Prospects of ratio and differential (δ) ratio based measurement-models: a case study for IRMS evaluation

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ABSTRACT

The suitability of a mathematical-model \( Y = f(\{X_i\}) \) in serving a purpose whatsoever (should be preset by the function \( f \) specific input-to-output variation-rates, i.e.) can be judged beforehand. We thus evaluate here the two apparently similar models \( Y_A = f_A(\delta R_i, W R_i) = (\delta R_i W R_i) \) and \( Y_\delta = f_\delta(\delta R_i, W R_i) = (\delta R_i W R_i - 1) = (Y_A - 1) \), with \( \delta R_i \) and \( W R_i \) representing certain measurable-variables (e.g. the sample \( S \) and the working-lab-reference \( W \) specific \( i^{th} \)-isotopic-abundance-ratios, respectively, for a case as the isotope ratio mass spectrometry “IRMS”). The idea is to ascertain whether “\( f_\delta \)” should represent a better model than “\( f_A \)”, specifically, for the well-known IRMS evaluation.

The study clarifies that “\( f_A \)” and “\( f_\delta \)” should really represent different model-families. For example, the possible variation, \( \varepsilon_A \), of an absolute estimate as the “\( y_A \)” (and/ or the risk of running a machine on the basis of the measurement-model “\( f_A \)” should be dictated by the possible \( R_i \)-measurement-variations \( (u_S \text{ and } u_W) \) only: \( \varepsilon_A = (\sum_i u_i) = (u_S + u_W) \); i.e., at worst: \( \varepsilon_A = 2u_i \). However, the variation, \( \varepsilon_\delta \), of the corresponding differential (i.e. \( S^W \delta_i \equiv Y_\delta \)) estimate “\( y_\delta \)” should largely be decided by “\( \delta R_i \) and \( W R_i \)” values: \( \varepsilon_\delta = \sum_i (|m_i| \times u_i) = 2(|m_i| \times u_i) = (|m_i| \times \varepsilon_\delta) \); with: \( m_i = (\delta R_i)(\delta R_i - W R_i) \).

Thus, any IRMS measurement (i.e. for which “\( |\delta R_i - W R_i| \to 0 \)” is a requirement) should signify that “\( |m_i| \to \infty \)”. Clearly, “\( y_\delta \)” should be less accurate than “\( y_A \)”, and/ or even turn out to be highly erroneous (\( \varepsilon_\delta \to \infty \)). Nevertheless, the evaluation as the absolute-ratio “\( y_A \)”, and
hence as the sample isotopic ratio “$S_{ri}$”, is shown to be equivalent to our previously reported finding that the conversion of a δ-estimate (here, $y_δ$) into “$S_{ri}$” should help to improve the achievable output-accuracy and -comparability.

1. INTRODUCTION

Evaluation should in general mean knowing any unknown (e.g. value of a variable, or relationship between variables, or ...) whatever. However, any conceivable result should be based on some defined standard(s) and/ or knowledge, i.e. refer to a relative fact only. For example, the understanding of a result (“x” Kg) of even simply weighing an unknown amount (“X” Kg of a solid-material) should need the ‘a priori’ knowledge of weighing-unit “Kg”. Further, the accountability of any estimate-of-indirect-measurement ($y$) should require the additional knowledge of relationship (viz.: $Y = f(\{X_i\})$) of desired variable ($Y$) with corresponding measurable variables ($X_i$, $i = 1, 2 ...$). However, the relationship (function “$f$”) may also happen to be unknown, and/ or be a proposed one. The latter, i.e. a possible relationship between any known (measurable) and unknown (desired) variables, is generally referred to as a “mathematical-model”. Again, for a given purpose, there might be several proposals. Thus, e.g. the comparison between two different quantities, $X_J$ and $X_K$, might be carried out in terms of their absolute ratio ($Y_A$) or differential ratio¹ ($Y_δ ≡ δ$):

$$Y_A = f_A(X_J, X_K) = (X_J/X_K)$$

$$Y_δ = f_δ(X_J, X_K) = ([X_J/X_K] - 1) = (Y_A - 1)$$

However, for any specified purpose whatever, how should really a proper model (or, if applicable, an appropriate derivable formula from many a possible one) be chosen?
This work considers the evaluation system to be the well-known isotope ratio mass spectrometry (IRMS),¹,² and discusses a simple means for resolving the issue.

2. TERMINOLOGIES AND PRINCIPLES

It is important pointing out that, irrespective of purpose (here, IRMS evaluation), any proposed model (“f₁” or “f₄”) should represent a specific method for bringing out a net systematic³ change in the corresponding independent variables (here: Xⱼ and Xₖ) and/ or estimates (“xⱼ ± uⱼ” and “xₖ ± uₖ”), and hence for dictating (the nature of) the output to be expected. Therefore, ‘a priori’ study of the possible properties³ of a proposed input-output relationship (e.g. rates of variations of the modeled variable “Y₄” or “Y₆” as a function of the measurable variables “Xⱼ and Xₖ”) should be a means for proper modeling.

2.1 Error and Uncertainty

As well-known⁴, the process “measurement” is subject to error. That is, even a directly measurable estimate “xᵢ” could be different from the corresponding unknown true-value “Xᵢ”; e.g.: \( Xᵢ = (xᵢ + Δᵢ) \), with \( Δᵢ \) representing the error (if any) in “xᵢ”. Thus, assessment of error should be an integral part of any evaluation. However, ascertainment of a true error as “Δᵢ” is inconceivable, and any result is generally reported as: \( Xᵢ = (xᵢ ± uᵢ) \). Clearly, “uᵢ” should represent the possible and, therefore the maximum, value of the error “Δᵢ” (i.e.³: \( uᵢ = Max |Δᵢ| \)); and be ensured ‘a priori’ (by the aid of relevant standards, i.e. while developing a chosen measurement technique) to be, at least acceptably, small.

Similarly, any indirect-measurement model “\( Yₐ = fₐ([Xᵢ]ᵢ=₁^N) \)” should in terms of corresponding independent (measurable input) and dependent (desired output) estimates be represented as: (\( yᵢ + Dᵢ \)) = \( fₐ([xᵢ + Δᵢ]ᵢ=₁^N) \); and/ or: (\( yᵢ ± εᵢ \)) = \( fₐ([xᵢ ± uᵢ]ᵢ=₁^N) \); where
“$D_d$” should stand for true *modeling* (output) error, and $\varepsilon_d$ for the corresponding *maximum possible value* (MPV); i.e.: $\varepsilon_d = \max |D_d|$.

However, it could also be mentioned that: (i) *method-development* may not always help to even identify small sources of systematic errors; i.e. even a *small* measurement-error ($\Delta_i$) may not be purely random by origin; and: (ii) any modeling error “$D_d$” should, in nature, be purely systematic: $D_d = f_d([\Delta_i]_i=1^N)$. Moreover, “$D_d$” should *never* vary for whether “$\Delta_i$” should be purely random or purely systematic or both by the origin. Thus, unlike the ref. [4], we refer to the “MPV of any (direct/ indirect measurement) error” as the (corresponding) *accuracy* or inaccuracy or *uncertainty*.

Further, only relative-error should be the measure of an error. Thus, by the error “$\Delta_i$”, we do mean that: $\Delta_i = \frac{x_i - x_i^*}{x_i^*}$. Similarly, we define (modeling/ output error): $D_d = \frac{y_d - y_d^*}{y_d^*}$. Therefore, by the uncertainty “$u_i$” or “$\varepsilon_i$”, we refer to the corresponding “*relative MPV*” only.

### 2.2 Evaluation of models

For any model “$Y_d = f_d([X_i]_i=1^N)$”, and hence for any modeled estimate: $(y_d + D_d) = f_d([x_i + \Delta_i]_i=1^N)$; and/ or: $(y_d \pm \varepsilon_d) = f_d([x_i \pm u_i]_i=1^N)$; the modeling-error ($D_d$) could be shown to be decided as:

$$D_d = \sum_{i=1}^{N} (M^d_t \times \Delta_i)$$  \hspace{1cm} (3)

And, the modeling-uncertainty ($\varepsilon_d$) can, really a priori, be ascertained as:

$$\varepsilon_d = \sum_{i=1}^{N} (M^d_t \times u_i) = ([UF]_d \times G u)$$  \hspace{1cm} (4)

where $M^d_t$ is a theoretical constant, representing the model (“$f_d$”) specific relative rate of variation of the modeled variable $Y_d$ as a function of the measurable variable $X_i$.
\[ M_i^d = \left( \frac{\partial Y_d}{\partial X_i} \right) \left( \frac{X_i}{Y_d} \right) = \left( \frac{\partial Y_d}{\partial X_i} \right), \quad i = 1, 2 \ldots N \]  
(5)

And, \( G_u \) stands for the measurement accuracy to be achieved (i.e. which is generally preset before developing a required experimental-methodology and/ or ascertaining the possible \( X_i \) specific “\( u_i \)”); so that: \( u_i = G_u \) (with: \( i = 1, 2 \ldots N \)); and:

\[ [UF]_d = (u_d/G_u) = \sum_{i=1}^{N} |M_i^d| \]  
(6)

Thus “[\( UF \)]_d”, which should be referred to\(^6\) as the uncertainty-factor of modeling (determining \( Y_d \)), really represents the collective rate-of variations of \( Y_d \) as a function of all different input/ measurable variables (\( X_i \), with: \( i = 1, 2 \ldots N \)). Therefore, the smaller should be the value of [\( UF \)]_d (viz.: [\( UF \)]_d < 1, rather: [\( UF \)]_d \ll 1) the better be the (evaluation method represented by the proposed) model “\( f_d \)”.

2.2.1 Clues for modeling: nature of parameters to be looked for

We may here go backward by examining certain formulae, e.g. Eqs 1 and 2, for their behavior.

“Eq. 1: \( Y_A = (X_J/X_K) \)” is, however, already shown elsewhere\(^3\) to be characterized by the following parameters (cf. Eq. 5): \( M_J^A = 1 \), and: \( M_K^A = -1 \); and thus (cf. Eq. 3):

\[ D_A = \sum_{i=1}^{2} (M_i^A \times \Delta_i) = (\Delta_J - \Delta_K) \]  
(3a)

And (cf. Eq. 4)

\[ e_A = \sum_{i=1}^{2} (|M_i^A| \times u_i) = (u_J + u_K) \]  
(4a)

Further (cf. Eq. 6):

\[ [UF]_A = \sum_{i=1}^{2} (|M_i^A|) = (|M_J^A| + |M_K^A|) = 2 \]  
(6a)

Therefore (for: \( u_J = u_K = G_u \); cf. Eq. 4 and/or 4a):

\[ e_A = ([UF]_A \times G_u) = (2 \times G_u) \]  
(4a')
Thus, what is signified is that even any elementary mathematical process should not be presumed to be (characterized by “\([UF]_d = 1\)”, and hence) non-biasing. For example, any estimated unknown ratio “\(y_A\)” (and hence any \(y_A\) based insight) could be twice as wrong as a corresponding monitored estimate “\(x_J\) or \(x_K\)”.

Yet, it is important pointing out that the “\(Y_A = (X_J/X_K)\)” specific parameters (viz. the individual rates-of-variations “\(M^\delta_J\) and, \(M^\delta_K\)”, and thus the collective rate-of-variation “\([UF]_A\)” and/ or the achievable output-accuracy “\(\varepsilon_A\)” should all be independent of the measureable variables “\(X_J\) and \(X_K\)”. Again, any analytical method should be valuable provided the corresponding desired result can ‘a priori’, i.e. irrespective of what and how much to be measured, be assured to be accurate. Thus, “\(Y_A = (X_J/X_K)\)” may stand out to represent a good evaluation model. Further, it could be shown below that “\(Y_A = (X_J/X_K)\)” helps minimize the effect of possible, i.e. even undetectable and/ or uncorrectable, systematic errors (say, \((SYS)\Delta_J\) and \((SYS)\Delta_K\) of measuring “\(X_J\) and \(X_K\)” (respectively) on the modeled estimate “\(y_A\)”, and hence, to improve the desired output accuracy (\(\varepsilon_A\)) as:

\[
\left(\frac{\Delta J}{X_J - X_K}\right)
\]

We now refer to the Eq. 2 (“\(Y_\delta = [(X_J/X_K) - 1] = [Y_A - 1]\)”, i.e. which signifies that the subtraction of an estimate as “\(y_A\)” from merely a constant “1” should yield the differential estimate “\(y_\delta\)”), and enquire: should “\(y_\delta\)” be equally as accurate as “\(y_A\)”?

However, “\(Y_\delta = [(X_J/X_K) - 1]\)” could be seen to be characterized by different kinds of parameters (cf. Eq. 5) as: \(M^\delta_J = \frac{x_J}{x_J - x_K}\), and: \(M^\delta_K = \frac{-x_J}{x_J - x_K}\); i.e. to imply that (cf. Eq. 3):

\[
D_\delta = \sum_{i=1}^{2} (M^\delta_i \times \Delta_i) = \left[\frac{x_J}{x_J - x_K} \times \Delta_J\right] - \left[\frac{x_J}{x_J - x_K} \times \Delta_K\right]
\]

And (cf. Eq. 4 and also Eq. 4a)
\[
\varepsilon_\delta = \sum_{i=1}^{2} (|M_i^\delta| \times u_i) = \left(\left[\frac{x_j}{x_j - x_K} \times u_j\right] + \left[\frac{-x_j}{x_j - x_K} \times u_K\right]\right)
\]

\[
= \left(\left[\frac{x_j}{x_j - x_K} \times [u_j + u_K]\right]\right) = \left(\left[\frac{x_j}{x_j - x_K} \times \varepsilon_A\right]\right) \quad (4b)
\]

Moreover (cf. Eq. 6):

\[
[U]^\delta = \left(\left[\frac{x_j}{x_j - x_K}\right] + \frac{-x_j}{x_j - x_K}\right) = \left(\left[\frac{x_j}{x_j - x_K}\right] \times 2\right) = \left(\left[\frac{x_j}{x_j - x_K}\right] \times [U]^A\right) \quad (6b)
\]

Thus, even for “\(u_j = u_K = g\ u\)” (cf. Eq. 4b and also Eq. 4a):\n
\[
\varepsilon_\delta = \left(\left[\frac{x_j}{x_j - x_K}\right] \times 2 \times g\ u\right) = \left(\left[\frac{x_j}{x_j - x_K}\right] \times \varepsilon_A\right) \quad (4b')
\]

Furthermore, the behavior of Eq. 2 might be studied as simply “\(Y_\delta = (Y_A - 1)\)”, i.e. “\(y_\delta\)” can be evaluated as the 2nd stage-estimate:\n
\[
(y_\delta \pm \varepsilon_\delta) = (y_A \pm \varepsilon_A) - 1 \quad (2')
\]

where, clearly, \(y_A\) should represent the 1st stage estimate (cf. Eq. 1 and also Eq. 4a or 4a'):

\[
(y_A \pm \varepsilon_A) = \left(\left[\frac{x_j \pm u_j}{x_K \pm u_K}\right]\right) \quad (1')
\]

However, the change of path should, on its own, never make the result to be different. For example, the rate of variation of the differential-ratio \((Y_\delta)\) as a function of the absolute-ratio \((Y_A)\), i.e. the 2nd stage output-variation, could be shown to be decided (cf. Eq. 5) as: \(M_\delta^A = \frac{y_A}{y_A - 1} = \frac{x_j}{x_j - x_K}\). Therefore, the 2nd stage output-uncertainty should be governed as (cf. Eq. 4 and also Eqs. (4a', 6a, 6b and so')):

\[
\varepsilon_\delta = \left(\left|M_\delta^A\right| \times \varepsilon_A\right) = \left(\left[\frac{x_j}{x_j - x_K}\right] \times \varepsilon_A\right) = \left(\left[\frac{x_j}{x_j - x_K}\right] \times [U]^A \times g\ u\right)
\]

\[
= \left(\left[\frac{x_j}{x_j - x_K}\right] \times [2 \times g\ u]\right) = ([U]^\delta \times g\ u) \quad (4b'')
\]
What may however be emphasized is that, on the one, the achievable accuracy ($\varepsilon_A$) of determining any absolute ratio ($Y_A$) should be governed by the achievable measurement-accuracies ($u_j$ and $u_K$) only, i.e. the measureable variables ($X_j$ and $X_K$) can in no way help in presetting $\varepsilon_A$. On the other, the achievable accuracy ($\varepsilon_\delta$) of determining a $\delta$-ratio as $Y_\delta$ should largely be fixed by “$X_j$ and $X_K$” themselves, rather by the difference “$|X_j - X_K|$”. For example, “$(|X_j - X_K|) \to 0$” should mean that “$\varepsilon_\delta \to \infty$”, i.e. (for a case, corresponding to which “$y_A$” should rather be accurate) the $\delta$-estimate “$y_\delta$” can turn out to be highly erroneous.

Thus, if “$Y_A = (X_j/X_K)$” and all other such models with “$|M'_i| = 1$, ($i = 1, 2 ...$)” should constitute the family3 no. F.1; then “$Y_\delta = ([X_j/X_K] - 1)$” should belong to another family (no. F.2). However, the implication of the family consideration is that, only for any possible “F.1” member, the output-accuracy and/ or modeling-performance should be independent of measureable variable(s) “$X_i(s)$”. On the contrary, the success of “F.2” modeling should be dictated by “$X_i(s)$”; e.g. the model “$Y_\delta = ([X_j/X_K] - 1)$” might lead to disaster in cases as “$(|X_j - X_K|) \to 0$” but help exert strong control (i.e. yield even unexpectedly good results) in cases where “$(|X_j - X_K|) \to \infty$”.

3 IRMS AND THE RATIO MODELS

The isotopic analysis of any lighter element, rather the study of possible variation in a corresponding source (S) specific isotopic-abundance-ratio ($^SR_i$), is since long1 proposed and continued to be carried out as a differential ratio ($\delta$), viz.: ($^{S/W}_i \delta_i \equiv Y_\delta = ([^SR_i/W_R_i] - 1)$; with $W$ representing a similar isotopic-source as $S$ so that “$[^SR_i - W_R_i] \to 0$”. The technique of $\delta$-measurement is, although lately supplemented by the laser mass spectrometry,7-9 well-known as the IRMS. Usually, $W$ stands for a relevant lab-available material, and is thus known as the
working-lab-reference. However, as different lab-specific $S/W\delta_{i}$-estimates cannot be inter-compared, any species-specific result is reported with reference to a corresponding recommended $D$. Thus, while “$Y\delta$” stands for the (measurable and/ or) IRMS variable, the desired variable is defined to be “$(S/D)\delta_{i} \equiv Z_{\delta}$) = ([$^S R_{i}/^D R_{i}$] − 1)”, with (in principle): $D R_{i} \approx S R_{i} \approx W R_{i}$.

However, why should at all the sample ($S$) measurement be accomplished by comparison with another similar isotopic material ($W$ or, $D$), and that too as a $\delta$-variable?

3.1 Measurement by comparison: why?

Any element, specifically a lighter one, should be subject to isotopic fractionation; i.e. isotopic abundances might vary as a function of geo/ bio/ environmental changes. Thus, by the isotopic analysis of an element, it should firstly mean the measurement of relevant isotopic-abundance-ratios ($R_{i}$, $i = 1, 2 \ldots$). Secondly, it is a requirement that “$R_{i}$” should remain invariant as a function of experimental conditions. However, in case of a lighter element, “$R_{i}$” (or even simply its estimate “$r_{i}$”) might significantly vary as a function of measurement-procedure and/ or -time only. Thus, for any specified source-of-sample ($S$), the measured estimate “$S r_{i}$” should be correlated to the unknown true value “$S R_{i}$”, at best, as:

$S R_{i} = (S r_{i} + \Delta_{S}) = (S r_{i} + [(^{RAN} \Delta_{S}) + (^{SYS} \Delta_{S})])$

where $\Delta_{S}$, $(^{RAN} \Delta_{S})$ and $(^{SYS} \Delta_{S})$ stand for total, random and systematic (isotopic-fractionation) errors, respectively; and where it could be a fact that “$(^{SYS} \Delta_{S}) \gg (^{RAN} \Delta_{S})$”.

Similarly, any other source ($W$) specific result can be expressed as:

$W R_{i} = (W r_{i} + \Delta_{W}) = (W r_{i} + [(^{RAN} \Delta_{W}) + (^{SYS} \Delta_{W})])$

However, if $S$ and $W$ should represent similar isotopic sources ( $|S R_{i} - W R_{i}| \rightarrow 0$), then the processing cum measurements of both $S$- and $W$-specific samples by employing identical
possible experimental conditions \textbf{(IPECs)} should cause corresponding fractionation errors to follow one another \((\text{SYS}\Delta_S \approx \text{SYS}\Delta_W)\). Moreover, the possible fractionation errors \((\text{SYS}\Delta_S)\) and \((\text{SYS}\Delta_W)\) (for measuring any isotopic-ratio “\(i\)”, viz. \(^2\text{H}/\text{H}\)) may differ from one another by magnitude but \textbf{never} by sign. This is the reason why certain mathematical operation on the estimates “\(S_r\) and \(W_r\)”, e.g. \textit{computation} of their ratio “\(y_A = (S_r/W_r)\)” should cause the difference-in-fractionation-errors \((\text{SYS}\Delta_S - \text{SYS}\Delta_W) \equiv \text{Add}\Delta\) only to turn out as the effective systematic error (rather, say, as an \textit{additional} random measurement error). For example, if it happens that: \(|\text{SYS}\Delta_S| > |\text{SYS}\Delta_W|\); then the error \((\mathcal{D}_A)\) of the estimated absolute ratio “\(y_A\)” should be decided as (cf. Eq. 3a, for “\(\Delta_f \equiv \Delta_S\)” and “\(\Delta_k \equiv \Delta_W\)”):

\[
\mathcal{D}_A = (\Delta_S - \Delta_W) = \left(\left[\text{RAN}\Delta_S + (\text{SYS}\Delta_S)\right] - \left[\text{RAN}\Delta_W + (\text{SYS}\Delta_W)\right]\right)
\]

\[
= \left(\text{RAN}\Delta_S + \text{Add}\Delta - \text{RAN}\Delta_W\right)
\]

(3a')

Similarly, for “\(|\text{SYS}\Delta_S| < |\text{SYS}\Delta_W|\)”:

\[
\mathcal{D}_A = (\text{RAN}\Delta_S - \text{RAN}\Delta_W + \text{Add}\Delta).
\]

(3a'')

Thus, even though the \(S\)- and \(W\)-measurement-uncertainties should be decided as: \(u_S = (\text{RAN}\Delta_S + (\text{SYS}\Delta_S)\); and: \(u_W = (\text{RAN}\Delta_W + (\text{SYS}\Delta_W)\)\), respectively; the ratio-uncertainty \((\varepsilon_A\text{, cf. Eq. 4a})\) should turn out to be \textbf{less} than the sum “\((u_S + u_W)\)”\). That is, \(\varepsilon_A\) should, although \textit{for a case of fractionation} be \textbf{difficult} to be \textit{predicted}, have a value as:

\[
\varepsilon_A = (\text{RAN}\Delta_S + \text{RAN}\Delta_W + |\text{SYS}\Delta_S - \text{SYS}\Delta_W|) = (\text{RAN}\Delta_S + \text{RAN}\Delta_W + \text{Add}\Delta)
\]

(4a'')

Moreover, the basic purpose of measuring \(S\) and \(W\) by employing \textbf{IPECs} is to ensure that “\(\text{Add}\Delta \to 0\)”\). Thus, there should be no alternative to ascertaining “\(\varepsilon_A\)” as the “\textit{lab-evaluated MPV of the error} \(\mathcal{D}_A\)” (i.e.: \(\varepsilon_A = \text{Max} |\mathcal{D}_A|\)).
However, any lighter elemental isotopic data is acquired and/or reported\textsuperscript{1,2,7-15} as a \textit{differential} ratio (viz.: \( y_\delta = \left[ (S R_i / W R_i) - 1 \right] = y_A - 1 \)), rather than as the \textit{absolute} ratio “\( y_A \)”. However, should the said-practice be justified?

### 3.2 Should “\( f_A \)” or “\( f_\delta \)” be the IRMS-model?

It is pointed out above that, if only the modeled \textit{system-functioning} (and/or achievable \textit{output-accuracy}) should be needed to be governed by the system-defining variables (viz. \( ^S R_i \) and \( ^W R_i \)) themselves, then only the “F.2” modeling (here “\( Y_\delta = \left( [S R_i / W R_i] - 1 \right) = (Y_A - 1) \)” has to be preferred over the “F.1” modeling (as “\( Y_A = (S R_i / W R_i) \)”)). However, this cannot be the requirement for any analytical method, at least, for the IRMS evaluation.

Further, \( Y_A = (S R_i / W R_i) \) and \( Y_\delta = (Y_A - 1) \) are shown to be so correlated (cf. e.g. Eq. 4b or 6b) that the \textit{ratio} of corresponding \textit{modeling-errors} (i.e. ratio of errors due to a pair of \textit{absolute} and \textit{differential} estimates “\( y_A \)” and “\( y_\delta \)”, respectively) should always be \textit{prefixed} as:

\[
\left( \frac{\Delta_\delta}{\Delta_A} \right) = \left( \frac{\varepsilon_\delta}{\varepsilon_A} \right) = \left( \frac{\left[ UF \right]_\delta}{\left[ UF \right]_A} \right) = \left| \frac{S R_i}{S R_i - W R_i} \right| \quad (7)
\]

Eq. 7 clarifies that the knowledge of relevant \( ^S R_i \) and \( ^W R_i \) \textit{certified} materials (or even simply \textit{theoretical} standards) should help to ‘a priori’ ensure whether \( Y_A = (S R_i / W R_i) \) or \( Y_\delta = \left( [S R_i / W R_i] - 1 \right) \)” be the appropriate IRMS-model. Thus, let’s consider the \( ^2\text{H}/^1\text{H} \) certified\textsuperscript{16} materials, IAEA-CH-7 and GISP, as the sample \( S \) and lab-reference \( W \), respectively, i.e. say that\textsuperscript{16,17} (true): \( S R_i = 14.013260 \times 10^{-5} \); and \( W R_i = 12.62076552 \times 10^{-5} \). Then (cf. Eq. 7) it is predicted that:

\[
\left( \frac{\Delta_\delta}{\Delta_A} \right) = \left( \frac{\varepsilon_\delta}{\varepsilon_A} \right) = \left( \frac{[UF]_\delta}{[UF]_A} \right) = 10.0634 \quad (7a)
\]

Therefore:
\[ D_\delta = (10.0634 \times D_A) \] (3b')

And/ or:

\[ e_\delta = (10.0634 \times e_A) = (10.0634 \times [2 \times g_u]) = (20.1268 \times g_u) \] (4b'Ⅰ)

where \( g_u \) should stand for bias corrected measurement-uncertainty (cf. Eq. 4a' or 4b')

It may also here be reminded that “\( |S_{R_i} - W_{R_i}| \to 0 \)” is a requirement for IRMS evaluation. However, “\( |S_{R_i} - W_{R_i}| \to 0 \)” should: (i) on the one ensure the (measurement-specific fractionation errors \( \Delta S \) and \( \Delta W \)” to be increasingly close to one another, and hence, in turn, the ratio-error “\( D_A \)” and/ or the ratio-uncertainty “\( e_A \)” to be small; i.e.) estimated absolute ratio \( Y_A \) to be accurate; and: (ii) on the other cause (“\([UF]_\delta \to \infty\)” and/ or “\( e_\delta \to \infty\)”, and therefore) the \( \delta \)-estimate \( Y_\delta \) to be increasingly inaccurate. Further, in practice (unknown case), “\( |S_{R_i} - W_{R_i}| \)” cannot be known beforehand. Therefore, the choice of “\( Y_\delta = ((S_{R_i}/W_{R_i}) - 1)\)”, rather than of “\( Y_A = (S_{R_i}/W_{R_i})\)”, as the IRMS-model should not only mean the lowering of achievable-accuracy but also cause, at least in some cases, the evaluated data (\( \delta \)-estimate as \( Y_\delta \), and hence the correspondingly extracted insight) to be misleading.

In our present known case, i.e. even for “\( |S_{R_i} - W_{R_i}| \)” to be somewhat significant, “\( Y_\delta \)” is predicted to be ≈10 times more erroneous than “\( Y_A \)”. However, are we correct?

3.2.1 Verification

For “\( S \)” as IAEA-CH-7 and “\( W \)” as GISP”, the nature of estimates (“\( S_{R_i} = x_J \)” and “\( W_{R_i} = x_K \)” to be expected for measurements under varying possible lab experimental set-ups (Nos. 1 and 2), and hence the corresponding possible variations of the modeled-estimates “\( Y_A \)” and “\( Y_\delta \)”, are exemplified (cf. Nos. 1-5) in Table 1. However, the Expt. No. 0 (i.e. which shows the measurement-errors “\( \Delta S \) and \( \Delta W \)” and thus the modeling errors “\( D_A \) and \( D_\delta \)” as zero) should
represent the true values, i.e.: \((true-S_{r_{l}} \equiv S_{r_{l}}) = 14.013260 \times 10^{-5}\) and \((true-W_{r_{l}} \equiv W_{r_{l}}) = 12.62076552 \times 10^{-5}\); and thus “\((true-y_{A} \equiv Y_{A}) = (S_{r_{l}}/W_{r_{l}}) = 1.1103336, and/or\((true-y_{\delta} \equiv Y_{\delta}) \equiv (Y_{A} - 1) = 0.1103336\)”. However, what is significant noting is that the evaluated ratio-of-modeling-errors, “\(D_{\delta}/D_{A}\)” (cf. Table 1 for any Lab and Expt. Nos.), is the same as the predicted value (10.0634, cf. Eq. 7a).

However, it should be more interesting to note that the measurement accuracy \((u_{i})\) is reflected, by Lab 1, to be reasonable (as: \(\max |\Delta_{i}| = 0.019\% \approx 0.02\%, \text{ cf. Example no. 5}\) and, by Lab 2, to be as worse as 0.12\%. Therefore, the modeled-estimates, e.g. \(y_{A}^{(\text{Lab1})}\) and \(y_{A}^{(\text{Lab2})}\), should be expected (i.e. from the viewpoint of measurement-accuracy only, cf. Eq. 4a) to be 04\% and 0.24\% accurate, respectively. However, even \(y_{A}^{(\text{Lab2})}\) has appeared to be 0.04\% accurate, rather as erroneous as \(y_{A}^{(\text{Lab1})}\) (because [cf. Table for any of Expt. Nos. 1-5]: “\(|D_{A}^{(\text{Lab1})}| \leq 0.034\%\)” and “\(|D_{A}^{(\text{Lab2})}| \leq 0.036\%\)”). Therefore, the presumable experimental conditions (“\text{IPECs}”), as at least those reflected by the Lab 2 data, should be fractionation prone.

3.2.2 Fractionation and achievable value of \(\varepsilon_{d}\)

It may be noted that the data \((S_{r_{l}}\) and \(W_{r_{l}})\) by Lab 1 do not help distinguish between the possible fractionation and random errors; i.e. appear to be unbiased. Moreover, the ratio-error “\(|D_{A}|\)” has, for the case of either Example No. 1 or 3, turned out to be less than even a corresponding measurement-error “\(|\Delta_{S}|\)” or “\(|\Delta_{W}|\)”. This supplements the above indicated fact that the computation of a ratio of any two estimates (here: \(S_{r_{l}}\) and \(W_{r_{l}}\)) should offer the possibility of partial or full cancellation (i.e. depending upon the signs and magnitudes) of the corresponding errors (\(\Delta_{S}\) and \(\Delta_{W}\), respectively); and thus controlling the ratio-error “\(D_{A}\)”. However, in the case of Example No. 2 or 4, “\(|D_{A}|\)” has equaled the measurement-error-sum
\(|\Delta S| + |\Delta W|\). Therefore, the prediction as Eq. 4a' (i.e. ratio-uncertainty: \(\varepsilon_A = [(u_S + u_W) \equiv (u_I + u_K)] = 2u_i\)) should, at least for unbiased cases of measurements, be a fact. Clearly, the reason is that the different measurement-specific random errors \(\Delta S \equiv \Delta J\) and \(\Delta W \equiv \Delta K\) can, even by the sign-of-error, differ from one another.

However, the Lab 2 data are (at least, with reference to Lab 1) highly erroneous and/ or biased, because (cf., for illustration, the Example No. 1): \((\Delta S^{(Lab2)} - \Delta S^{(Lab1)}) = -0.09\%\) and: \((\Delta W^{(Lab2)} - \Delta W^{(Lab1)}) = -0.09\%\). That is, the fractionation errors \((^{SYS}\Delta S\) and \((^{SYS}\Delta W\) appear to be as high as 0.09% or so. However, the measurements of \(S\) and \(W\), i.e. even by employing IPECs, should not ensure that: \((^{SYS}\Delta S = (^{SYS}\Delta W\). In other words, the \(S\) and \(W\) specific fractionation and random errors can, in case of a real world experiment as the Example No. 1, have any combination of values as:

(i) \(\Delta S = -0.07\% = (^{SYS}\Delta S + ^{(RAN)}\Delta S) = (-0.09\% + 0.02\%)\); and \(\Delta W = -0.079\% = (^{SYS}\Delta W + ^{(RAN)}\Delta W) = (-0.09\% + 0.011\%)\);

(ii) \(\Delta S = -0.07\% = (^{SYS}\Delta S + ^{(RAN)}\Delta S) = (-0.08\% + 0.01\%)\); and \(\Delta K = -0.079\% = (^{SYS}\Delta W + ^{(RAN)}\Delta W) = \left[-0.09\% + 0.011\%\right] = (^{SYS}\Delta W + \left[Add_{\Delta} + ^{(RAN)}\Delta W\right]) = (-0.08\% + \left[0.01\%\right])\);

Yet, any modeled estimate (“\(y_A\)” or, “\(y_\delta\)”) could be seen to be accountable by the theory. Thus, e.g. whether the Example No 1 should correspond to the error-combination no. either (i) or (ii) or some other, the ratio-error \(^{D_A(Expt.1)}\) is here predicted (cf. Eq. 3a or Eq. 3a') to be 0.009%. Moreover, Table 1 (cf. for Lab 2) verifies that: \(^{D_A(Expt.1)} = 0.009\%;\) and/ or that: \(^{D_A(Lab2)} = ^{D_A(Lab1)}\).
Thus, as shown here, the **MPV of modeling error** “\( \text{Max} |D_A| \)’’ should be more or less independent of the labs (because: \( \text{Max} |D_{A}^{(\text{Lab1})}| = 0.0342\% \); and: \( \text{Max} |D_{A}^{(\text{Lab2})}| = 0.0363\% \)).

That is the ratio-uncertainty \( e_A \) should, for a case of fractionations, be less than the sum of established measurement-uncertainties “(\( u_S + u_W \))”.

In other words, *lab observed value* of the error “\( \text{Max} |D_A| \)” should be, as indicated by Eq. 4a, or so, the authentic measure of “\( e_A \)”.

Moreover, the \( \text{Lab2} \delta \)-estimates (with: \( |D_{\delta}^{(\text{Lab2})}| \leq 0.363\% \)) are also difficult to be distinguished from the \( \text{Lab1} \delta \)-estimates (because: \( |D_{\delta}^{(\text{Lab1})}| \leq 0.342\% \)). This means that the measure of even the accuracy “\( \varepsilon_\delta \)” should be the lab-evaluated \( \text{Max} |D_{\delta}| \)”.

Therefore, if the aim of modeling should be to have a means for simply cancelling the possible \( S \)- and \( W \)-specific fractionation errors, i.e. **not** really for achieving the best possible accuracy in the desired (modeled) result, then “\( Y_\delta = (S_{R/}^{W}R_i - 1) = (Y_A - 1) \)” should be equally as suitable a model as “\( Y_A = (S_{R/}^{W}R_i) \)” for the case of IRMS. However, it is demonstrated that (cf. Table 1), and/or explained why (cf. Eq. 4b or Eq. 7a or so), the usual IRMS-estimate “\( y_\delta \)” should be more erroneous than the corresponding absolute ratio “\( y_A \)”.

### 3.3 Result: \( S/D \delta \)-estimate (\( z_\delta \)) or absolute estimate (\( y_A \) or \( S_{R/} \))?

It is pointed out above that, for enabling the comparison between different possible lab-results, any lab (\( W \)) specific \( S/W \delta \)-estimate (\( y_\delta \)) should be translated into the corresponding recommended\(^{10,11} \) standard (\( D \)) specific \( S/D \delta \)-estimate (\( z_\delta \)); i.e. reference-scale-transformation “\( W \rightarrow D \)” is a general requirement. Thus, by any IRMS evaluation, it should mean that:

\[
Z_\delta = [h_\delta(Y_\delta) \equiv h_\delta(f_\delta(Y_A))] \tag{8}
\]

Or, in terms of estimates:

\[
(z_\delta \pm \varepsilon_\delta) = [h_\delta([y_\delta \pm \varepsilon_\delta]) \equiv h_\delta(f_\delta(y_A \pm \varepsilon_A))] \tag{8'}
\]
where (the desired result, i.e. scale converted $\delta$-ratio): $z_\delta = (|[{}^S r_i/ {}^D r_i]| - 1) = (z_A - 1)$; and $z_{\varepsilon_\delta}$ is the corresponding (i.e. $\delta$-scale conversion) uncertainty.

Further, let’s refer to the uncertainty of the scale converted absolute ratio ($z_A$) as “$Z_{\varepsilon_A}$”. However, it is (in terms of “$S/W$” estimates) shown above that “$\varepsilon_\delta > \varepsilon_A$”. Then, shouldn’t it be true that “$Z_{\varepsilon_\delta} > Z_{\varepsilon_A}$”?

Therefore, it is felt imperative to examine whether the IRMS principle (cf. Eq. 8) “$Z_\delta = h_\delta(Y_\delta)$” should itself be worth reformulating as “$Z_A = h_A(Y_A)$” or so.

As: $Y_\delta = (|[{}^S r_i/ {}^W r_i]| - 1) = (Y_A - 1)$, and: $Z_\delta = (|[{}^S r_i/ {}^D r_i]| - 1) = (Z_A - 1)$; the evaluation of a result as “$Z_\delta$” (or even $Z_A$, or $z_i$) should require $^2,13-15,18$ “$W$” to be a calibrated reference material. Else, $^{2,13-15,18}$ certain other calibrated materials (we say, $^{17,19}$ auxiliary reference-standards “$A_i$, with: $i = 1, 2 \ldots$”) should also, i.e. in addition to the usual sample $S$ and by employing the investigating lab-established “IPECs”, be measured.

It may further be pointed out that a true value (i.e. any variable, e.g. “$Z_\delta$” or, $^S r_i$ or so) cannot be method-specific. However, any estimate as “$Z_\delta$” (i.e. achievable output-accuracy “$Z_{\varepsilon_\delta}$”) should be method-dependent. Thus, simply for distinguishing between the different possible characteristics of different typical scale-conversion-methods, we may refer to the employing of “calibrated $W$”, “only one “$A_i$” and “two different $A_i$-standards” as the Mtd-1, Mtd-2 and Mtd-3, respectively.

3.3.1 Mtd-1: $W$ calibrated method of scale conversion

♦ 1. Scale conversion of ratio-of-ratios ($Y_A \rightarrow Z_A$)

The expression “$Z_A = (^S r_i/ ^D r_i)$” should itself help derive the formula “$Z_A = h_A(Y_A)$”:

$$Z_A = \left( \frac{^S r_i}{^D r_i} \right) = \left( \frac{^S r_i}{^W r_i} \times \frac{^W r_i}{^D r_i} \right) = (Y_A \times C_A) = (Y_A \times [C_\delta + 1]) \quad (9)$$
Therefore, in terms of estimates, Eq. 9 could be rewritten as:

\[(Z_A^{(Mtd-1)} \pm z_A^{(Mtd-1)}) = (y_A \pm \varepsilon_A) \times (C_\delta + 1)) \]  

(9')

where \(C_\delta\) stands for the known “\(W\) vs. \(D\)" isotopic calibration constant (i.e.: \(C_\delta = [(W_{Ri}/D_{Ri}) - 1] = [C_A - 1]\)); e.g. here,\(^{16}\) i.e. for “\(W\) as GISP” and “\(D\) as VSMOW” hydrogen: \(C_\delta = -0.18973\).

However, Eq. 9 should, like Eq. 1, belong to the F.1 family, i.e. “\(Z_A\)” could be shown to be equally as sensitive as “\(Y_A\)” towards a possible measurement-variation, and thus (uncertainty-factor, cf. Eq. 5/ 6): \(Z[UF]_A^{(Mtd-1)} = |A M_{S/D}^{S/W}| = 1\). Therefore, the uncertainty, \(Z \varepsilon_A^{(Mtd-1)}\), of determining the scale converted absolute value (\(Z_A^{(Mtd-1)}\)) should be decided\(^6\) as (cf. also Eq. 4):

\[Z \varepsilon_A^{(Mtd-1)} = (Z[UF]_A^{(Mtd-1)} \times \varepsilon_A) = \varepsilon_A \]  

(4c)

That is, \(Mtd-1\) specific (\(S/D\)) ratio-of-ratios (\(Z_A^{(Mtd-1)}\)) is predicted to be as accurate as the lab-estimated, i.e. “\(S/W\)”, ratio-of-ratios (\(y_A\)).

Further, if the measurement conditions “\(IPECs\)” should (like the Lab 1 in Table 1) help suppress the fractionation to the effects that (the \(S\)- and \(W\)-measurement-uncertainties): \(u_S = (RAN) u_S\), and \(u_W = (RAN) u_W\) (respectively); and if also: \(u_S = u_W = \varepsilon u\); then “\(Z \varepsilon_A\)” can be expressed as (cf. Eq. 4a’):

\[Z \varepsilon_A^{(Mtd-1)} = \varepsilon_A = (u_S + u_W) = (2 \times \varepsilon u) \]  

(4c’)

\(\textbf{1.1. Evaluation of sample isotopic abundance ratio (}\(Z_A \rightarrow S_{Ri}\))\)

As \(^{D}R_i\) should ever be known, the estimate “\(^S\!R_i\)” can also always be computed:

\[S_{Ri} = (^D R_i \times Z_A) \]  

(10)

And hence:

\[(S_{Ri} \pm \varepsilon_{Si}) = (^D R_i \times [Z_A^{(Mtd-1)} \pm Z \varepsilon_A^{(Mtd-1)}]) \]  

(10')
Eq. 10 could also be shown to belong to the F.1 model-family; i.e. (cf. Eq. 5/6): \[ [UF]_{ZA}^{S_{Ri}} = M_{ZA}^{S_{Ri}} = \begin{vmatrix} 1 \end{vmatrix} \] Thus the uncertainty \( S_{\varepsilon_i} \) should be fixed as (cf. Eq. 4 and/or Eq. 4c):

\[
S_{\varepsilon_i} = ([UF]_{ZA}^{S_{Ri}} \times Z_{\varepsilon_i}^{(Mtd-1)}) = Z_{\varepsilon_i}^{(Mtd-1)} = \varepsilon_i
\] (4d)

And, for the possible bias (fractionation) free cases (as those referred to by Eq. 4c):

\[
S_{\varepsilon_i} = Z_{\varepsilon_i}^{(Mtd-1)} = \varepsilon_i = (u_s + u_w) = (2 \times G' u)
\] (4d')

That is, “\( S_{\varepsilon_i} \)” should turn out equally as accurate as the corresponding “\( S/D \)” ratio-of-ratios (here, \( Z_{\varepsilon_i}^{(Mtd-1)} \)), and/or as the “\( S/W \)” (i.e. lab-estimated) ratio-of-ratios (\( y_A \)).

2. \( \delta \)-Scale conversion (\( Y_\delta \rightarrow Z_\delta \))

Eq. 8 (i.e. “\( Z_\delta = h_\delta (Y_\delta) \)” should, like Eq. 9, be arrived at as follows\(^{17,19} \):

\[
Z_\delta = \left( \frac{S R_i^D - 1}{S R_i^D} - 1 \right) = \left( \frac{S R_i^W \times W R_i^D - 1}{W R_i^D} - 1 \right) = ([Y_\delta + 1] \times [C_\delta + 1] - 1) \] (11)

Thus Eq. 8' (i.e. “[\( Z_\delta \pm Z_{\varepsilon_\delta} \) = h_\delta (Y_\delta \pm \varepsilon_\delta) \)” should take the description as:

\[
(Z_\delta^{(Mtd-1)} \pm Z_{\varepsilon_\delta}^{(Mtd-1)}) = ((Y_\delta \pm \varepsilon_\delta) + 1) \times [C_\delta + 1] - 1) \] (11')

However, it is already shown elsewhere\(^{17,19} \) that Eq. 11 belongs to the F.2 family; i.e. the variation of “\( Z_\delta \)” as a function of “\( Y_\delta \)” should be fixed as\(^{17} \) (cf. Eq. 5/6):

\[
Z_{[UF]_\delta}^{(Mtd-1)} = \left| \frac{\delta M_{S/W}^{S/D}}{\delta M_{S/W}^{S/D}} \right| = \left| (S R_i^W - W R_i^D)/(S R_i^D - D R_i^D) \right| ; \ i.e. \ the \ uncertainty \ Z_{\varepsilon_\delta}^{(Mtd-1)} \ (cf. \ Eq. \ 4 \ or \ 4b \ or \ so) \ as:
\[
Z_{\varepsilon_\delta}^{(Mtd-1)} = (Z_{[UF]_\delta}^{(Mtd-1)} \times \varepsilon_\delta) = \left( \left| \frac{S R_i^W}{S R_i^D} - \frac{W R_i^D}{D R_i^D} \right| \times \varepsilon_\delta \right) \] (4E)

Further, “\( D, S \) and \( W \)” should all represent similar (viz. natural) isotopic materials. Therefore, “\( Z_{[UF]_\delta}^{(Mtd-1)} \)” should be close to unity. However, for illustration, say that “\((D R_\delta^W R_i^D) < 1 \)”.

Then, the \( \delta \)-scale conversion uncertainty “\( Z_{\varepsilon_\delta}^{(Mtd-1)} \)” should be somewhat higher than the corresponding IRMS (i.e. \( \delta \)-measurement) uncertainty “\( \varepsilon_\delta \)”.

Otherwise (i.e. for: \([D R_\delta^W R_i^D] > 1 \)
the $S/D\delta$-estimate ($z_\delta^{(\text{Mtd-1})}$) should turn out more accurate than the corresponding lab, i.e. $S/W\delta$-estimate ($y_\delta$). Thus, as $^{16} D R_i = 15.576 \times 10^{-5}$, the present known case should imply that: $Z_{[UF]}^{(\text{Mtd-1})} = 0.891$; and/or that: $Z_{\varepsilon_\delta}^{(\text{Mtd-1})} = (0.891 \times \varepsilon_\delta)$.

However, as (cf. Eqs. 4b$^{///}$): $\varepsilon_\delta = (10.0634 \times \varepsilon_A)$; and (cf. Eq. 4c$^{'}$): $Z_{\varepsilon_A}^{(\text{Mtd-1})} = \varepsilon_A = (u_s + u_W)$

$= (2 \times ^G u)$; the $\delta$-scale conversion uncertainty “$Z_{\varepsilon_\delta}^{(\text{Mtd-1})}$” could be re-expressed as:

$Z_{\varepsilon_\delta}^{(\text{Mtd-1})} = (0.891 \times [10.0634 \times \varepsilon_A]) = (8.967 \times \varepsilon_A) = (8.967 \times Z_{\varepsilon_A}^{(\text{Mtd-1})})$

$= (8.967 \times [u_s + u_W]) = (8.967 \times [2 \times ^G u]) = (17.934 \times ^G u)$

(4E$'$)

where $^G u$ should stand for bias free measurement-uncertainty: $^G u = (u_s \equiv ^{(\text{RAN})} u_s) = (u_W \equiv ^{(\text{RAN})} u_W)$.

**Alternative process** ($Z_A \rightarrow Z_\delta$)

The result ($z_\delta$) can also be evaluated from “$z_A$”; i.e. Eq. 11 should be equivalent to:

$Z_\delta = (Z_A - 1)$

(11a)

And, therefore:

$Z_\delta^{(\text{Mtd-1})} \pm Z_{\varepsilon_\delta}^{(\text{Mtd-1})} = ([Z_A^{(\text{Mtd-1})} \pm Z_{\varepsilon_A}^{(\text{Mtd-1})}] - 1)$(11a$'$)

The “$Z_\delta$ versus $Z_A$” variation-rate could be shown to be fixed as (cf. Eq. 5/ 6): $Z_{[UF]}^{\delta} = |Z_M^{\delta}| = |Z_A^{(\text{Mtd-1})} - 1| = |(\delta R_i/|\delta R_i - D R_i|)| = 8.9671$; and thus (cf. Eq. 4, and also Eq. 4E$'$):

$Z_{\varepsilon_\delta}^{(\text{Mtd-1})} = (Z_{[UF]}^{\delta} \times Z_{\varepsilon_A}^{(\text{Mtd-1})}) = (8.967 \times Z_{\varepsilon_A}^{(\text{Mtd-1})}) = (8.967 \times \varepsilon_A)$

(4E$''$)

Eq. 4E$'''$ supplements the prediction (cf. the context of Eq. 2 and Eq. 2$'$) that a result should not vary for varying the evaluation-path only. That is, irrespective of whether one should go by Eq. 11 or Eq. 11a, the $S/D\delta$-estimate $z_\delta^{(\text{Mtd-1})}$ is predicted to turn out more erroneous (here, $\approx 9$ times) than any corresponding absolute ratio (as either “$S/D$” estimate $z_A^{(\text{Mtd-1})}$, or lab-“$S/W$”-estimate $y_A$).
2.1. Should the estimates \( ^{S}r_{i} = f_{S}(z_{A}) \) and \( ^{S}r_{i} = f_{S}(z_{D}) \) be different?

The computation of \( ^{S}r_{i} \) from \( z_{D} \) should be an equally simple task as Eq. 10:

\[
^{S}R_{i} = (^{D}R_{i} \times [Z_{D} + 1])
\]

That is:

\[
(^{S}r_{i} \pm ^{S}\varepsilon_{i}) = (^{D}R_{i} \times [(Z_{D}^{(Mtd-1)} \pm Z_{\varepsilon_{D}}^{(Mtd-1)}) + 1])
\]

The uncertainty-factor of evaluating \( ^{S}R_{i} \) from \( Z_{D} \) could be shown to be decided as:

\[
[U]^R_{z_{D}} = \left| (Z_{D}/[Z_{D} + 1]) \right| = \left| (^{S}R_{i} - ^{D}R_{i})/^{S}R_{i} \right| \equiv \left( ^{S}R_{i}/^{D}R_{i} \right) < 1
\]

and in the present known case): \([U]^{R}_{z_{D}} = (1/7)^{R}_{A} = 1/8.9671\); and thus (cf. Eq. 4 or so) the uncertainty:

\[
^{S}\varepsilon_{i} = ([U]^{R}_{z_{D}} \times Z_{\varepsilon_{D}}^{(Mtd-1)}) = (Z_{\varepsilon_{D}}^{(Mtd-1)}/8.9671)
\]

The finding here (cf. Eq. 4d///) is really in corroboration with the previous report\(^{17,19}\) that estimated sample ratios \( ^{S}r_{i}^{(Lab1)}, ^{S}r_{i}^{(Lab2)} \ldots \) should better represent the sample (\( S \)) and be more closely intercomparable than the corresponding \( \delta \)-estimates \( z_{D}^{(Lab1)}, z_{D}^{(Lab2)} \ldots \). Moreover, as (cf. Eq. 4E///): \( Z_{\varepsilon_{D}}^{(Mtd-1)} = 8.967 \times Z_{\varepsilon_{A}}^{(Mtd-1)} \); Eq. 4d/// should be equivalent to Eq. 4d. That is, irrespective of whether the path chosen is Eq. 10 or Eq. 10a, the \textbf{Mtd-1} specific uncertainty \( ^{S}\varepsilon_{i}^{(Mtd-1)} \) should be the one and the same:

\[
^{S}\varepsilon_{i}^{(Mtd-1)} = (Z_{\varepsilon_{D}}^{(Mtd-1)}/8.9671) = Z_{\varepsilon_{A}}^{(Mtd-1)} = \varepsilon_{A} = (u_{S} + u_{W}) = (2 \times G_{u})
\]

Eq. 4d/// further emphasizes the point that a mere change of evaluation path should not cause the desired output (here: \( ^{S}r_{i} \)) to be different.

However, the important finding is that the \textit{differential-to-absolute uncertainty-ratio} as either \( (Z_{\varepsilon_{D}}/Z_{\varepsilon_{A}}) \equiv (^{S}D_{\varepsilon_{D}}/^{S}D_{\varepsilon_{A}}) \) or \( (Z_{\varepsilon_{D}}/\varepsilon_{A}) \equiv (^{S}D_{\varepsilon_{D}}/^{S}W_{\varepsilon_{A}}) \) or even \( (Z_{\varepsilon_{D}}/^{S}\varepsilon_{i}) \equiv (^{S}D_{\varepsilon_{D}}/^{S}\varepsilon_{i}) \) should be >1; and/ or equal to the factor as: \( |(^{S}R_{i}/[^{S}R_{i} - ^{D}R_{i}]| \). That is the \textit{ratio} of possible errors “in any usual IRMS result (i.e. \textit{S/D}-estimate} \( z_{D} \)” and “in any corresponding absolute
estimate (as either “$S/D$” ratio-of-ratios $z_A$ or “$S/W$” ratio-of-ratios $y_A$ or even sample isotopic ratio $\delta ri$)” should, depending only on the difference in isotopic composition (IC) between $S$ and $D$, be prefixed as $>1$; e.g. (here, in the known case [see also Eq. 7a]):

$$\frac{Z_{D_S}}{Z_{D_A}} = \frac{Z_{D_S}}{D_A} = \frac{Z_{D_S}}{S_{D_i}} = \left| \frac{S_{R_i} - D_{R_i}}{S_{R_i}} \right| = 8.9671 \tag{7b}$$

Moreover, all the different “$S/W$” estimates ($y_A$ and $y_\delta$) in Table 1 are translated into the corresponding: (i) “$S/D$” estimates ($z_A$ and $z_\delta$, respectively) and: (ii) also $S_{RT}$-values; and furnished in Table 2, which shows that the estimated error-ratios (cf. columns 7 and 9) are the same as predicted (cf. Eq. 7b). Thus, Table 2 confirms the finding that the results of the evaluations as “(Eq. 9): $Z_A = h_A(Y_A)$”, “(Eqs. 9-10): $S_{RT} = h_S(Z_A) = h_S(h_A(Y_A))” and even “(Eqs. 10a-11): $S_{RT} = h_S(Z_\delta) = h_S(h_\delta(Y_\delta))” should turn out equivalent (i.e. equally well represent the sample-source $S$), and be more accurate (i.e. be better representatives) than the usual IRMS result to be obtained as (Eq. 11): $Z_\delta = h_\delta(Y_\delta)$.

### 3.3.2 Scale conversion with the aid of $Ai$-standards

It is indicated above that the employing of even a single $Ai$-standard (i.e. Mtd-2: $Y_\delta \xrightarrow{A1} Z_\delta \rightarrow S_{R_i}$) should require an $Ai$-measurement, i.e. cause any desired result ($z_\delta$ and, in turn, $S_{R_i}$) to be subject to an additional source of error. Thus, even though the Mtd-3 ($Y_\delta \xrightarrow{A1,A2} Z_\delta$) is believed $11,14,15,18$ to ensure “$z_\delta$” to be more accurate than that to be obtained by the Mtd-2; it has already been clarified elsewhere $17,19$ that “$Y_\delta \xrightarrow{A1} Z_\delta \rightarrow S_{R_i}$” “$Y_\delta \xrightarrow{A1 (or A2)} Z_\delta \rightarrow S_{R_i}$” and “$Y_\delta \rightarrow Z_\delta \rightarrow S_{R_i}$” (i.e. Mtd-3, Mtd-2 and Mtd-1) should yield the least, moderate and most accurate results, respectively. Yet, we may verify, below, the generality of the finding $17,19$ in terms of ratio-of-ratios (i.e.: $Y_A \overset{Ai(s)}{\longrightarrow} Z_A \rightarrow S_{R_i}$) even.
However, it may here be reminded that there is a finite possibility\(^3\) for any \textit{multivariable} result (e.g. “\(y_A\)” or “\(y_δ\)” in Table 1) to turn out to be \textbf{100\%} accurate. Thus, e.g. Eq. 3a or 3a\(^{1/}\) clarifies that the estimate “\(y_A\)” should, even in a case where the corresponding individual measurement-errors be \textit{non-zero} but equal to one another (i.e. even when: \([\Delta S = \Delta W] \neq 0\)), represent the true value “\(Y_A\)” (i.e. “\(D_A = 0\)”, and hence “\(D_δ = 0\)”, should be true). However, measurement-errors can \textit{never} be preset (i.e. “\(D_δ = 0\)” or so cannot be achieved). Thus, “uncertainty” should not be confused with the triviality as “\(D_A = 0\)” or “\(D_δ = 0\)” or so.

We should also keep in mind that, although any measurement-uncertainty as “\(u_S\)” should represent the “\textit{MPVs}” of both random and fractionation errors: \(u_S = (|_{(RAN)}\Delta S| + |_{(SYS)}\Delta S|)\); the \textit{ratio-error} as “\(D_A\)” should practically be governed (cf. Eq. 3a\(^{1/}\) or 3a\(^{1/}\)) by the \textit{random} measurement-errors (as \((RAN)\Delta S\) and \((RAN)\Delta W\)) only. Thus the ratio-uncertainty (\(\varepsilon_A\)), although needs to be experimentally established under the investigating lab’s “\textit{IPECs}” (cf. Eq. 4a\(^{1/}\)), is expressed below as: \(\varepsilon_A \approx (RAN)u_S + (RAN)u_W\). Moreover, the formula “\(\varepsilon_A = 2^Gu\)” (cf. Eq. 4a\(^{1/}\)) should in the present context refer to “\(G^u\)” as the fractionation \textit{corrected} measurement uncertainty, and signify that “\(G^u = (RAN)u_S = (RAN)u_W\)” ; or (if applicable) “\(G^u = (RAN)u_{A1} = (RAN)u_{A2} = (RAN)u_W\)”.

3.3.2.1 \textbf{Mtd-2: use of single} \textit{Ai}-standard (A1)

\begin{itemize}
  \item 1. Scale conversion of \textit{ratio-of-ratios} \(Y_A \xrightarrow{A1} Z_A\)
\end{itemize}

Let’s, like “\(Y_A\)”, denote the \textit{auxiliary} variable as “\(Y_1A\)”, i.e.: \(Y_1A = (A1\, R_i/W_i)\). Then the required formula “\(Z_A = f_A(Y_A, Y_1A)\)” can, like Eq. 9, be derived as follows:

\[
Z_A = \left(\frac{S_{R_i}}{D_{R_i}}\right) = \left(\frac{S_{R_i} \times \frac{W_{R_i}}{A1R_i} \times \frac{A1\, R_i}{D_{R_i}}}{Y_1A}\right) = \left(\frac{Y_A \times C1_A}{Y_1A}\right) = \left(\frac{Y_A \times [C\delta + 1]}{Y_1A}\right) \quad (9a)
\]

That is, in terms of estimates:

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\[
(z_{A}^{(\text{Mtd-2})} \pm Z_{\varepsilon A}^{(\text{Mtd-2})}) = (|y_{A} \pm \varepsilon_{A}| \times |C_{1A} + 1|)/|y_{1A} \pm \varepsilon_{1A}) \quad (9a^{'})
\]

where \(C_{1A}\) is the known \(A\) vs. \(D\) calibration constant (i.e.: \(C_{1A} = ([^{14}R_{p}^{D}R_{i}] - 1) = [C_{1A} - 1]\)); and “\(\varepsilon_{A}\) and \(\varepsilon_{1A}\)” represent the lab-established uncertainties of the estimates “\(y_{A}\) and \(y_{1A}\)”, respectively; i.e. (cf. Eq. 4a’): \(\varepsilon_{A} \approx (\text{RAN})u_{S} + (\text{RAN})u_{W}\), or (cf. Eq. 4a’): \(\varepsilon_{A} = ([U_{F}]_{A} \times G_{u}) = 2^{G_{u}}\); and thus: \(\varepsilon_{1A} \approx (\text{RAN})u_{A1} + (\text{RAN})u_{W}\), and/or: \(\varepsilon_{1A} = (Y_{1}[U_{F}]_{A} \times G_{u}) = 2^{G_{u}}\).

However, Eq. 9a could be shown to belong, like Eq. 9, to the F.1 family. That is, even Eq. 9a specific individual variation-rates should be invariable (cf. Eq. 5): \(M_{Y_{A}}^{Z_{A}} = 1\), and: \(M_{Y_{1A}}^{Z_{A}} = -1\). Therefore, the uncertainty \(Z_{\varepsilon_{A}}^{(\text{Mtd-2})}\) should be decided as (cf. Eq. 4):

\[
Z_{\varepsilon_{A}}^{(\text{Mtd-2})} = \sum_{i=1}^{2} (|M_{i}^{Z_{A}}| \times \varepsilon_{i}) = [(|M_{Y_{A}}^{Z_{A}}| \times \varepsilon_{A}) + (|M_{Y_{1A}}^{Z_{A}}| \times \varepsilon_{1A})] = (\varepsilon_{A} + \varepsilon_{1A}) \quad (4f)
\]

Or (recollecting that [cf. e.g. Eq. 4d’’’]: \(Z_{\varepsilon_{A}}^{(\text{Mtd-1})} = \varepsilon_{A} = S_{ \varepsilon_{i}}^{(\text{Mtd-1})} = 2^{G_{u}}\)):

\[
Z_{\varepsilon_{A}}^{(\text{Mtd-2})} = (\varepsilon_{A} + \varepsilon_{1A}) = (Z_{\varepsilon_{A}}^{(\text{Mtd-1})} + \varepsilon_{1A}) \quad (4f^{'})
\]

Or (in terms of “\(G_{u}\)’’):

\[
Z_{\varepsilon_{A}}^{(\text{Mtd-2})} = (\varepsilon_{A} + \varepsilon_{1A}) = ([U_{F}]_{A} \times G_{u}) + ([Y_{1}[U_{F}]_{A} \times G_{u}] = [(U_{F}]_{A} + Y_{1}[U_{F}]_{A}) \times G_{u}] = (2 + 2) \times G_{u} = (Z_{[U_{F}]_{A}}^{(\text{Mtd-2})}) \times G_{u}) = (2 \times [2 \times G_{u}]) = (2 \times Z_{\varepsilon_{i}}^{(\text{Mtd-1})}) \quad (4f^{'})
\]

Thus, even in terms of ratio-of-ratios, the Mtd-1 (i.e. “\(Z_{A} = h_{A}(Y_{A})\)” that should yield more accurate results than the Mtd-2 (“\(Z_{A} = f_{A}(Y_{A}, Y_{1A})\)”).

\[\cdot 1.1. \] Evaluation of \(S_{R_{i}}\)-value \((z_{A}^{(\text{Mtd-2})} \rightarrow S_{R_{i}}^{(\text{Mtd-2})})\)

The formula \(S_{R_{i}} = f_{S}(Z_{A})\)” (cf. Eq. 10) cannot be different for different scale conversion methods. Thus, as already clarified (cf. Eq. 4d’’’): \(S_{ \varepsilon_{i}}^{(\text{Mtd-1})} = Z_{\varepsilon_{A}}^{(\text{Mtd-1})}\), the estimates \(S_{R_{i}}^{(\text{Mtd-2})}\) and \(Z_{A}^{(\text{Mtd-2})}\) should also be equally accurate: \(S_{ \varepsilon_{i}}^{(\text{Mtd-2})} = Z_{\varepsilon_{A}}^{(\text{Mtd-2})}\). In other words, even the findings here (i.e. which are based on the considerations of ratio-of-ratios) are in conformity with the
previously pointed out fact\textsuperscript{17,19} that the aid of any single $A_i$-standard should cause the result (here: $z_A$, or: $S_r$) to be rather inaccurate: $Z_{E_A}(\text{Mtd-2}) > Z_{E_A}(\text{Mtd-1})$, or: $S_{E}^{(\text{Mtd-2})} > S_{E}^{(\text{Mtd-1})}$.

2. $\delta$-Scale conversion ($Y_\delta \xrightarrow{A_1} Z_\delta$)

“$Z_\delta = f_\delta(Y_\delta, Y1_\delta)$” should have description as:\textsuperscript{17,19}

$$Z_\delta = \left(\frac{S R_i}{D R_i} \right) - 1 = \left[ \frac{S R_i}{W R_i} \right] \times \frac{A_1 R_i}{A_1 R_i} - 1 = \left[ \frac{[Y_\delta + 1] \times [C1_\delta + 1]}{Y1_\delta + 1} - 1 \right]$$

(11a)

And, therefore:

$$(Z_{E_\delta}^{(\text{Mtd-2})} \pm Z_{E_\delta}^{(\text{Mtd-2})}) = \left( [Y_\delta \pm \varepsilon_\delta] \times [C1_\delta + 1] \right) / (Y1_\delta \pm \varepsilon1_\delta)$$

(11a')

However, any “$Y_\delta = ([S R_i]^W R_i] - 1$” type of relationship should a member of the F.2 family; i.e. (cf. Eqs. 4a' and 7a): $\varepsilon_\delta = \left( \frac{S R_i}{S R_i - W R_i} \right) \times \varepsilon_A = \left( \frac{S R_i}{S R_i - W R_i} \right) \times 2 \times G u$; and (one can verify)

that: $\varepsilon1_\delta = \left( \frac{A_1 R_i}{A_1 R_i - W R_i} \right) \times \varepsilon1_A = \left( \frac{A_1 R_i}{A_1 R_i - W R_i} \right) \times 2 \times G u$.

Moreover, as already shown elsewhere\textsuperscript{17}, Eq. 11a should be characterized by the parameters (cf. Eq. 5) as: $M_{Y_\delta}^{Z_{E_\delta}} = \frac{S R_i - W R_i}{S R_i - D R_i}$; and: $M_{Y1_\delta}^{Z_{E_\delta}} = -\frac{S R_i - W R_i}{A_1 R_i - W R_i}$; and thus (cf. Eq. 4, or so):\textsuperscript{6}

$$Z_{E_\delta}^{(\text{Mtd-2})} = \sum_{i=1}^{2} \left( \left[ M_{Y_\delta}^{Z_{E_\delta}} \right] \times \varepsilon_i \right) = \left( \left[ M_{Y_\delta}^{Z_{E_\delta}} \right] \times \varepsilon_\delta \right) + \left( \left[ M_{Y1_\delta}^{Z_{E_\delta}} \right] \times \varepsilon1_\delta \right) = \left( \left[ \frac{S R_i}{S R_i - D R_i} \right] \times \varepsilon_A \right) +$$

$$\left( \left[ \frac{S R_i}{S R_i - D R_i} \right] \times \varepsilon1_A \right) = \left( \left[ \frac{S R_i}{S R_i - D R_i} \right] \times \left[ \varepsilon_A + \varepsilon1_A \right] \right) = \left( \left[ \frac{S R_i}{S R_i - D R_i} \right] \times Z_{E_A}^{(\text{Mtd-2})} \right)$$

(4g)

Or, even for: $\varepsilon_A = \varepsilon1_A = 2G u$ (cf. further Eq. 4f').
\[ Z_{\epsilon_\delta}^{(\text{Mtd-2})} = \left( \frac{S_{R_i}}{S_{R_i} - D_{R_i}} \right) \times \left[ \epsilon_A + \epsilon_{1\text{A}} \right] = \left( \frac{S_{R_i}}{S_{R_i} - W_{R_i}} \right) \times 4 \times G_u = \left[ \left( \frac{S_{R_i}}{S_{R_i} - W_{R_i}} \right) \times Z_{\epsilon_A}^{(\text{Mtd-2})} \right] \]

\[ = (8.967 \times Z_{\epsilon_A}^{(\text{Mtd-2})}) = (2 \times [8.967 \times 2 \times G_u]) = (2 \times Z_{\epsilon_\delta}^{(\text{Mtd-1})}) \]  

That is, “\(Z_{\epsilon_\delta}^{(\text{Mtd-2})}\)” can turn out even twice more erroneous than “\(Z_{\epsilon_\delta}^{(\text{Mtd-1})}\)”.

### 2.1. Conversion: \(Z_{\delta}^{(\text{Mtd-2})} \rightarrow S_{r_i}^{\text{Mtd-2}}\)

As “\(Z_{\delta} \rightarrow S_{r_i}\)” conversion formula cannot vary for varying the scale conversion method, it could here again be shown that (cf. Mtd-1, viz. Eq. 4d/// or Eq. 7b or so):  
\[ S_{\epsilon_i}^{(\text{Mtd-2})} = Z_{\epsilon_A}^{(\text{Mtd-2})} = \left( \frac{Z_{\epsilon_\delta}^{(\text{Mtd-2})}}{\left| \left( \frac{S_{r_i} - D_{r_i}}{S_{r_i}} \right)^{S_{r_i}} \right|} \right) = \left( \frac{Z_{\epsilon_\delta}^{(\text{Mtd-2})}}{8.9671} \right) \]

\[ (9b) \]

That is, in terms of estimates:

\[ Z_A^{(\text{Mtd-3})} = Z_{\epsilon_A}^{(\text{Mtd-3})} = \left[ y_A \pm \varepsilon_A \right] \times \frac{C_{1\delta} - C_{2\delta}}{y_1A \pm \varepsilon_{1A}} \]  

\[ (9b') \]

where:: \(C_{2\delta} = \left( \frac{A_{2\delta} - D_{r_i}}{A_{2\delta}} \right) - 1 = \left( \frac{A_{2\delta} - D_{r_i}}{A_{2\delta}} \right) - 1\); i.e. \(C_{2\delta}\) is the “\(A_2\) vs. \(D\)” calibration constant; \(Z_{\epsilon_A}^{(\text{Mtd-3})}\) represents the uncertainty of (the present method-specific estimate) \(Z_A^{(\text{Mtd-3})}\); and \(\varepsilon_{2A}\) stands (like \(\varepsilon_A\) and \(\varepsilon_{1A}\)) for the lab-established uncertainty of the absolute estimate “\(y_{2A}\)”.

3.3.2.2 **Mtd-3**: aid of two different \(Ai\)-standards (\(A_1, A_2\))

#### 1. Scale conversion of ratio-of-ratios \(Y_A \xrightarrow{A_1,A_2} Z_A\)

Let: \(Y_{2A} = \left( \frac{A_{2\delta} - D_{r_i}}{A_{2\delta}} \right) \). Then the relation “\(Z_A = f_A(Y_A, Y_{1A}, Y_{2A})\)” can, like Eq. 9a, be derived as follows:

\[ Z_A = \left( \frac{S_{r_i}}{D_{r_i}} \right) = \left( \frac{S_{r_i}}{W_{r_i}} \times \frac{W_{r_i}}{A_{1\delta} - A_{2\delta}} \times \frac{A_{1\delta} - A_{2\delta}}{D_{r_i}} \right) \]

\[ = \left( Y_A \times \frac{C_{1\delta} - C_{2\delta}}{Y_{1A} - Y_{2A}} \right) = Y_A \times \frac{C_{1\delta} - C_{2\delta}}{Y_{1A} - Y_{2A}} \]

\[ (9b) \]

That is, in terms of estimates:

\[ (Z_A^{(\text{Mtd-3})} = Z_{\epsilon_A}^{(\text{Mtd-3})} = \left[ y_A \pm \varepsilon_A \right] \times \frac{C_{1\delta} - C_{2\delta}}{y_{1A} \pm \varepsilon_{1A}} \]  

\[ (9b') \]

where:: \(C_{2\delta} = \left( \frac{A_{2\delta} - D_{r_i}}{A_{2\delta}} \right) - 1 = \left( \frac{A_{2\delta} - D_{r_i}}{A_{2\delta}} \right) - 1\); i.e. \(C_{2\delta}\) is the “\(A_2\) vs. \(D\)” calibration constant; \(Z_{\epsilon_A}^{(\text{Mtd-3})}\) represents the uncertainty of (the present method-specific estimate) \(Z_A^{(\text{Mtd-3})}\); and \(\varepsilon_{2A}\) stands (like \(\varepsilon_A\) and \(\varepsilon_{1A}\)) for the lab-established uncertainty of the absolute estimate “\(y_{2A}\)”.

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Further, Eq. 9b could be seen to be characterized by the parameters (cf. Eq. 5) as:

\[ M_{Y_A}^{Z_A} = 1; \text{ but: } M_{Y_{1A}}^{Z_A} = -(41R_i/[41R_i - 42R_i]) \text{ and: } M_{Y_{2A}}^{Z_A} = (42R_i/[41R_i - 42R_i]). \]

That is (even though both Eq. 9 and Eq. 9a belong to the F.1 model family) Eq. 9b is a member of the F.2 family. Therefore, the choice of even (the present ratio-of-ratios’ based formula) Eq. 9b as the IRMS evaluation model should be risky. Clearly, the reason is that the uncertainty “\( Z_\varepsilon_{A(Mtd-3)} \)” should not only be higher (than either “\( Z_\varepsilon_{A(Mtd-1)} \)” or “\( Z_\varepsilon_{A(Mtd-2)} \)” but also be dependent on the \( A_i \)-standards to be used (cf. Eq. 4 or so):

\[
Z_\varepsilon_{A(Mtd-3)} = \left[ (|M_{Y_A}^{Z_A}| \times \varepsilon_A) + (|M_{Y_{1A}}^{Z_A}| \times \varepsilon_1A) + (|M_{Y_{2A}}^{Z_A}| \times \varepsilon_2A) \right] \\
= \left[ \varepsilon_A + \left( \frac{41R_i}{41R_i - 42R_i} \right) \times \varepsilon_1A \right] + \left( \frac{42R_i}{41R_i - 42R_i} \times \varepsilon_2A \right) \tag{4h}
\]

Or (for [cf. e.g. Eq. 4a] \( \varepsilon_A = \varepsilon_1A = \varepsilon_2A = 2^G u \)):

\[
Z_\varepsilon_{A(Mtd-3)} = \left( 2 \times \left( 1 + \left| \frac{41R_i + 42R_i}{41R_i - 42R_i} \right| \right) \times ^G u \right) = (Z[U_F]_A^{(Mtd-3)} \times ^G u) \tag{4h'}
\]

Clearly, \( Z[U_F]_A^{(Mtd-3)} \) should be >4 (and hence cause: \( Z_\varepsilon_{A(Mtd-3)} > Z_\varepsilon_{A(Mtd-2)} \)); i.e. “\( Z_\varepsilon_{A(Mtd-3)} \)” should be more erroneous than even “\( Z_\varepsilon_{A(Mtd-2)} \)”.

\( (Z_\varepsilon_{A(Mtd-3)} \rightarrow S_{R_i(Mtd-3)}) \) Conversion

The formula “\( S_{R_i} = f_S(Z_{A}) \)” is fixed (cf. Eq. 10). Thus, like other methods (cf. e.g. Eq. 4d), it could be shown that: \( S_{\varepsilon_i}^{(Mtd-3)} = Z_{\varepsilon_i}^{(Mtd-3)} \).

\( \delta \)-Scale conversion (\( Y_\delta \xrightarrow{A1,A2} Z_\delta \))

“\( Z_\delta = f_\delta(Y_\delta,Y_1\delta,Y_2\delta) \)” should, like Eq. 9b, take the description as:

\[
Z_\delta = \left( \frac{S_{R_i}}{D_{R_i}} - 1 \right) = \left[ \frac{S_{R_i}}{W_{R_i}} \times \frac{W_{R_i}}{A1}_{R_i - A2}_{R_i} \times \frac{42R_i}{41R_i - 42R_i} \right] - 1
\]
Therefore:

\[
(z_\delta^{(Mtd-3)} \pm \varepsilon_\delta^{(Mtd-3)}) = \left([Y_\delta \pm \varepsilon_\delta] \times \frac{C_{1\delta} - C_{2\delta}}{[Y1_\delta \pm \varepsilon1_\delta] - [Y2_\delta \pm \varepsilon2_\delta]}\right)
\]

(11b')

However, it should be pointed out that, although the literature\textsuperscript{14,15} based “\(Z_\delta = f_\delta(Y_\delta, Y1_\delta)\)” formula is identical with Eq. 11a, the commonly used “\(Z_\delta = f_\delta(Y_\delta, Y1_\delta, Y2_\delta)\)” formula is as follows:\textsuperscript{14,15}

\[
Z_\delta = \left([Y_\delta - Y2_\delta] \times \frac{C_{1\delta} - C_{2\delta}}{Y1_\delta - Y2_\delta}\right) + C_{2\delta}
\]

(12)

However, it is already clarified elsewhere\textsuperscript{17,19} that, as “\(C_{1\delta}\) and \(C_{2\delta}\)” are constants and “\(Z1_\delta\) and \(Z2_\delta\)” are variables (and thus, as: \(\left(\langle 41 R_i^D R_i \rangle \times \langle 42 R_i^W R_i \rangle \right) \neq \left(\langle 41 R_i^W R_i \rangle \times \langle 42 R_i^D R_i \rangle \right)\)); the right side of Eq. 12 cannot be reduced to the left side “\((\langle 5 R_i^D R_i \rangle - 1)\)”, i.e. Eq. 12 cannot represent any possible form of the “\(Y_\delta \xrightarrow{A1A2} Z_\delta\)” conversion process.

Anyway, Eq. 11b should, like any simple \(\delta\)-expression (e.g. Eq. 2), belong to the F.2 model family. Thus, recollecting that (cf. Eqs. 4a' and 7a): \(\varepsilon_\delta = \left(\left|\langle 4 R_i^D R_i \rangle \times \langle 5 R_i^W R_i \rangle \right| \times \varepsilon_A\right), \varepsilon1_\delta = \left(\left|\langle 41 R_i^D R_i \rangle \times \langle 4 R_i^W R_i \rangle \right| \times \varepsilon_A\right)\); the uncertainty of evaluation \(Z_{\varepsilon_\delta^{(Mtd-3)}}\) could be shown to be decided as (cf. Eq. 4 and also Eq. 4h):\textsuperscript{17,19}

\[
Z_{\varepsilon_\delta^{(Mtd-3)}} = \left([M_{Y_\delta}^{Z\delta}] \times \varepsilon_\delta\right) + \left([M_{Y1_\delta}^{Z\delta}] \times \varepsilon1_\delta\right) + \left([M_{Y2_\delta}^{Z\delta}] \times \varepsilon2_\delta\right)
\]

\[
= \left(\frac{S R_i^D R_i - W R_i}{S R_i^D R_i}\right) \times \varepsilon_\delta + \left(\frac{-S R_i \times (A1 R_i^D R_i - W R_i)}{(A1 R_i - A2 R_i) \times (S R_i^D R_i)}\right) \times \varepsilon1_\delta + \left(\frac{-S R_i \times (A2 R_i^D R_i - W R_i)}{(A1 R_i - A2 R_i) \times (S R_i^D R_i)}\right) \times \varepsilon2_\delta
\]

\[
= \left(\frac{S R_i}{S R_i^D R_i}\right) \times \varepsilon_A + \left(\frac{A1 R_i}{A1 R_i - A2 R_i}\right) \times \varepsilon1_A + \left(\frac{A2 R_i}{A1 R_i - A2 R_i}\right) \times \varepsilon2_A
\]
\[
\begin{align*}
\text{Or, even for: } & \varepsilon_4 = \varepsilon_1 = \varepsilon_2 = 2^G u \quad \text{(see also Eq. 4h')} \\
& Z_{\varepsilon_\delta}^{(Mtd-3)} = \left( \frac{S_{R_i}}{S_{R_i} - D_{R_i}} \right) \times 2 \times G u \times \left[ 1 + \frac{A_1 R_i + A_2 R_i}{A_1 R_i - A_2 R_i} \right] \\
& = \left( \frac{S_{R_i}}{S_{R_i} - D_{R_i}} \right) \times 2 \times \left[ 1 + \frac{A_1 R_i + A_2 R_i}{A_1 R_i - A_2 R_i} \right] \times G u \\
& = \left( \frac{S_{R_i}}{S_{R_i} - D_{R_i}} \right) \times Z^{[UF]_A^{(Mtd-3)}} \times G u = \left( Z^{[UF]_\delta^{(Mtd-3)}} \times G u \right) \\
\end{align*}
\]

It is clarified above that \(Z^{[UF]_A^{(Mtd-3)}}\) should itself be >4. Therefore, for present known case, \(Z^{[UF]_\delta^{(Mtd-3)}}\) should be as high as >36; i.e.: \(Z_{\varepsilon_\delta}^{(Mtd-3)} = (36 \times G u)\).

Moreover, it is already exemplified elsewhere\(^{17}\) that \textit{any method specific error-ratio} as \(Z_{D_\delta/S_{D_i}}\) does turn out to be a constant equaling to \(\left\lvert \left( \frac{S_{R_i}}{S_{R_i} - D_{R_i}} \right) \right\rvert\).

However, the findings: (i) \(Z_{\varepsilon_4}^{(Mtd-1)} < Z_{\varepsilon_4}^{(Mtd-2)} < Z_{\varepsilon_4}^{(Mtd-3)}\) (cf. the different \textit{ratio-of-ratios} based scale conversion methods as Eqs. 9, 9a and 9b); (ii) \(Z_{\varepsilon_\delta}^{(Mtd-1)} < Z_{\varepsilon_\delta}^{(Mtd-2)} < Z_{\varepsilon_\delta}^{(Mtd-3)}\) (cf. the \(\delta\)-scale conversion methods as Eq. 11, 11a and 11b); and: (iii) \(S_{\varepsilon_i}^{(Mtd-1)} < S_{\varepsilon_i}^{(Mtd-2)} < S_{\varepsilon_i}^{(Mtd-3)}\) (i.e. in terms of even sample isotopic ratio obtained by either Eq. 10 or 10a); should represent the simple fact that the uncertainty of any evaluation should be proportional to the number of individual measurements to be involved. In other words, the claim\(^{11,14,15,18}\) that \(Z_{\varepsilon_\delta}^{(Mtd-2)} < Z_{\varepsilon_\delta}^{(Mtd-3)}\) can never represent any real world event.

What is however significant is that, \textit{irrespective} of scale conversion method, the \textit{absolute} estimate (either \(Z_A\) or \(Z_{S_{R_i}}\)) is shown to be \textbf{more} accurate than the \(\delta\)-estimate \(Z_\delta\). Furthermore, the \textit{ratio} of \(\delta\)-to-\textit{absolute} errors (i.e. ratio of achievable \(\delta\)-to-absolute
accuracies and/or uncertainty factors) should, for using any scale conversion method, be a constant as “\( |(\delta R_i/[\delta R_i - D R_i])| \); cf. Eq. 7b”. That is the said constant (error-ratio) should be prefixed by only the sample “\( S \)” and the reference-standard “\( D \)” involved. Therefore, if “\( \delta R_i \)” should happen to be very close to “\( D R_i \)”, then the evaluated absolute estimate (\( Z_A \), or even \( \delta r_i \)) should be highly accurate, but the corresponding \( \delta \)-estimate “\( z_\delta \)” might turn out to be highly erroneous.

CONCLUSIONS

The above study clarifies that even simply specifying a mathematical relationship “\( Y_d = f_d(X_i) \)” should mean evaluating the proposed function “\( f_d \)” as a model for any purpose whatever. The reason is, as clarified above, that the “\( f_d \)” specific individual and, hence the collective, input-to-output variation-rates (\( M_i^d \) and \( [UF]_d \), respectively) should also thus get specified: 
\[
M_i^d = \left( \frac{\partial Y_d}{\partial X_i} \right) \left( \frac{X_i}{Y_d} \right), \quad \text{with: } i = 1, 2 \ldots N; \text{ and: } [UF]_d = \sum_{i=1}^{N} \left| M_i^d \right|.
\]

In other words, it is signified above that any conceivable input-output variation should, in nature, be purely systematic (i.e. “\( f_d \)” specific). It is thus elaborated that, for a given variation (viz.) “\( \delta u = 1\% \)” in the measurable and/or input variables (\( X_i \), with: \( i = 1, 2 \ldots N \)), the possible maximum value (\( \epsilon_d \)) of output-variation can ‘a priori’ be ascertained as: 
\[
\epsilon_d = ([UF]_d \times \delta u) = [UF]_d \%.
\]
Clearly, the smaller should be the “[\( UF \)]_d” value (viz.: “[\( UF \)]_d \ll 1”) the better suitable the model “\( f_d \)” be for any purpose whatsoever.

Depending upon the exact description of “\( f_d \)” one or the other “\( M_i^d \)”, and hence “[\( UF \)]_d”, might turn out to be decided by the system-specific \( X_i \)-value(s). However, the above study supports the classification of all conceivable models into two families: (i) all models but for each of which cases “[\( UF \)]_d” should be independent of “system (viz. \( X_i \))” be a single family
The significance of the model-families is that, while the F.1 modeling/output accuracy (and hence the accuracy of driving any corresponding model based machine) should solely be decided by achievable $X_i$-measurement accuracies ($\varepsilon_d^{(F.1)} = \sum_{i=1}^{N} (|M_i^d| \times u_i) = \sum_{i=1}^{N} u_i$; and/or $\varepsilon_d^{(F.1)} = [N \times G_u]$, with: $u_1 = u_2 = \ldots = u_N = G_u$); the achievable F.2 modeling accuracy is shown to be governed as: $\varepsilon_d^{(F.2)} = f_d(X_i, u_i)$.

Clearly, any F.2 model should generally be risky to employ in practice. This is because that, for specific $X_i$-value(s), the possible (net) $X_i$-measurement-error might happen to even be reduced in the process of defining the output-error (and thus may offer an unexpected control over a corresponding output based machine). However, for certain other possible value(s) of system defining $X_i(s)$, the net input-error might even be enhanced as the output-error (i.e. may lead a corresponding machine to disastrous consequences).

A simple example of the F.1 models is the elementary mathematical expression of any absolute ratio (viz.: $Y_A = \left[\frac{S_i R_i}{W_i R_i}\right]$, with “$S_i$ and $W_i$” representing the well-known IRMS sample $S$ and working-lab-reference $W$ specific $i^{th}$ isotopic abundance-ratios, respectively); and that of the F.2 models is (any differential “$\delta$” ratio): $Y_\delta = (\left[\frac{S_i R_i}{W_i R_i}\right] - 1) = (Y_A - 1)$. However, what is important is that, for any specific case of $S$ and $W$ measurements, the ratio of the possible true-errors $D_A$ and $D_\delta$ (and hence of the uncertainties, $\varepsilon_A$ and $\varepsilon_\delta$, of the evaluated unknown absolute and $\delta$-ratios, $y_A$ and $y_\delta$, respectively) should be prefixed as:

$$
\left(\frac{D_\delta}{D_A}\right) = \left(\frac{\varepsilon_\delta}{\varepsilon_A}\right) = \left(\frac{[UF]_\delta}{[UF]_A}\right) = \left|\frac{\frac{S_i R_i}{W_i R_i} - 1}{\frac{S_i R_i}{W_i R_i}}\right|
$$
Further, \( |S_R_i - W_R_i| \to 0 \) is a requirement for IRMS measurement. Therefore, any \( \delta \)-estimate (\( y_{\delta} \)) should clearly be *more erroneous* than the corresponding absolute estimate (\( y_A \)) and, at least for a case of very close isotopic compositions (ICs) of \( S \) and \( W \), turn out *highly* erroneous.

Again, the \( \delta \)-scale conversion: \( y_{\delta} \to z_{\delta} \) (with: \( z_{\delta} = [(\delta_r_i / D_R_i) - 1] = [z_A - 1] \); and “\( D \)” as the recommended reference-standard) is unavoidable for *reporting* any IRMS result (\( \delta \)-estimate).

However, the scale conversion of ratio-of-ratios “\( y_A \to z_A \)” is shown above to rather be a simpler task. Further, “\( D R_i \)” should be known. Therefore, the *sample isotopic abundance ratio* (\( \delta_r_i \)) can also be evaluated, i.e. from “\( z_{\delta} \)” as: \( \delta_r_i \pm \delta_{\epsilon_i} = (D R_i \times [(z_{\delta} \pm z_{\epsilon_{\delta}}) + 1]) \); and/ or from “\( z_A \)” as: \( \delta_r_i \pm \delta_{\epsilon_i} = (D R_i \times z_A \pm z_{\epsilon_A}) \).

However, the above study supplements the previously reported fact\(^{17,19} \) that the scale conversion with the aid of any single auxiliary (\( A_i \)) standard should, though help avoid the requirement of calibrating “\( W \)” , cause the desired result (viz. \( \delta \)-estimate “\( z_{\delta} \)” , or even any *absolute* estimate “\( z_A \)” or “\( S_r_i \)” ) to be more erroneous than that to be obtained by the \( W \)-calibration method. In other words, the claim\(^{11,14,15,18} \) that the process “\( (Y_{\delta} \xrightarrow{A_1} Z_{\delta}) \)”, rather than “\( (Y_{\delta} \xrightarrow{A_1} Z_{\delta}) \)”, should ensure “\( z_{\delta} \)” to be accurate is simply baseless. The employing of increasing number of \( A_i \)-standards should require increasing number of measurements, and hence subject any scale converted data (either \( z_{\delta} \) or \( z_A \) ) to increasing number of different measurement-errors.

Moreover, the present study emphasizes the fact\(^{17} \) that, for whatsoever *method* might be chosen, the ratio of “\( \delta \)-to-absolute” scale conversion uncertainties (i.e. “\( Z_{\epsilon_{\delta}} / Z_{\epsilon_A} \)” , or “\( Z_{\epsilon_{\delta}} / S_{\epsilon_i} \)” ) and/ or the ratio of possible true-errors (i.e.: “\( Z_{D_{\delta}} / Z_{D_A} \)” , or “\( Z_{D_{\delta}} / S_{\epsilon_i} \)” ) should be *prefixed* by, only, the sample \( S \) and the standard \( D \) involved:
Again, “\( D_i \approx S_i \approx W_i \)” is a basic requirement for any IRMS evaluation. Thus, the \( \delta \)-estimate \( z_\delta \) might even turn out, i.e. for a possible case of very similar ICs of \( S \) and \( D \), misleading. This further emphasizes the fact\(^{17,19} \) that different possible absolute lab-results (either ratio-of-ratios: \( z_A^{(\text{Lab-1})}, z_A^{(\text{Lab-2})} \ldots \); or sample isotopic ratios: \( S_{i}^{(\text{Lab-1})}, S_{i}^{(\text{Lab-2})} \ldots \)) should more accurately represent the sample “\( S \)” and/ or more closely be intercomparable than the corresponding \( \delta \)-estimates (\( z_\delta^{(\text{Lab-1})}, z_\delta^{(\text{Lab-2})} \ldots \)).

Essentially, the basic IRMS evaluation principle “\( Z_\delta = f_\delta(Y_\delta) \)” is shown to be worth reformulating as either “\( Z_\delta = f_\delta(Y_\delta) \)” or simply as “\( Z_A = f_A(Y_A) \)”.

Of course, it should generally be difficult to calibrate any possible lab-specific working-reference (\( W \)). Therefore, for scale conversion, the aid of a suitable \( A_i \)-standard (and hence the allowance of certain additional uncertainty in the result) should also be unavoidable. Yet, as shown above, the replacement of the \( \delta \)-ratio based evaluation process “\( Y_\delta \rightarrow Z_\delta \)” by the absolute-ratio based evaluation process as either “\( Y_\delta \rightarrow Z_\delta \rightarrow S_i \)” or simply “\( Y_A \rightarrow Z_A \)” should help avoid the reporting of (relatively or even highly) erroneous \( \delta \)-results. Moreover, either “\( Y_A \rightarrow Z_A \)” or “\( Y_A \rightarrow Z_A \)” should mean simplification of required computations.
REFERENCES

1. McKinney, C. R., McCrea, J. M., Epstein, S, Allen H. A. & Urey U. C. Rev. Sci. Instum. 21, 724 (1950).
2. IAEA-TECDOC-825, IAEA, Vienna (1995).
3. Datta, B. P. arXiv:0712.1732.
4. ISO, Guide to the Expression of Uncertainty in Measurement (1995).
5. Scarborough J. B. Numerical Mathematical Analysis, Oxford & IBH Publishing Co., Kolkata (1966).
6. Datta, B. P. arXiv:0909.1651.
7. IAEA-TECDOC-1247, IAEA, Vienna (2001).
8. Kerstel, E. R. Th., Trigt, R. van, Dam, N., Reuss, J. & Meijer, H. A. Anal. Chem. 71, 5297 (1999).
9. Kerstel, E. R. Th. & Gianfrani, L. Appl. Physics B 92, 439 (2008).
10. Coplen T. B. Pure and Appl. Chem. 66, 273 (1994).
11. Coplen T. B., Brand, W. A., Gehre, M., Groning, M., Meijer, H.A., Toman, B. & Verkouteren, R. M. Anal. Chem. 78, 2439 (2006).
12. Verkouteren R. M., Klouda G. A. & Currie L. A. IAEA-TECDOC-825, IAEA, Vienna, 1995, pp. 111-129.
13. Allison, C. E., Francey, R. J. & Meijer H. A. J. IAEA-TECDOC-825, p. 155, IAEA, Vienna (1995).
14. Verkouteren, R. M. & Lee, J. N. Fresenius J. Anal. Chem. 370, 803 (2001).
15. Paul, D., Skrzypek, G. & Forizs, I. Rapid Commun. Mass Spectrom. 21, 3006 (2007).
16. Gonfiantini, R., Stichler, W. & Rozanski, K. *IAEA-TECDOC*-825, p. 13, IAEA, Vienna (1995).

17. Datta, B. P. arXiv:1401.1094.

18. Gonfiantini R. *Nature* **271**, 534 (1978).

19. Datta, B. P. arXiv:1101.0973.

20. Groning, M., Frohlich, K., Regge, P. De & Danesi P. P. INTENDED USE of THE IAEA REFERENCE MATERIALS PART II, p. 5, IAEA, Vienna (2009).

21. Vienna (2009).
Table 1. Possible measured estimates ($\delta r_i^*$ and $\delta r_i^w$, with errors $\Delta r_i$ and $\Delta r_i^w$) of the $^{2}$H/$^{1}$H isotopic standards “IAEA-CH-7 and GISP” (respectively) and the corresponding modeled, i.e. “$S/W$” absolute and differential, estimates ($y_A$ and $y_\delta$; with errors $\Delta y_A$ and $\Delta y_\delta$, respectively)

| LAB No | Example No. | Measured “$S$ or $W$” specific isotopic abundance ratio ($r_i$) (Measurement error $\Delta$) | LAB reflected uncertainty “$u_i$”, (%) | Output estimate “$y_d$” (output-error $\Delta y_d$) | Observed error-ratio $|\Delta y_\delta|/|\Delta y_A|$ |
|--------|-------------|---------------------------------------------------------------------------------------------|--------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1      | 0           | 14.013260 (0)                                                                                   | 12.62076552 (0)                      | -                                             | 1.1103336 (0)                                  | 0.1103336 (0)                                  | 0                  | 0                  |
|        | 1           | 14.01606265 (0.02)                                                                            | 12.62215380 (0.011)                 | 0.02                                          | 1.1104335 (0.009)                              | 0.1104335 (0.009)                              | 10.0634           | 10.0634           |
| 2      | 1           | 14.01157841 (−0.012)                                                                          | 12.62291105 (0.017)                 | 1.1100117 (−0.029)                            | 0.1100117 (−0.029)                            | 10.0634           |
|        | 2           | 14.01424093 (0.007)                                                                            | 12.62240622 (0.013)                 | 1.1102670 (−0.006)                            | 0.1102670 (−0.006)                            | 10.0634           |
| 3      | 3           | 14.01550212 (0.016)                                                                            | 12.61849378 (−0.018)                | 1.1107112 (0.034)                             | 0.1107112 (0.034)                             | 10.0634           |
|        | 4           | 14.01059748 (−0.019)                                                                          | 12.62013448 (−0.005)                | 1.1101781 (−0.014)                            | 0.1101781 (−0.014)                            | 10.0634           |
| 5      | 5           | 14.01013260 (0)                                                                                   | 12.62076552 (0)                      | -                                             | 1.1103336 (0)                                  | 0.1103336 (0)                                  | 0                  | 0                  |
| 2      | 1           | 14.00345072 (−0.07)                                                                            | 12.61079512 (−0.079)                | 1.1104335 (0.009)                              | 0.1104335 (0.009)                              | 10.0634           |
|        | 2           | 13.99869647 (−0.102)                                                                           | 12.61142615 (−0.074)                | 1.1100225 (−0.1280)                            | 0.1100225 (−0.1280)                            | 10.0634           |
| 3      | 3           | 14.00106846 (−0.087)                                                                            | 12.61068981 (−0.08)                 | 1.1102558 (−0.007)                            | 0.1102558 (−0.007)                            | 10.0634           |
|        | 4           | 14.00289019 (−0.074)                                                                           | 12.80688268 (−0.11)                 | 1.1107338 (0.03604)                            | 0.1107338 (0.03604)                            | 10.0634           |
| 5      | 5           | 13.99644409 (−0.12)                                                                            | 12.60814475 (−0.10)                 | 1.1101113 (−0.02002)                          | 0.1101113 (−0.02002)                          | 10.0634           |
Table 2. “Mtd-1” specific scale converted results \( z_A \) and \( z_\delta \) (i.e. corresponding to the possible lab-estimates \( y_A \) and \( y_\delta \), respectively, in Table 1); and also the sample isotopic ratio \( ^8s_{ri} \) obtained by the process as either \( Z_A \rightarrow ^8S_{ri} \) (cf. Eq. 10) or \( Z_\delta \rightarrow ^8S_{ri} \) (cf. Eq. 10a).

| Lab No. | Example No. | Ratio-of-ratios | Differential (\( \delta \)) ratios | (S/D)-error-ratio | \( ^8s_{ri} \)-value | Error ratio |
|---------|-------------|-----------------|-------------------------------|------------------|----------------------|-------------|
|         |             | Estimated (S/W)-ratio “\( y_A \)” | \( (S/D) \)-estimate “\( z_A \)” | \( (S/D) \)-error-ratio | \( (S/D) \)-error-ratio | \( ^8s_{ri} \)-value | Error ratio |
|         |             | \( (S/D) \times 10^2 \) | \( (S/D) \times 10^2 \) | \( (S/D) \times 10^2 \) | \( (S/D) \times 10^2 \) | \( ^8s_{ri} \times 10^5 \) | \( ^8s_{ri} \times 10^5 \) |
|         |             | \( z_A \times 10^2 \) | \( z_A \times 10^2 \) | \( z_A \times 10^2 \) | \( z_A \times 10^2 \) | \( z_A \times 10^2 \) | \( z_A \times 10^2 \) |
| 1       | 0           | 1.1103336 \( \times 10^2 \) | 0.8996700 \( \times 10^2 \) | 0.1103336 \( \times 10^2 \) | 0 | 14.013260 \( \times 10^5 \) | 0 |
|         | 1           | 1.1104335 \( \times 10^2 \) | 0.89975097 \( \times 10^2 \) | 0.1104335 \( \times 10^2 \) | 0 | 14.014521 \( \times 10^5 \) | 0 |
| 2       | 1           | 1.1101117 \( \times 10^2 \) | 0.8994092 \( \times 10^2 \) | 0.1101117 \( \times 10^2 \) | 0 | 14.009197 \( \times 10^5 \) | 0 |
|         | 2           | 1.1102670 \( \times 10^2 \) | 0.8996103 \( \times 10^2 \) | 0.1102670 \( \times 10^2 \) | 0 | 14.014521 \( \times 10^5 \) | 0 |
| 3       | 1           | 1.1107112 \( \times 10^2 \) | 0.89997595 \( \times 10^2 \) | 0.1107112 \( \times 10^2 \) | 0 | 14.014521 \( \times 10^5 \) | 0 |
| 4       | 2           | 1.1107112 \( \times 10^2 \) | 0.89997595 \( \times 10^2 \) | 0.1107112 \( \times 10^2 \) | 0 | 14.014521 \( \times 10^5 \) | 0 |
|         | 2           | 1.1102670 \( \times 10^2 \) | 0.8996103 \( \times 10^2 \) | 0.1102670 \( \times 10^2 \) | 0 | 14.014521 \( \times 10^5 \) | 0 |
| 5       | 3           | 1.1101782 \( \times 10^2 \) | 0.89954405 \( \times 10^2 \) | 0.1101782 \( \times 10^2 \) | 0 | 14.009197 \( \times 10^5 \) | 0 |
| 4       | 4           | 1.1107112 \( \times 10^2 \) | 0.89997595 \( \times 10^2 \) | 0.1107112 \( \times 10^2 \) | 0 | 14.014521 \( \times 10^5 \) | 0 |
| 5       | 5           | 1.1101782 \( \times 10^2 \) | 0.89954405 \( \times 10^2 \) | 0.1101782 \( \times 10^2 \) | 0 | 14.009197 \( \times 10^5 \) | 0 |

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