Study of variations as desired-relative (δ), rather than absolute, differences: falsification of the purpose of achieving source-representative and closely comparable lab-results

B. P. Datta (email: bibek@vecc.gov.in)
Radiochemistry Laboratory, Variable Energy Cyclotron Centre, 1/AF Bidhan Nagar, Kolkata 700 064, India

ABSTRACT

Recently (arXiv:1101.0973), it has been pointed out by us that the possible variation in any source (S) specific elemental isotopic (viz. ^2H/^1H) abundance ratio S^R can more accurately be assessed by its absolute estimate S^r (viz. as “(S^r - D^R)”, with D as a standard-source) than by either corresponding measured-relative (S/W δ) estimate “[(S/W) - 1]” or δ-scale-converted-relative (S/D δ) estimate “[(S/D) - 1]”. Here, we present the fundamentals behind scale-conversion, thereby enabling to understand why at all “S^r” should be the source- and/or variation-characterizing key, i.e. why different lab-specific results should be more closely comparable as absolute estimates (S^r_{Lab1}, S^r_{Lab2} …) than as desired-relative (S/D δ_{Lab1}, S/D δ_{Lab2} …) estimates. Further, the study clarifies that: (i) the δ-scale-conversion “S/W δ → S/D δ” (even with the aid of calibrated auxiliary-reference-standard(s) Ai(s) “S/W δ → Ai(s) S/D δ”) cannot make the estimates (as S/D δ, and thus S^r) free of the measurement-reference W; (ii) the employing of (increasing number of) Ai-standards should cause the estimates to be rather (increasingly) inaccurate and, additionally, Ai(s)-specific; and (iii) the S/D δ-estimate may, specifically if S happens to be very close to D in isotopic composition (IC), even misrepresent S; but the corresponding “S^r” should be very accurate. However, for S and W to be increasingly closer in IC, the S/D δ-estimate and also S^r are shown to be increasingly accurate, irrespective of whether the S/W δ-measurement accuracy could thus be improved or not. Clearly, improvement in measurement-accuracy should ensure additional accuracy in results.
1. INTRODUCTION

Isotopic composition (IC) of any element, specifically lighter, is variation prone for geo, bio, environmental ... changes. Thus, variations-in-ICs of stable lighter elements (as a function of sample-source/time...) are themselves used as the tools for diagnosing the causes of IC-variations, origins-of-sample-sources, and so. The (variation of) IC in any sample \( S \) is usually measured as a “\( \delta \)”-variable: \( S/W \delta = (S/R - W/R - 1) \); with \( S \) as any sample-isotopic [e.g. \(^2\text{H}/\text{H}\)] abundance ratio in question, and \( W/R \) as the corresponding ratio in a working-lab-reference \( W \).

The \( \delta \)-measurement-technique is rather known as the isotope ratio mass spectrometry (IRMS); i.e. though the IRMS is supplemented from time to time in different ways\(^{1-6}\), and even lately by the laser mass spectrometry\(^{6-8}\). However, lab specific choice of \( W \) should cause different lab-results to be incomparable. Thus, any (species-specific) result is evaluated with reference to a (corresponding) recommended\(^9,10\) reference-standard \( (D) \). In other words, the desired variable is generally considered to be \( \frac{S}{D} \delta \) [with: \( \frac{S}{D} \delta = (S/R\cdot D - 1) \)], but without examining whether the \( \delta \)-scale-conversion: \( S/W \delta \rightarrow \frac{S}{D} \delta \) can only remove the barrier for, or really ensure accurate, inter-comparison of lab-results \( (\frac{S}{D} \delta_{\text{Lab1}}, \frac{S}{D} \delta_{\text{Lab2}} \ldots) \). We are, therefore, concerned here.

The benefit of performing the measurement as \( \frac{S}{W} \delta \) is that the effects of (uncorrectable) technical-biases should largely be eliminated. However, by an estimate \( (r) \) of any isotopic-abundance-ratio \( \frac{S}{R} \), it should mean: \( R = (r + \Delta) \), or: \( R = (r \pm u) \), with \( \Delta \) as [true] measurement-error and \( u \) as uncertainty\(^{11}\). Therefore, the ratio \( \frac{S}{R/W} \) (of even ratios \( \frac{S}{R} \pm \frac{S}{u} \) and \( \frac{W}{R} \pm \frac{W}{u} \), which are acquired under identical possible experimental conditions) should\(^{12}\), though sometimes [when their true-measurement-errors, \( S\Delta \) and \( W\Delta \), might equal to one another] represent the true-ratio \( \frac{S}{R/W} \), generally be more erroneous than either the estimate \( \frac{S}{r} \) or
“$W_r$”. That is\footnote{12: $\langle S/W_r \rangle = ([S/W_r] \pm [u + W])$}; and is because that $S\Delta$ and $W\Delta$ may, even in direction, differ from one another. Essentially, any measured-data as even $S/W\delta$ could be at variance ($\pm S/W\mu$) over corresponding [unknown] true value. Thus, the conversion: ($S/W\delta \pm S/W\mu$) → ($S/D\delta \pm S/D\varepsilon$) should be desirable provided it ensures (the output-uncertainty) $S/D\varepsilon$ as $\leq S/W\mu$. We here, therefore, analyze the implications of $\delta$-scale-conversion from the basic standpoint.

2. FORMALISM

Generally, even measurement-procedure is (by the aid of relevant standards) established beforehand, i.e. uncertainty $S/W\mu$ is ensured to be acceptably small. However the conversion “($S/W\delta \pm S/W\mu$) → ($S/D\delta \pm S/D\varepsilon$)” should, like any other evaluation, mean the incorporation of a desired systematic (i.e. given “$S/D\delta$ vs. $S/W\delta$” relationship based) change in the measured-data $S/W\delta$. Thus, uncertainty $S/D\varepsilon$ should\footnote{12: Based on change in the measured-data $S/W\delta$.} also stand for a desired change in the uncertainty $S/W\mu$. For example, if the slope ($M_{s/W}^{S/D}$) of “$S/D\delta$ vs. $S/W\delta$” variation curve should be unity, then the result $S/D\delta$ should be equally as comparable as the measured data $S/W\delta$. However, for $M_{s/W}^{S/D}$ to be $>1$ (or, $<1$), $S/D\delta$ should be less (or, even more) accurate than $S/W\delta$. Thus, here, we should really study the behavior of different possible “$S/D\delta$ vs. $S/W\delta$” relationships and so.

However, for simplicity, we henceforth imply that “$S/W\delta$ ≡ $X$”, “$S/D\delta$ ≡ $Y$”, “$S/W\mu$ ≡ $u_X$”, and “$S/D\varepsilon$ ≡ $\varepsilon_Y$”. Similarly, true error, though should usually be ever unknown, is in the case of a measured estimate “$X$” referred to as $\Delta X$, and that in the desired estimate “$y$” as $D_Y$. However, only relative errors should be meaningful\footnote{13: Only relative errors should be meaningful.}. Therefore, we define: $\Delta X = \frac{\Delta X}{X} = \frac{x - X}{X}$; and: $D_Y = \frac{\Delta Y}{Y} = \frac{y - Y}{Y}$. Further, any result is generally reported as: $X = (x \pm u_X)$, which clarifies that “$u_X$” should represent the possible [and, therefore, the maximum] value of the true-error $\Delta X$, i.e.\footnote{12:} $u_X =$...
and output accuracies (or inaccuracies or uncertainties), respectively. Moreover, considering, e.g.: \( Y = g(\{X_i\}_{i=1}^N) \); i.e. for: \( (y + D_Y) = g(\{x_i + \Delta_i\}_{i=1}^N) \); and: \( (y + \varepsilon_Y) = g(\{x_i \pm u_i\}_{i=1}^N) \); the output-error \( (D_Y) \) could be shown to be decided as:

\[
D_Y = \sum_{i=1}^N (M_i^Y \times \Delta_i)
\]

And, the output-uncertainty \( (\varepsilon_Y) \) could, even a priori, be ascertained as:

\[
\varepsilon_Y = \sum_{i=1}^N (|M_i^Y| \times u_i) = \left[ \sum_{i=1}^N (|M_i^Y| \times F_i) \right] \times G_u = (UF)_Y \times G_u
\]

where \( M_i^Y \) is a theoretical constant, representing the relationship “\( g \)” specific (relative) rate of variation of \( Y \) as a function of \( X_i \):

\[
M_i^Y = \left( \frac{\partial Y}{\partial X_i} \right) \left( \frac{x_i}{Y} \right) = \left( \frac{\partial Y}{\partial X_i / X_i} \right), \quad i = 1, 2 \ldots N
\]

And, \( G_u \) is any \( u_i \)-value [viz. which could be believed to be achieved before establishing \( u_i(s) \)]; \( F_i = (u_i / G_u) \); and \( (UF)_Y \) may be called as uncertainty-factor. Clearly, if all \( X_i \)-measurements should be subject to equal uncertainty \( (u_i = G_u, \) i.e. if: \( F_i = 1, \) with: \( i = 1, 2 \ldots N \), then:

\[
(UF)_Y = \sum_{i=1}^N (|M_i^Y| \times F_i) = \sum_{i=1}^N |M_i^Y|
\]

However the important point is that, if only “\( (UF)_Y \) is <1”, the function as “\( g \)” should really represent a desirable evaluation method.

Further, let us represent “\( X \xrightarrow{Al(s)} Y \)” as: \( Y = f(X, Z_1, Z_2 \ldots) \), cf. below. Then, corresponding \( \{M_i^Y\} \) may be referred to as “\( M_{X^Y}, M_{Z_1^Y}, M_{Z_2^Y} \ldots \)”; and \( \{u_i\} \) as “\( u_X, u_{Z_1}, u_{Z_2} \ldots \)”.

We now look into the exact functions as “\( g \)” (evaluation-methods). As “\( R \)” cannot be zero or infinity, the expression “\( Y = (1^{SR/DR} - 1) \)” can itself be transformed into the required scale-conversion (“\( ^{SW} \delta \rightarrow ^{SD} \delta \)” = “\( X \rightarrow Y \)” formula:
\[ Y = \left( \frac{S}{D} - 1 \right) = \left( \frac{S}{R} \times \frac{w}{R} \times \frac{d}{R} - 1 \right) = ([X + 1] \times [C + 1] - 1) = f(X) \] (5)

where \( C \) is the \( W \) vs. \( D \) isotopic calibration constant \( C = [{}^W R/{}^D R] - 1 \), and should be known.

However, the determining of “\( C \)” could be avoided by employing one or more calibrated-auxiliary-standards \( (A_1, A_2, \text{ etc}) \) in the process: \( X \rightarrow Y \). The corresponding scale conversion formulae can also, like Eq. 5, be easily derived:

\[ Y = \left( \frac{S}{D} - 1 \right) = \left( \frac{S}{R} \times \frac{w}{R} \times \frac{A_1}{R} \times \frac{A_2}{R} - 1 \right) = \left( \frac{(X + 1) \times (C_1 + 1)}{(Z_1 + 1)} - 1 \right) = f(X, Z_1) \] (6)

\[ Y = \left( \frac{S}{R} \times \frac{w}{R} \times \frac{A_1 - A_2}{R} \times \frac{d}{R} - 1 \right) = \left( \frac{(X + 1) \times (C_1 - C_2)}{(Z_1 - Z_2)} - 1 \right) = f(X, Z_1, Z_2) \] (7)

... where \( C_1 \) and \( C_2 \) are known \( (Ai \text{ vs. } D \text{ calibration}) \) constants \( [C_1 = ([A_1^R/{}^D R] - 1) \text{ and: } C_2 = ([A_2^R/{}^D R] - 1)] \); and \( Z_1 \) and \( Z_2 \) are the \( Ai \)-measured variables: \( Z_1 = ([A_1^R/{}^W R] - 1) \) and: \( Z_2 = ([A_2^R/{}^W R] - 1) \).

It may, however, be pinpointed that the formula normally used in practice for employing (single \( Ai \) is the same as Eq. 6, but) two different \( Ai \)-standards is \( (\text{different from Eq. 7}) \)\(^{16,17} \):

\[ Y = (X - Z_2) \times \left( \frac{C_1 - C_2}{Z_1 - Z_2} \right) + C_2 \] (8)

Unfortunately, Eq. 8 cannot represent a scale conversion method\(^{19} \): as \( C_1 \) and \( C_2 \) are constants, and \( Z_1 \) and \( Z_2 \) are variables [i.e. as: \( (C_1 \times Z_2) \neq (C_2 \times Z_1) \)]; the right hand side cannot even be reduced to “\( Y \)”.

However (irrespective how “\( Y \)” is estimated): \( Y = ([^S R/{}^D R] - 1) \); and \( ^D R \) is ever known. Therefore, the absolute ratio \( (^S R) \) can, at least, be readily estimated:

\[ ^S R = ^D R \times (Y + 1) \] (9)
3. RESULTS AND DISCUSSION

3.1 Appropriate scale conversion method

We, for visualizing a priori which design of evaluation should be appropriate, consider both $X$ and $Y$ as known, viz. sample $S$ and lab-reference $W$ to be (the $^2$H/$^1$H certified materials as) IAEA-CH-7 and GISP, respectively. That is, say that\(^{20}\): \( Y \equiv \frac{S}{D} \delta_{2/1} = -0.10033 \); and \( C \equiv \frac{W}{D} \delta_{2/1} = -0.18973 \) (with $D$ as VSMOW $[\frac{D}{D} \delta_{2/1} = 0$, but: $^D R = 15.576 \times 10^{-5}$]); so that: $S \delta_{2/1} = 14.013260 \times 10^{-5}$; and $W \delta_{2/1} = 12.62076552 \times 10^{-5}$, and/ or that: \( X = ([^S R]^W R) - 1 = 0.110336 \).

Further [cf. Eq. 7], we choose $A_1$ to be NBS-1 (“$C_1 \equiv \frac{A_1}{D} \delta_{2/1} = -0.0476$”), and $A_2$ to be NBS-1A (“$C_2 \equiv \frac{A_2}{D} \delta_{2/1} = -0.1833$”),\(^{21}\) i.e.: \( Z_1 = ([^A_1 R]^W R) - 1 = 0.175410665 \), and: \( Z_2 = ([^A_2 R]^W R) - 1 = 7.9356264 \times 10^{-3} \). However, for the method as Eq. 6, we use either NBS-1 or NBS-1A as $A_1$.

The natures of variation to be expected in the desired $\delta$-estimate “$y$” as a function of scale-conversion-method (cf. Eqs. 5-7), and thus in the absolute result “$S_r$” (cf. Eq. 9), are exemplified in Table 1, where all method specific measured estimates are considered to be either 100% accurate (cf. example no. 0); or at ±1% errors (i.e.: $x = [X \pm 0.01X]$; and: $z_i = [Z_i \pm 0.01Z_i]$; cf. example nos. 1 and 2). It may be noted that, corresponding to example no. 0 (i.e. for: $x = X$; and if appropriate: $z_i = Z_i$), the results have also turned out 100% accurate ($y = Y$, and: $S_r = ^S R$; irrespective of method/ BLOCK); thereby clarifying, from purely experimental viewpoint, that any of Eqs. 5-7 should represent a valid scale conversion method. However, as indicated by example no. 1 and/ or no. 2, Eq. 5 should yield the most accurate $Y$-value. In other words, the employing of $A_i$-standard(s), viz. as Eq. 6/ Eq. 7, should cause the desired $\delta$-estimate ($y$, and hence the absolute estimate $^S r$) to be: (i) rather inaccurate, and: (ii) $A_i(s)$-specific [comparison
between BLOCK Nos. 2 and 2a]. Further, it should be interesting to note that, irrespective of method, \( S_r \) is reflected to be less erroneous than \( y \) by a constant-factor as \( \left| \frac{D_Y}{D_R} \right| \).

### 3.2 Can the (accuracy of) desired \( S/D \delta \)-estimate be decided by the lab-reference \( W \)?

In order for ascertaining whether scale-conversion can make the estimate \( y \) to be free of the measurement-reference \( W \), we now replace the \( W \)-material, GISP, by e.g. SLAP (i.e. consider: \( C \equiv \frac{W/D_2}{\delta_{2/1}} = -0.428 \)) and hence: \( W_R = 8.909472 \times 10^{-5} \), and/or: \( X = 0.57284965 \), \( Z_1 = 0.665034965 \), and \( Z_2 = 0.427797203 \), reevaluate all the results (as Table 1) and present them in Table 2. However, the new estimates as example no. 1 or 2 [cf. any BLOCK in Table 2] are different from (truly, more erroneous than) the corresponding estimates in Table 1. That is, even the \( \delta \)-estimate as \( y \), and thus the absolute estimate \( S_r \) (and/or achievable accuracies, \( \varepsilon_Y \) and \( S \varepsilon_R \), respectively), are signified to be \( W \)-specific. Moreover, the indication (Table 1) that \( ^{S/D} \delta \equiv y \) to \( S_r \) conversion helps improve accuracy is rather confirmed in Table 2, which signifies the accuracy-enhancement-factor \( \left| \frac{D_Y}{D_R} \right| \) to be independent of even \( W \).

### 3.3 Are the above findings fictitious?

The uncertainties \( \varepsilon_Y \) and \( S \varepsilon_R \) [with: \( G_u = 1\% \)], i.e. the uncertainty-factors \( [UF]_Y \) and \( [UF]_R \) (for determining \( Y \) [by either of the methods as Eqs. 5-7] and the [corresponding] absolute-ratio \( S \delta \), respectively), are exemplified, and even in terms of their governing factors illustrated, in Table 3, where any 1\(^{st}\) set of data (e.g. “\( M_X^Y = -0.891 \)” relates to the employing of GISP as \( W \) [cf. Table 1], and any 2\(^{nd}\) set of data [e.g.: \( M_X^Y = (\approx -3.266) \)] corresponds to SLAP as \( W \) [cf. Table 2]. In any case, the \( W \)-specific predictions [for \( W \) as GISP and, e.g. scale conversion method as Eq. 5]: \( \varepsilon_Y^{Eq.5} = (\times G_u) = (0.891 \times G_u) = 0.891\% \); and [even for \( W \) to be SLAP]: \( \varepsilon_Y^{Eq.5} = 3.266\% \); are in corroboration with the findings as \( (\left| D_Y \right| = 0.891\% \) and: \( \left| D_Y \right| = 3.266\% \) in) Tables 1 and 2, respectively.
3.3.1 Why should the results be lab-reference (\(W\)) specific?

Perhaps, variation of (the IC of the) lab-reference \(W\) is believed to affect the achievable-measurement-accuracy \(G_u\) only. That is the estimates (e.g. corresponding to Eq. 5 and example no. 1, but which were obtained for equal [1\%] errors in the \(W\)-specific \(SW\) \(\delta\)-estimates “\(x^{(GISP)}\) and \(x^{(SLAP)}\)” were not expected to vary between Tables 1 and 2. However, it is already illustrated by the considerations as Eqs 1-3 above that the “\(x \rightarrow y\)” translation should be equivalent to the error-transformation as “\(\Delta_X \xrightarrow{M^Y_X} D_Y\), or “\(u_X \xrightarrow{|M^Y_X|} e_Y\).” Further (cf. Table 3): \(M^Y_X = ([\hat{R}^W - W R] / [\hat{R}^D - D R])\); i.e. the \(SD\) \(\delta\)-estimate, \(y\), has to be \(W\)-specific. Again, “\(\omega^{SLAP} R\)” is \(\langle GISP R\rangle\), which explains why the results for employing SLAP (cf. Table 2), than GISP (cf. Table 1), as \(W\) are more erroneous.

3.3.2 Why could the results vary for simply the choice of \(Ai\)-standard(s)?

Table 3 (cf. for Eq. 6) confirms that the employing of even single auxiliary-reference \(A1\) should cause “\(y\)” to be (\(Ai\)-specific and/ or) subject to additional measurement-variation at the rate as: \(M^Y_{Z1} = ([\hat{R}^W - W R - A1 R] / [A1 R(\hat{R}^D - D R)])\). Further, “\(|W R - NBS-1 A1 R|\)” is \(\langle |W R - NBS-1 R|\) (with \(W\) as either GISP or SLAP). This explains why, even though the \(A1\)-measurement-accuracy \(u_{Z1}\) is considered to be unchanged, the employing of \(A1\) as NBS-1A (cf. block 2a in Table 1 or 2), rather than as NBS-1 (cf. block 2), is observed to yield better representative result(s).

3.3.3 Should the aid of \(Ai\)-standards be at all worth?

It was often meant in the literature\(^{10,16-18}\) that the method as Eq. 7 (\(X \xrightarrow{A1,A2} Y\), specifically for employing sample bracketing \(Ai\)-standards, should yield more accurate estimate “\(y\)” than the method as Eq. 6 (\(X \xrightarrow{A1} Y\)) or Eq. 5 (\(X \rightarrow Y\)). Unfortunately, the selection of sample-bracketing
Ai-references should require the desired-unknown “Y” itself to be known beforehand. Again, as shown by considering a known case (“S/D δ ≡ Y” = −0.10033) here, “y” obtained by employing Eq. 7 (with sample-bracketing Ai-standards [“A1/D δ ≡ NBS-1/D δ” = −0.0476; and “A2/D δ ≡ NBS-1A/D δ” = −0.1833]; cf. example no. 1/2 in BLOCK no. 3 of Table 1 or 2) is more erroneous than the “y” obtained for using either NBS-1 (cf. BLOCK no. 2) or NBS-1A (cf. BLOCK no. 2a] as A1 or for no Ai (cf. BLOCK no. 1). In any case, the rate-of-variation (M_Y^X) of Y as a function of X (i.e. the effect of any possible error, u_X, in measuring the sample S, on the desired result “y”) is shown to be fixed, irrespective scale-conversion-method (cf. Table 3). Thus, “y” by Eq. 6/7 can never be more accurate than the “y” by Eq. 5.

Further, Eq. 6 requires only one Ai-measurement, but Eq. 7 involves two. That is, uncertainty “ε_Y^Eq.7” should even be expected to be “>ε_Y^Eq.6”. Yet, it may be pointed out that “M_Y^Z_1” (and hence “ε_Y^Eq.6”, cf. Table 3 for Eq. 6) could be varied by varying either or both “W- and A1-materials” [i.e. the difference “|W_R - A1_R|” and the ratio “S/R/A1”]; but “ε_Y^Eq.7” (i.e. “M_Y^Z_1” and “M_Y^Z_2” corresponding to Eq. 7) should vary as a function of even the difference “|A1_R - A2_R|”.

Thus, though “ε_Y^Eq.7” cannot (in any unknown case) be ensured to be “<ε_Y^Eq.6”, hypothetical-systems [of the type as: “1 < (S/R/A1) > (S/R/A2)”] may be designed to yield: ε_Y^Eq.7 < ε_Y^Eq.6.

### 3.3.4 Why did absolute estimate (S_R) turn out more accurate than S/D δ-estimate (y)?

The estimate “S_R” is obtained from the estimate “y” (cf. Eq. 9), and is why (cf. Table 3)18,19: S ε_R = (|M_Y^T| × ε_Y) = (|M_Y^T| × |UF_R| × G_U) = (|UF_R| × G_U). Further: M_Y^T = (|S_R - D_R| / S_R), i.e. “|M_Y^T|” has to be <1, and/ or error-reduction [“(ε_R/ε_Y) ≡ (|UF_R|/|UF_T|)” < 1] should be a feature of the transformation “y → S_R”. Over and above, if only sample S and standard D are fixed, then “M_Y^T” should also be fixed. This explains why the accuracy-enhancement-factor
“( |DY| / |DR| ) ≡ [εYsεR]” is observed (cf. Tables 1 and 2) to be fixed (as “[1|M_Y|] = 8.9671”) and/or independent of the measurement-reference W, scale-conversion-method, and Ai-material(s).

3.4 Could our findings be trivial (source-specific)?

Remembering that [output-uncertainty, cf. Eq. 2]: ε = ([UF] × gu), the variations of [UF]Y and [UF]R (i.e. uncertainty-factors for δ-scale-conversion by each of the methods as Eqs. 5-7, and for determining [δ-method-specific value of] the sample-isotopic-ratio sR [cf. Eq. 9]) as a function of the measurable sWδ-quantity “X” (with a specific material [GISP] as “W”, and hence against sR itself, cf. the top-axis), are depicted in Figures 1 and 2, respectively. Clearly (cf. the considerations for innumerable s-sources as the IAEA-CH-7 “X = 0.1103336” in. Fig. 1), the above finding “εY Eq.7 > εY Eq.6 > εY Eq.5” has to be a source-independent fact.

3.4.1 Can any sWδ-estimate “y” be free of W?

As Fig. 1 implies, “[UF]Y Eq.5” (actually, as already clarified in Table 3, the rate-of-variation “|M_Y|”, i.e. [UF]Y but relating to S-measurement alone, and hence which is an integral part of any method-specific-[UF]Y) should decrease for decreasing “|X|” (rather “|sR – "R|” only), and be zero (if S and W happen to have the same IC, i.e.) at “X = 0”. Thus, the other observations, viz.: (i) δ-scale-conversion doesn’t make the estimate “y” free from the measurement-reference W, but (ii) accuracy of any method-specific “y” is improved for simply considering W to be closer to the sample-S [in IC], should also represent general facts. Above all, the prediction that the measurement of even the Ai/Wδ-quantity (Zi) should cause y to be W-specific (cf. Table 3, which clarifies the rate-of-variation “[M_YZi” to also be decided by, among others, “"R”) is verified by the fact that neither “[UF]Y Eq.6”, nor “[UF]Y Eq.7” is zero at “X = 0” (cf. Fig. 1, which has considered the Ai(s) as being different [in IC] from W).
3.4.2 Variation-identifying tool: $^{S/D}\delta$-estimate ($y$) or absolute-estimate ($^{S}r$)?

Usually, any measured (e.g. $^{S/W}\delta$) estimate ($x$) is a priori ensured to be accurate. Similarly, (corresponding) reference-standard $D$ is also a prefixed one. Thus, sample-$S$ can happen to be very close, in IC, to $D$. However, what is revealed here (cf. Fig. 1 for $X = 0.235$ or so) is that the $^{S/D}\delta$-estimate $y$ should, for $|^{S}R - ^{D}R| \to 0$, turn out increasingly erroneous.

Nevertheless, for $D$ to be very different (viz. here, a highly $^{2}H$-enriched material) from any corresponding unknown-$S$, “$y$” would be accurate (cf. Fig. 1 for: $X = \pm 0.6$ or so). Unfortunately, the latter should cause the measure-of-variation “$|^{S}R - ^{D}R|$” itself to be larger than the source-value “$^{S}R$” (i.e. [cf. Table 3] “$|M_{y}^{R}|$” to be $>1$), and hence be inconceivable as a viable proposal.

In any case (cf. Table 3), the product “$|M_{y}^{R}| \times [UF]_{y}$” defines “[UF]_{R}”. This is why, the variation of the method-independent parameter “$|M_{y}^{R}|$” (against “$X$”) is also described as an insert in Fig. 1, thereby explaining why (although “[UF]_{y}$-curves” pass through the peak as infinity) “[UF]_{R}$-curves” [cf. Fig. 2] are of valley-shapes. However (cf. here above), any real world “$|M_{y}^{R}|$” should be $<1$, i.e. the above finding “uncertainty-$^{S}\varepsilon_{R}$ is $<^{S}\varepsilon_{Y}$” has also to be a general one. In other words, “$|M_{y}^{R}| > 1$ (cf. Fig. 1)”, and hence “$^{S}\varepsilon_{R} > ^{S}\varepsilon_{Y}$”, should represent hypothetical cases. Moreover, for unknown-$S$ to be close to $D$, the $^{S/D}\delta$-estimate $y$ may even misrepresent “$S$” (cf. Fig. 1: $[UF]_{Y} \gg 1$). However, what is interesting (cf. Fig. 2, e.g. the $[UF]_{R}$ Eqs.(5&9)-curve) is that any real world absolute estimate “$^{S}r$” (specifically, for $^{S}R \approx ^{D}R$, i.e. corresponding to a highly inaccurate $^{S/D}\delta$-estimate “$y$”) should be (highly) accurate.

Further, for a case characterized by either “[UF]_{Y} = 0” or “$|M_{y}^{R}| = 0”$, [UF]_{R} (and hence $^{S}\varepsilon_{R}$) should also equal zero. Thus, as Fig. 2 clarifies, any method-specific “minima” corresponds to “$X = 0$ (i.e. $S$ as identical with $W$)”. For example, “$^{S}\min.UF$ Eqs.(5&9)” equals zero, and is because...
that (cf. Fig. 1): $\text{Min. } UF_Y \text{ Eq. } 5 = 0$. However, why shouldn’t “$|M_Y^R| = 0$” ($S$ as identical with $D$, cf. the insert in Fig. 1 for: $X = 0.2341565$) cause even corresponding $UF_R \text{ Eqs.(5&9)}$ to be zero?

As “$|R - D| \to 0$” simultaneously implies “$|M_X^Y| \to \infty$” (i.e.: $|UF_Y \to \infty$) and “$|M_Y^R| \to 0$”; the corresponding $UF_R$ should be decided (cf. Table 3: $UF_R \text{ Eqs.(5&9)} = \left| 1 - \left( \frac{w}{SR} \right) \right| \text{ and hence as: } Lim.(S \to D)\left| UF_R \text{ Eqs.(5&9)} \right| = \left| 1 - \left( \frac{w}{SR} \right) \right| = \left| C \right| = 0.18973$. Similarly, one may verify that: $\text{Lim.(S \to D)}\left| UF_R \text{ Eqs.(6&9)} \right| = \left( |C| + |(\frac{w - A^1}{R})A^2\right| \right) = 0.33896$; and: $\text{Lim.(S \to D)}\left| UF_R \text{ Eqs.(7&9)} \right| = \left( |C| + |(\frac{w - A^1}{R}) + (\frac{A^2}{R} - \frac{w}{R})\right| \right) = 1.28450$.

We may, for illustration, consider a specific unknown-source ($uS$) to be “$uSR = 15.6 \times 10^{-5}$” (i.e.: “$X = (|uSR|/w) - 1 = (|uSR/GISP| - 1) = 0.23605814$ and: “$Y = (|uSR|/w) - 1 = 1.5408291 \times 10^{-3}$”). Then, as Fig. 1 predicts: “$e_Y \text{ Eq. } 5 = \left( |UF_Y \text{ Eq. } 5 \times G\right) = 124.1G\text{; and as Fig. 2 implies: } uS \text{ Eqs.(5&9)} = |(\left| UF_Y \text{ Eq. } 5 \right| \times uY \text{ Eq. } 5) = |(\left| M_Y^R \right| \times uUF_Y \text{ Eq. } 5 \times G\right) = |(\left| UF_R \text{ Eqs.}(5&9) \times G\right) = 0.191G\text{. That is, for a possible measurement-error } G\text{, the absolute-estimate (}$uS$) should turn out } \approx 650 \text{ times more accurate than the } uS/D\delta\text{-estimate (}$uY$).

However, say, measurement (for $uS$ by Lab1) has yielded: “$X \text{ Lab1} = (uX + u\Delta X) = (uX + 0.1%) = 0.236294$. That is, one may verify (cf. Eq. 5): “$Y \text{ Lab1} = 0.0017321 = (uY + uD_Y) = (uY + 12.4%)$; and in turn (cf. Eq. 9): “$S \text{ Lab1} = 15.60298 \times 10^{-5} = (uS + uS_D) = (uS + uS + 0.0191\%)$. Clearly, the results are in corroboration of the above predictions. However, the point to note is that the true variation in $uS \text{ from } D \text{ is } (|uS - D| = 0.024 \times 10^{-5} = 0.1508291\%$, which is) more or less accurately represented by the estimate $uS \text{ Lab1}$ (as: $[uS \text{ Lab1} - D] = 0.027 \times 10^{-5} = 0.173\%$, and rather misrepresented by the $uS/D\delta\text{-estimate } uY \text{ Lab1}$ (as: $[uY \text{ Lab1} - Y] = 1.913 \times 10^{-4} = 12.4\%$).
Similarly, another equally suitable lab might be considered to yield: \( u_{X_{\text{lab2}}} = (u_X - 0.1\%) = 0.235822 \), thereby giving \( u_{Y_{\text{lab2}}} = 0.001350 = (u_Y - 12.4\%) \) and \( u_{Sr_{\text{lab2}}} = 15.59702 \times 10^{-5} = (u_{Sr} - 0.0191\%) \). Thus the scatter, while between the \textit{absolute} lab-results is only \textbf{0.027\%}, between the differential \( (u_{\text{S/D} \delta}) \) lab-results is as high as \textbf{17.5\%}.

\textbf{4. CONCLUSIONS}

The above study clarifies that different absolute lab-results \( (Sr_{\text{lab1}}, Sr_{\text{lab2}}, \ldots) \) should always be more closely comparable than their desired-relative (i.e. \( S/D \delta \)) estimates \( (y_{\text{lab1}}, y_{\text{lab2}}, \ldots) \). In other words, the variation, if at all any, in a source \( S \) (from a source as \( D \), i.e. as a function of time and so) could be accurately ascertained by the corresponding absolute estimate \( S_r \) (viz. as \( |Sr - Dr| \)) rather than by the \( S/D \delta \)-estimate \( y \). This is, as shown above, best supported by the fact that the \( S/D \delta \)-estimate \( y \) can turn out to even be \textit{non-representative} of source-\( S \) (e.g. in a case where \( S \) could be close, in IC, to the reference-standard \( D \)). Most importantly, the \( "Sr" \) (\textit{corresponding to}: \( S_r \approx D_r \)) should be (highly) accurate.

It is demonstrated that, and also explained why: (i) the scale conversion (as either: \( "S/W \delta \rightarrow S/D \delta" \) \( \equiv \) \( X \rightarrow Y \) or: \( "S/W \delta \rightarrow A(\delta) \rightarrow S/D \delta" \)) cannot make the results (the \( S/D \delta \)-estimate \( y \), and hence the absolute estimate \( S_r \)) free from the measurement-reference \( W \); and: (ii) the employing of (\textit{increasing} number of) \( A\delta \)-standards should cause the estimates (\( y \) and \( S_r \)) to be, though assumed\textsuperscript{10,15-18} accurate, (\textit{increasingly}) \textit{inaccurate}, however.

\textbf{REFERENCES}

1. McKinney, C. R., McCrea, J. M., Epstein, S, Allen H. A. & Urey U. C. Rev. Sci. Insttum. \textbf{21}, 724 (1950).
2. Craig, H. *Geochim. Cosmochim. Acta* **12**, 133 (1957).
3. IAEA-TECDOC-825, IAEA, IAEA, Vienna (1995)
4. Brenna, J. T., Corso, T. N., Tobias, H. J. & Caimi, R. J. *Mass Spectrom. Rev.* **16**, 227 (1997).
5. Ribas-Carbo, M., Still, C., & Berry J. *Rapid Commun. Mass Spectrom.* **16**, 339 (2002).
6. IAEA-TECDOC-1247, IAEA, IAEA, Vienna (2001).
7. Kerstel, E. R. Th., Trigt, R. van, Dam, N., Reuss, J. & Meijer, H. A. *Anal. Chem.* **71**, 5297 (1999).
8. Kerstel, E. R. Th. & Gianfrani, L. *Appl. Physics B* **92**, 439 (2008).
9. Coplen T. B. *Pure and Appl. Chem.* **66**, 273 (1994).
10. Coplen T. B., Brand, W. A., Gehre, M., Groning, M., Meijer, H.A., Toman, B. & Verkouteren, R. M. *Anal. Chem.* **78**: 2439 (2006).
11. ISO, *Guide to the Expression of Uncertainty in Measurement* (1995).
12. Datta, B. P. *arXiv:0712.1732*.
13. Scarborough J. B. *Numerical Mathematical Analysis*, Oxford & IBH Publishing Co., Kolkata (1966).
14. Datta, B. P. *arXiv:0909.1651*.
15. Allison, C. E., Francey, R. J. & Meijer H. A. J. *IAEA-TECDOC-825*, p. 155, IAEA, Vienna (1995).
16. Verkouteren, R. M. & Lee, J. N. *Fresenius J. Anal. Chem.* **370**, 803 (2001).
17. Paul, D., Skrzypek, G. & Forizs, I. *Rapid Commun. Mass Spectrom.* **21**, 3006 (2007).
18. Gonfiantini R. *Nature* **271**, 534 (1978).
19. Datta, B. P. *arXiv:1101.0973*.
20. Gonfiantini, R., Stichler, W. & Rozanski, K. *IAEA-TECDOC-825*, p. 13, IAEA, Vienna (1995).

21. Groning, M., Frohlich, K., Regge, P. De & Danesi P. P. INTENDED USE of THE IAEA REFERENCE MATERIALS PART II, p. 5, IAEA, Vienna (2009).
Table 1. Examples of variations in the scale-conversion-method specific \( S/W \delta \)-estimate (\( y \)), and thus in the absolute-estimate (\( S_r \)), as a function of required (\( S/W \delta \)- and, if applicable, \( A/W \delta \)-) data of a given accuracy (\( \epsilon^u = 1\% \)): use of GISP as the measurement-reference \( W \)

| BLOCK (Method) No. (Eq. No.) | Example No. | Input (measured) \( S/W \delta \)-estimate \( x \), its (relative) error \( \Delta x \) \((\Delta x \times 10^2)\) | \( A/W \delta \)-estimate \( z_1 \), and its error \( \Delta z_1 \) \((\Delta z_1 \times 10^2)\) | \( A/W \delta \)-estimate \( z_2 \), and its error \( \Delta z_2 \) \((\Delta z_2 \times 10^2)\) | Output (\( S/W \delta \), or absolute) estimate and (relative) error \( D \) \((D_y \times 10^2)\) | Error-ratio \( |D_y|/|D_R| \) \| Projected output accuracy \( \epsilon \) \((\epsilon_y \times 10^2)\) \((\epsilon_r \times 10^2)\) |
|-----------------------------|-------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|--------|-----------------|
| 1 (Eq. 5)                   | 0           | 0.11033360 (0)                                  | -                                                | -                                                | -0.100330 (0)                                      | 14.013260 (0) | 0               | 0.891          | 0.1            |
|                            | 1           | 0.11143694 (1.0)                                | -                                                | -                                                | -0.0994360 (−0.891)                               | 14.027185 (0.0994) | 8.9671         |
|                            | 2           | 0.10923026 (−1.0)                               | -                                                | -                                                | -0.1012234 (0.891)                                | 13.999335 (−0.0994) | 8.9671         |
| 2 (Eq. 6, with \( A_1 \) as NBS-1) | 0           | 0.11033360 (0)                                  | 0.175410665 (0)                                 | -                                                | -0.100330 (0)                                      | 14.013260 (0) | 0               | 2.23           | 0.25           |
|                            | 1           | 0.11143694 (1.0)                                | 0.1736566 (−1.0)                                 | -                                                | -0.0980901 (−2.23)                                | 14.048149 (0.249) | 8.9671         |
|                            | 2           | 0.10923026 (−1.0)                               | 0.1771648 (1.0)                                 | -                                                | -0.1025633 (2.226)                                | 13.978474 (−0.2482) | 8.9671         |
| 3 (Eq. 7)                   | 0           | 0.11033360 (0)                                  | 0.175410665 (0)                                 | 7.9356264×10^3 (−1.0)                             | -0.100330 (0)                                      | 14.013260 (0) | 0               | 10.8           | 1.21           |
|                            | 1           | 0.11143694 (1.0)                                | 0.1736566 (−1.0)                                 | 8.01498×10^3 (1.0)                                | -0.089468 (−10.83)                                 | 14.182447 (1.207) | 8.9671         |
|                            | 2           | 0.10923026 (−1.0)                               | 0.1771648 (1.0)                                 | 7.85627×10^3 (−1.0)                               | -0.110957 (10.59)                                  | 13.847732 (−1.181) | 8.9671         |
| 2a (Eq. 6, with \( A_1 \) as NBS-1A) | 0           | 0.11033360 (0)                                  | 7.9356264×10^3 (−1.0)                            | -                                                | -0.100330 (0)                                      | 14.013260 (0) | 0               | 0.962          | 0.11           |
|                            | 1           | 0.11143694 (1.0)                                | 7.85627×10^3 (−1.0)                              | -                                                | -0.0993651 (−0.9617)                               | 14.028289 (0.1073) | 8.9671         |
|                            | 2           | 0.10923026 (−1.0)                               | 8.01498×10^3 (1.0)                               | -                                                | -0.1012948 (0.9616)                                | 13.998233 (−0.1072) | 8.9671         |
Table 2. Variations of scale-conversion-method specific $S/D\delta$-estimate ($y$), and thus of absolute-estimate ($Sr$), and/or (their) accuracies for employing SLAP (i.e. instead of GISP, cf. Table 1) as the measurement-reference $W$

| Block (Method) No. (Eq. No.) | Example No. | Input (measured) $S/W\delta$-estimate $x$, its (relative) error $\Delta x$, $A/W\delta$-estimate $z$, and its error $\Delta z$ | Output ($S/D\delta$, or absolute) estimate and (relative) error $D$ | Error-ratio $|D|R| \times 10^2$ | Projected output accuracy $\varepsilon$ |
|-------------------------------|-------------|---------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------|---------------------|
| 1 (Eq. 5)                     | 0           | $0.57284965 (0)$ $\Delta x \times 10^2$                                                                                           | $-0.100330 (0)$ $\Delta y \times 10^2$                                                                 | $14.013260 (0)$ $\Delta Sr \times 10^2$ | $3.266$ $0.364$     |
|                              | 1           | $0.57858 (1.0)$ $\Delta z1 \times 10^2$                                                                                          | $-0.097053 (3.266)$ $\Delta z1 \times 10^2$                                                                   | $14.06430 (0.364)$ $\Delta Sr \times 10^2$ | $8.9671$           |
|                              | 2           | $0.56712 (1.0)$ $\Delta z2 \times 10^2$                                                                                          | $-0.103607 (3.266)$ $\Delta z2 \times 10^2$                                                                   | $13.962222 (-0.3642) \Delta Sr \times 10^2$ | $8.9671$           |
| 2 (Eq. 6, with 41 as NBS-1)   | 0           | $0.57284965 (0)$ $\Delta x \times 10^2$                                                                                           | $-0.100330 (0)$ $\Delta y \times 10^2$                                                                 | $14.013260 (0)$ $\Delta Sr \times 10^2$ | $6.87$ $0.767$     |
|                              | 1           | $0.57858 (1.0)$ $\Delta z1 \times 10^2$                                                                                          | $-0.093432 (-6.87)$ $\Delta z1 \times 10^2$                                                                    | $14.12070 (0.7667) \Delta Sr \times 10^2$ | $8.9671$           |
|                              | 2           | $0.56712 (1.0)$ $\Delta z2 \times 10^2$                                                                                          | $-0.107173 (6.82)$ $\Delta z2 \times 10^2$                                                                    | $13.906677 (-0.7606) \Delta Sr \times 10^2$ | $8.9671$           |
| 3 (Eq. 7)                     | 0           | $0.57284965 (0)$ $\Delta x \times 10^2$                                                                                           | $-0.100330 (0)$ $\Delta y \times 10^2$                                                                 | $14.013260 (0)$ $\Delta Sr \times 10^2$ | $46.7$ $5.2$       |
|                              | 1           | $0.11143694 (1.0)$ $\Delta z1 \times 10^2$                                                                                         | $-0.05345 (-46.7)$ $\Delta z1 \times 10^2$                                                                    | $14.74345 (5.21) \Delta Sr \times 10^2$ | $8.9671$           |
|                              | 2           | $0.10923026 (1.0)$ $\Delta z2 \times 10^2$                                                                                         | $-0.14308 (42.6)$ $\Delta z2 \times 10^2$                                                                    | $13.34738 (-4.75) \Delta Sr \times 10^2$ | $8.9671$           |
| 2a (Eq. 6, with 41 as NBS-1A) | 0           | $0.57284965 (0)$ $\Delta x \times 10^2$                                                                                           | $-0.100330 (0)$ $\Delta y \times 10^2$                                                                 | $14.013260 (0)$ $\Delta Sr \times 10^2$ | $6.0$ $0.67$       |
|                              | 1           | $0.11143694 (1.0)$ $\Delta z1 \times 10^2$                                                                                         | $-0.094340 (-5.97) \Delta z1 \times 10^2$                                                                     | $14.106564 (0.666) \Delta Sr \times 10^2$ | $8.9671$           |
|                              | 2           | $0.10923026 (1.0)$ $\Delta z2 \times 10^2$                                                                                         | $-0.106284 (5.935)$ $\Delta z2 \times 10^2$                                                                    | $13.920513 (-0.662) \Delta Sr \times 10^2$ | $8.9671$           |
Table 3: Scale-conversion (SC) processes (and also the process as Eq. 9) specific parameters

| SC-Formula | Process-specific rate-of-variation ($M_Y^V$, cf. Eq. 3) | $[UF]_Y$ (cf. Eq. 4) | Output-Uncertainty ($\varepsilon$, cf. Eq. 2) | $\varepsilon_Y$/$\varepsilon_R$ |
|------------|--------------------------------------------------------|----------------------|---------------------------------|------------------------|
| Eq. 5      | $M_X^Y = \left( \frac{dY}{dX} \right) \frac{X}{Y} = \frac{x(C+1)}{(X+1)(C+1)-1} = \frac{S R^{-W} R}{S R^{-D} R} = -0.891^{*2}; (-3.266)^{*3}$ | $[UF]_Y^{\text{Eq. 5}} \times \left| M_X^Y \right| = 0.891^{*2}; (3.266)^{*3}$ | $\varepsilon_Y^{\text{Eq. 5}} \times \left( \frac{[UF]_Y^{\text{Eq. 5}}}{\varepsilon_Y^{\text{Eq. 5}}} \right) = (0.891^{*2}; (3.266)^{*3})$ |
|            |                                                        |                      | $\varepsilon_Y^{\text{Eq. 5}} \times \varepsilon_Y^{\text{Eq. 5}} = (\left| M_X^Y \right| - \left| \varepsilon_Y^{\text{Eq. 5}} \right|) = (0.0994^{*2}; (0.3642)^{*3})$ |
|            |                                                        |                      | $\varepsilon_Y^{\text{Eq. 5}} \times \varepsilon_Y^{\text{Eq. 5}} = (\left| M_X^Y \right| - \left| \varepsilon_Y^{\text{Eq. 5}} \right|) = (0.0994^{*2}; (0.3642)^{*3})$ |
| Eq. 6*4    | $M_X^Y = \left( \frac{dY}{dX} \right) \frac{X}{Y} = \frac{x(C+1)}{p (Z1+1)} = \frac{S R^{-W} R}{S R^{-D} R} = -0.891^{*2}; (-3.266)^{*3}$ | $[UF]_Y^{\text{Eq. 6}} \times \left( \left| M_X^Y \right| + \left| M_Z^Y \right| \right) = 2.23^{*2}; (6.85)^{*3}; [0.962^{*2}; (5.95)^{*3}]^{*5}$ | $\varepsilon_Y^{\text{Eq. 6}} \times \varepsilon_Y^{\text{Eq. 6}} = (2.23^{*2}; (6.85)^{*3}; [0.9617^{*2}; (5.953)^{*3}]^{*5}$ |
|            |                                                        |                      | $\varepsilon_Y^{\text{Eq. 6}} \times \varepsilon_Y^{\text{Eq. 6}} = (2.23^{*2}; (6.85)^{*3}; [0.9617^{*2}; (5.953)^{*3}]^{*5}$ |
| Eq. 7*6    | $M_X^Y = \left( \frac{dY}{dX} \right) \frac{X}{Y} = \frac{x(C1 - C2)}{q} = \frac{S R^{-W} R}{S R^{-D} R} = -0.891^{*2}; (-3.266)^{*3}$ | $[UF]_Y^{\text{Eq. 7}} \times \left( \left| M_X^Y \right| + \left| M_Z^Y \right| + \left| M_Z^Y \right| \right) = 10.7^{*2}; (44.6)^{*3}$ | $\varepsilon_Y^{\text{Eq. 7}} \times \varepsilon_Y^{\text{Eq. 7}} = (10.71^{*2}; (44.57)^{*3}$ |
|            |                                                        |                      | $\varepsilon_Y^{\text{Eq. 7}} \times \varepsilon_Y^{\text{Eq. 7}} = (10.71^{*2}; (44.57)^{*3}$ |

*1: $\varepsilon_Y \times \varepsilon_Y = (\left| [UF]_Y \right| \times \left( \varepsilon_Y^{\text{Eq. 5}} \right) = \left( \left| [UF]_Y \right| \times \left( \varepsilon_Y^{\text{Eq. 6}} \right) \times \left( \varepsilon_Y^{\text{Eq. 7}} \right) \right) = (0.11152 \times [UF]_Y)$

*2: This data refers to the measurement-reference “$W$” as GISP (cf. the text and Table 1).

*3: This value corresponds to SLAP as “$W$” (cf. the text and Table 2).

*4: $p = (X + 1) \times (C1 + 1) - (Z1 + 1)$; cf. [corresponding to Eq. 6] the expression of “$M_Y^Y$”.

*5: These values refer to NBS-1A (i.e. instead of NBS-1) as “$A1$” (cf. the text and the BLOCK nos. 2a in Tables 1 & 2).

*6: $q = (X + 1) \times (C1 - C2) - (Z1 - Z2)$; cf. [corresponding to Eq. 7] the expression of “$M_Y^Y$”.

18
Figure 1. Variation of method-specific-$[UF]_Y$ as a function of sample $S$ ($^2\text{H}/^1\text{H}$ abundance ratio)
Figure 2. Plot of $[UF]_R$ against sample $S$ ($^2H/^1H$ abundance ratio)