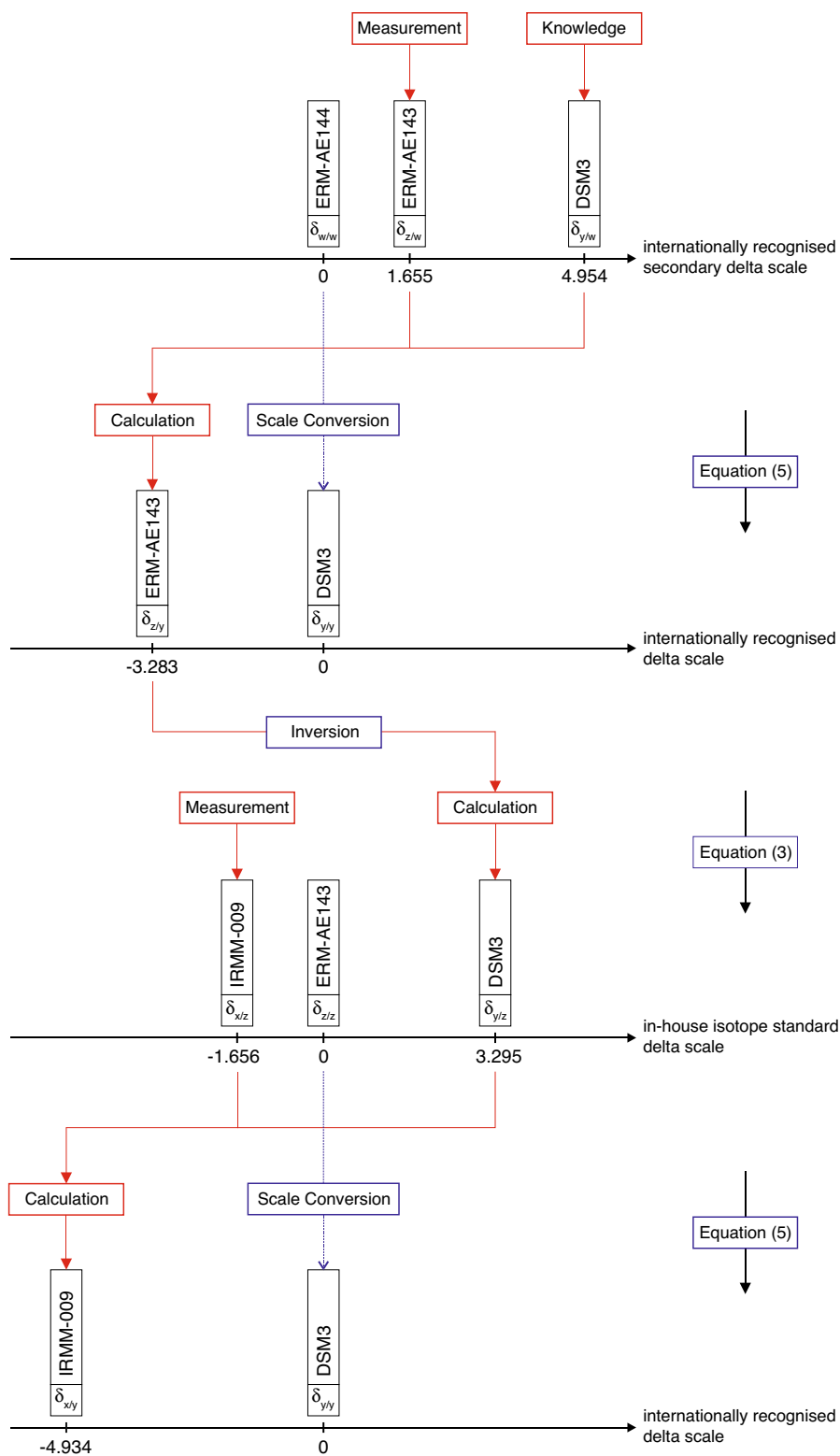
$\delta_{\text{ERM-AE144/ERM-AE143}}^{26/24}(\text{Mg})$  value and its associated combined uncertainty were calculated.

With  $\delta_{\text{ERM-AE144/ERM-AE143}}^{26/24}(\text{Mg})$ , its associated combined standard uncertainty from Table 3 and  $\delta_{\text{ERM-AE143/DSM3}}^{26/24}(\text{Mg}) = -3.284\text{‰}$  and its associated combined standard uncertainty of  $u_c(\delta_{\text{ERM-AE143/DSM3}}^{26/24}(\text{Mg})) = 0.013\text{‰}$  from Vogl *et al.* (2020) the final result can be calculated as  $\delta_{\text{ERM-AE144/DSM3}}^{26/24}(\text{Mg}) = -4.928\text{‰}$  with its associated combined standard uncertainty  $u_c(\delta_{\text{ERM-AE144/DSM3}}^{26/24}(\text{Mg})) = 0.028\text{‰}$ .

### Repeated measurements of $\delta_{\text{ERM-AE144/ERM-AE143}}^{26/24}(\text{Mg})$

A series of twelve Mg isotope ratios in ERM-AE144 was measured at PTB by MC-ICP-MS as described in Vogl *et al.* (2020) by applying ERM-AE143 as the bracketing standard. The twelve measurements were carried out in groups of four within three independent sequences (on three different days). Each of the twelve measurements as well as the necessary bracketing measurements consisted of eighteen cycles with 8 s integration time per cycle. The signal intensities of all ratios were corrected for blanks prior to any calculations. The final delta value and its associated combined standard uncertainty were calculated according to Equation (13) from the section *Measurement uncertainty for repeated measurements*.

A final result of  $\delta_{\text{ERM-AE144/ERM-AE143}}^{26/24}(\text{Mg}) = (-1.643 \pm 0.042)\text{‰}$  with  $k = 1$  was obtained. The calculation is shown in detail in the Excel file of the online supporting information on the tab "MU Repeated



**Figure 5.** The link between the in-house isotope standard z (ERM-AE143) and the first (original) scale anchor y (DSM3) is missing, but instead its link  $\delta_{y/w}$  to a second scale anchor w (ERM-AE144) is known. The in-house isotope standard z is measured against w and Equation (5) yields  $\delta_{z/y}$ , which has to be inverted to  $\delta_{y/z}$ . Measuring the actual sample x (IRMM-009) against the in-house isotope standard z, enables finally the calculation of  $\delta_{x/y}$  linked to the first (original) delta scale via a second scale anchor w and the in-house isotope standard z.

measurements". Since it mainly uses the three mean values of the three sequences, to a certain degree the day-to-day variance is already accounted for.

### Special case: in-house isotope standard vs. secondary isotope standard vs. primary isotope standard

Where  $\delta_{y/z}$  has not been published and the first (original) delta standard  $y$  is not available, the in-house isotope standard  $z$  has to be calibrated vs. a second delta isotope standard  $w$ . This requires the application of Equation (5) a second time and in between the use of Equation (3): firstly, for linking the in-house isotope standard  $z$  to the first (original) standard by measuring  $z$  against  $w$  ( $\delta_{z/w}$ ) while knowing  $y$  against  $w$  ( $\delta_{y/w}$ ). Since applying Equation (5) yields  $\delta_{z/y}$  it has to be inverted to  $\delta_{y/z}$  using Equation (3), resulting in Equation (14). Then, Equation (5) is applied a second time, for linking the measured delta value  $\delta_{x/z}$  of the sample  $x$  against the in-house isotope standard  $z$  to the first isotope standard  $y$ , which leads to Equation (15). Equation (15) provides the link of sample  $x$  via the in-house isotope standard  $z$  and the second isotope standard  $w$  to the first (original) isotope standard  $y$ .

$$\delta_{y/z} = \frac{\delta_{y/w} + 1}{\delta_{z/w} + 1} - 1 \quad (14)$$

$$\delta_{x/y} = \frac{(\delta_{x/z} + 1) \times (\delta_{z/w} + 1)}{\delta_{y/w} + 1} - 1 \quad (15)$$

A practical example is the use of an in-house isotope standard for  $\delta^{26/24}(\text{Mg})$  measurements while the first (original) standard DSM3 is not available. Then, the in-house isotope standard can be linked to ERM-AE143, which for the link to DSM3 is established (Vogl *et al.* 2020). Figure 5 illustrates for the above example the links between the known and measured values as well as the steps in which Equation (5) and Equation (3) are applied. Another example is the use of an in-house isotope standard for  $\delta^{34/32}(\text{S})$  measurements which needs to be linked to IAEA-S1, the delta standard for sulfur, which itself needs to be linked to the virtual VPDB scale.

The calculation is shown in detail in the Excel file of the online supporting information on the tab "Example Special case".

## Conclusions

The exact equations are provided for converting any delta value of a specific isotope ratio measured on a specific

delta scale to a delta value of the same isotope ratio but on another scale. The equations are set up for the three cases, namely the interchanging of sample and standard, the use of a secondary scale anchor and the scale conversion. Real-world examples explain and illustrate the application of the provided equations. Additionally, these calculations are carried out for a wide range of numerical delta values and are compared with the linear approximations. The bias of the linear approximation amounts to values of up to several ‰, depending on the numerical values of the involved delta values. This clearly demonstrates that the linear approximation is a very rough estimate and may not be used for exact calculations.

The exact calculation or conversion of the delta value to a specific delta scale / scale anchor is one prerequisite for realising comparability of delta values obtained in different studies and laboratories. The second main prerequisite is the measurement uncertainty associated with the delta value to be compared. Therefore, two alternatives for obtaining measurement uncertainties associated with delta values are presented. The first alternative is based on the approach developed by Rosner *et al.* (2011) and focuses on a single measurement (or very few SSB measurements). It considers the contributions by sample preparation and matrix separation in a pragmatic way by inserting factors  $\kappa_i$ , which have the value one and an uncertainty that represents the individual contribution. The second approach focuses on delta measurements, which are carried out more often to obtain smaller uncertainties. The higher number of measurements is mainly applied for reference measurements, such as the certification of a reference material or the assessment of an in-house isotope standard. This uncertainty approach considers correlations between standard and sample measurements, thus leading to reduced measurement uncertainties. This second approach can be expanded as well to processed samples by adding the individual contributions for sample preparation and matrix separation.

Finally, the application of in-house isotope standards is explained in a step-by-step procedure and the calculation of the measurement uncertainty associated with the sample measurement is described. For the application of an in-house isotope standard, as well as for all calculations within this work, an Excel file is provided in the online supporting information that offers spreadsheets for the individual calculations. With the equations presented here and the Excel spreadsheets provided, it is manageable for every analyst to estimate reliable and reasonable measurement uncertainties for the measured delta values. This will improve the comparability and lead to higher reliability of delta values.

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## Data availability statement

The data that supports the findings of this study are available in the supplementary material of this article.

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## Supporting information

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The following supporting information may be found in the online version of this article:

Appendix S1. Derivation of the equations needed to realise a scale conversion.

Appendix S2. Approximations/simplifications of Equations (3), (4) and (5).

Appendix S3. Derivation of Equation (10).

Appendix S4. Derivation of Equation (13).

Appendix S5. Special case: Derivation of Equation (15).

Appendix S6. References.

Appendix S7. Simplifications, delta-scale conversions and worked examples.

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