

Determination of the δ values: problems with different approaches

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Delta, δ, definition (according to **IUPAC**, International Union of Pure and Applied Chemistry)

 $^{A/B}\delta_{i/STI}$

$$= \frac{A/B_{R_i}}{A/B_{R_{STI}}} - 1 \qquad \text{e.g. } \left[\frac{\frac{18}{16}R_i}{\frac{18}{16}R_{STI}} - 1\right]$$

^{A/B}δ_{i/STI}

$$= \left[\left(\frac{A/B_{R_i}}{A/B_{R_{STI}}} - 1 \right)^* 10^3 \right]^* 10^{-3} = X^* 10^{-3}$$
$$= X \%_0$$

i STI A, B	material of interest primary standard (e.g. : V-SMOW, V-PDB, V-CDT, etc) rare and dominant isotope of element E, respectively
$n^A E, n^B E$	number of moles of the isotope ^A E and ^B E in the treated substance
A/BR	$n^{A}E/n^{B}E$

Fundamental equations for δ (**w** = working standard)

(1)

Starting from the definition

$$\frac{R_i}{R_{STI}} = \delta_{i/STI} + 1$$

the following relations are obtained:

$$\frac{R_{i}}{R_{STI}} = \frac{R_{w}}{R_{w}} \frac{R_{i}}{R_{STI}} = (1/\frac{R_{STI}}{R_{w}}) \frac{R_{i}}{R_{w}} \rightarrow \rightarrow$$

$$\rightarrow \quad \delta_{i/STI} + 1 = [1/(\delta_{STI/w} + 1)] (\delta_{i/w} + 1)$$

$$= [k (\delta_{i/w} + 1)]$$

Using a secondary standard, st, as intermediary, we get

$$\frac{R_{i}}{R_{STI}} = \frac{R_{st}}{R_{st}} \frac{R_{w}}{R_{w}} \frac{R_{i}}{R_{STI}} = \left(\frac{R_{st}}{R_{STI}} / \frac{R_{st}}{R_{w}}\right) \frac{R_{i}}{R_{w}} \rightarrow$$

$$\rightarrow \delta_{i/STI} + 1 = \frac{(\delta_{st/STI} + 1)}{(\delta_{st/w} + 1)} \quad (\delta_{i/w} + 1) =$$

 $= [1/(\delta_{STI/w} + 1)] \ (\delta_{i/w} + 1) =$

$$= \mathbf{k} \left(\delta_{i/w} + 1 \right)$$

δ determination with only one standard, *st*

Linearity of the measured parameters (linearity is here defined in a general and elementary way)

^AEM, ^BEM, molecules containing isotopes ^AE and ^BE, respectively
 n^AE, n^BE, number of moles of isotopes ^AE and ^BE, respectively

- Linearity of the spectrometric response, I

 $I(AEM) = a n^AE$, $I(BEM) = b n^BE$

where **a** and **b** do not depend on **nE**

- Linearity of the measured isotope ratio, R_(m)

$${}^{A/B}\mathbf{R}_{(m)} = \frac{\mathbf{I}({}^{A}\mathbf{E}\mathbf{M})}{\mathbf{I}({}^{B}\mathbf{E}\mathbf{M})} = \frac{\mathbf{a}}{\mathbf{b}} \frac{\mathbf{n}({}^{A}\mathbf{E})}{\mathbf{n}({}^{B}\mathbf{E})} = \mathbf{c} \frac{\mathbf{n}({}^{A}\mathbf{E})}{\mathbf{n}({}^{B}\mathbf{E})} = \mathbf{c} \frac{A/B}{\mathbf{R}}$$

where **c** does not depend on **nE**

- Linearity of measured $\delta_{i/h}$

 $A/B\delta_{i/h(m)}$ + 1 is independent on the number of moles nE of the treated materials *i* and *h*; i.e.:

$$\frac{A/B}{\delta_{i/h(m)}} + 1 = \frac{A/B}{R_{i(m)}} / \frac{A/B}{R_{h(m)}} = \frac{c_i \frac{n({}^{A}E_i)}{n({}^{B}E_i)}}{c_h \frac{n({}^{B}E_h)}{n({}^{B}E_h)}} = \frac{c_i \frac{A/B}{R_i}}{c_h \frac{A/B}{R_h}}$$
$$= \frac{d}{d} \left(\frac{A/B}{\delta_{i/h}} + 1\right)$$

 $d = c_i / c_h$

where $A/B\delta_{i/h}$ is the true value h = reference material

δ determination with only one standard, st

Linearity conditions

 $\delta_{i/STI} + 1 = \frac{(\delta_{st/STI} + 1)}{(\delta_{st/w} + 1)} \quad (\delta_{i/w} + 1)$ st = generic standard with known $\delta_{st/STI}$

value (e.g. GISP)

Assume that there is linearity that the experimental values (m) are not affected by errors: $(\delta_{st/w(m)} + 1)$ and $(\delta_{i/w(m)} + 1)$ i.e. $\delta_{st/w(m)} + 1 = d (\delta_{st/w} + 1)$ $\delta_{i/w(m)} + 1 = d (\delta_{i/w} + 1)$



In the case of lineartity the laboratories may obtain different values for *d* but the same $\delta_{i/STI}$ value

Actually, the measured values $\delta_{st/w(m)}$ and $\delta_{i/w(m)}$ are at least affected by random error; thus in general in two different laboratories L1 and L2, different K values will be obtained.

For the same spectrometric response $(\delta_{i/w(m)} + 1)$ we may write

$$\begin{split} \widehat{\delta}_{i/\text{STI}(\text{L1})} + 1 &= \frac{(\delta_{st/\text{STI}} + 1)}{(\delta_{st/\text{w}(\text{m},\text{L1})} + 1)} \left(\delta_{i/\text{w}(\text{m})} + 1\right) = \mathbf{k}_{\text{L1}} \left(\delta_{i/\text{w}(\text{m})} + 1\right) \\ \widehat{\delta}_{i/\text{STI}(\text{L2})} + 1 &= \frac{(\delta_{st/\text{STI}} + 1)}{(\delta_{st/\text{w}(\text{m},\text{L2})} + 1)} \left(\delta_{i/\text{w}(\text{m})} + 1\right) = \mathbf{k}_{\text{L2}} \left(\delta_{i/\text{w}(\text{m})} + 1\right) \end{split}$$

Subtracting the equations above, we get:

$$\widehat{\boldsymbol{\delta}}_{i/STI(L1)} - \widehat{\boldsymbol{\delta}}_{i/STI(L2)} = (\mathbf{k}_{L1} - \mathbf{k}_{L2}) (\boldsymbol{\delta}_{i/w(m)} + 1)$$

The discrepancy between the estimated values obtained in the two different laboratories increases linearely as $(\delta_{i/w(m)} + 1)$ increases!

Experience on δ measurements tell us that, generally,

a) different laboratories *do not give the same* $\hat{\delta}_{i/STI}$ estimation

b) for a given $(\delta_{i/w(m)} + 1)$ value, the discrepancy of the results cannot be explained only by the difference $(K_{L1} - K_{L2})$

It's the case, for instance, of the data for **SLAP** (Gonfiantini, 1978) which gives a range of values:

from -452.1 to -418.1 ‰ from -49.8 to -44.7 ‰

The differences are one order of magnitude higher than the analytical uncertainties!

δ determination with more than one standard, *st1*, *st2*, *etc*.

Linearity condition:

Assume that uncertainty on $\delta_{st/STI}$ is much lower than uncertainty on $\delta_{st/w(m)}$,

i.e.
$$\mathbf{u}(\boldsymbol{\delta}_{st/STI}) \ll \mathbf{u}(\boldsymbol{\delta}_{st/w(m)})$$

Consider the couples of *experimental* and the *accepted* data for the standards:

$$\begin{split} &(\delta_{st1/STI} + 1, \delta_{st1/w(m)} + 1) \\ &(\delta_{st2/STI} + 1, \delta_{st2/w(m)} + 1) \\ &(\dots, \dots, \dots) \\ &(\delta_{stn/STI} + 1, \delta_{stn/w(m)} + 1) \\ &On \ the \ basis \ of \ OSL \ (Ordinary \ Last-Square \ regression) \\ &Y = \delta_{st/w(m)} + 1 \ on \ X = \delta_{st/STI} + 1 \ we \ obtain \ the \ straight \ line \ dettermined by the straight line \ dettermined by the straight line \ dettermined by the straight \ dettermined by the straight \ line \ dettermined by the straight \ detter$$

$$\delta_{\mathbf{i}/\mathbf{w}(\mathbf{m})} + \mathbf{1} = (1/\mathbf{k})_{\mathbf{exp}} (\delta_{\mathbf{i}/\mathbf{STI}} + \mathbf{1})$$

The reverse equation is used to estimate $\delta_{i/STI}$ from $\delta_{i/w(m)}$ for a new material **i**.

$$\widehat{\delta}_{i/STI} + 1 = \mathbf{k}_{exp} \left(\delta_{i/w(m)} + 1 \right)$$

valid only in case of linearity

No-linearity conditions

$$\delta_{i/w(m)} + 1 \neq c_i \frac{n({}^{A}E_i)}{n({}^{B}E_i)} / c_w \frac{n({}^{A}E_w)}{n({}^{B}E_w)} = c \ (\delta_{i/w} + 1)$$

where *c* is not constant but dependent on $(\delta_{i/w} + 1)$

$$\widehat{\delta}_{i/STI} + 1 = \mathbf{f} \left(\delta_{i/w(m)} + 1 \right)$$

thus $\hat{\delta}_{i/STI}$ +1 is a non linear function of $(\delta_{i/w(m)} + 1)$, but a CURVE

(where **f** indicates the function)

CURVES of calibration L1 and L2 obtained in laboratories 1 and 2

As an example assume that the curves L1 and L2 are a 2^d order polynomial function which fits *perfectly* the point O (origin of the coordinate), STI, ST1, ST*
 δ_{i/STI} + 1 = H (δ_{i/STI(m)} + 1)² + G (δ_{i/STI(m)} + 1)



- Straight line *stl*

$$\widehat{\delta}_{i/STI} + 1 = \mathbf{k}_{exp} (\delta_{i/STI(m)} + 1)$$

passing for the points of $\delta+1$ coordinates0(0,0) (not reported in Figure)STI(1,1)



Therefore

1) the best calibration line is, theoretically, a **curve** (since the spectrometric response never is *perfectly* linear) obtained

2) using $\delta_{st/STI} = (R_{st} / R_{STI}) - 1$ values calculated from absolute isotope ratio R obtained on several standards, st, and on a primary standard, STI

Unfortunately, absolute ratio analyses are difficult to obtain!

However, also in the case these ratios were measured, the scientific community preferred to follow another way for isotope value calculation of new samples: the so called

two-point linear "normalization".

Actually, both the values of the standards (or, at least, the value of one of the two standards), are (is) accepted *by agreement (agr)* by the scientific community

e.g. SLAP: $^{2/1}\delta_{SLAP/V-SMOW(agr)}$ P/V-SMOW from measured ^{2/1}R_{SLAP} and ^{2/1}R_{V-SMOW} - 428 ‰ - 428.8 % (Gonfiantini, 1978) (Wit et al, 1980)

Primary and secondary standards frequently used for "two-point normalization

Name	Nature	Isotope ratio	10 ³ *δ	Primary standard
V-SMOW	water	$^{2}H/^{1}H$	0.00*	V-SMOW
		¹⁸ O/ ¹⁶ O	0.00*	V-SMOW
V-SMOW 2	water	$^{2}H/^{1}H$	0.0 ±0.3	V-SMOW
		¹⁸ O/ ¹⁶ O	0.00 ±0.02	V-SMOW
SLAP	water	$^{2}H/^{1}H$	-428.0*	V-SMOW
		¹⁸ O/ ¹⁶ O	-55.5*	V-SMOW
SLAP 2	water	${}^{2}H/{}^{1}H$	-427.5 ±0.3	V-SMOW
		¹⁸ O/ ¹⁶ O	-55.50 ±0.02	V-SMOW
NBS 19	Ca-carbonate	¹³ C/ ¹² C	+1.95*	V-PDB
		¹⁸ O/ ¹⁶ O	-2.20*	V-PDB
LSVEC	Li-carbonate	¹³ C/ ¹² C	-46.6*	V-PDB
		¹⁸ O/ ¹⁶ O	-26.7 ±0.2	V-PDB
IAEA-N-1	NH ₄ -sulfate	$^{15}N/^{14}N$	+ 0.4 ±0.2	Atmospheric N ₂
USGS 32	NH ₄ -nitrate	$^{15}N/^{14}N$	+180*	Atmospheric N ₂
IAEA-S-1	Ag ₂ S	$^{34}S/^{32}S$	-0.3*	V-CDT
IAEA-S-2	Ag ₂ S	$^{34}S/^{32}S$	+22.62 ±0.08	V-CDT
IAEA-S-3	Ag ₂ S	³⁴ S/ ³² S	-32.49 ±0.08	V-CDT

*, values accepted by agreement

Two-point linear «normalization»

Usual form presented in the literature

(e.g. Gonfiantini 1978, 1984, Blattner & Ulston 1978, Blattner 1984, Coplen 1988, Böhlke & Coplen, 1995)

$$\delta_{i/norm} = f (\delta_{i/w(m)} - \delta_{ST/w(m)}) + \delta_{ST/STI(agr)}$$

where

$$\mathbf{f} = \frac{\delta_{\mathrm{ST}^*/\mathrm{STI(agr)}} - \delta_{\mathrm{ST}/\mathrm{STI(agr)}}}{\delta_{\mathrm{ST}^*/\mathrm{W(m)}} - \delta_{\mathrm{ST}/\mathrm{W(m)}}}$$

Rearranging the equation above:

$$\frac{\delta_{i/norm} - \delta_{ST/STI(agr)}}{\delta_{ST^*/STI(agr)} - \delta_{ST/STI(agr)}} = \frac{\delta_{i/w(m)} - \delta_{ST/w(m)}}{\delta_{ST^*/w(m)} - \delta_{ST/w(m)}}$$

which is simply a straight line passing for 2 standards instead of for only 1 : two is better than one!

$$\frac{\mathbf{Y}_{\mathbf{i/norm}} - \mathbf{Y}_{ST}}{\mathbf{Y}_{ST^*} - \mathbf{Y}_{ST}} = \frac{\mathbf{X}_{\mathbf{i}(\mathbf{m})-} \mathbf{X}_{ST(\mathbf{m})}}{\mathbf{X}_{ST^*(\mathbf{m})-} \mathbf{X}_{ST(\mathbf{m})}} \rightarrow \frac{\delta_{\mathbf{i/norm}} - \delta_{ST/STI(agr)}}{\delta_{ST^*/STI(agr)} - \delta_{ST/STI(agr)}} = \frac{\delta_{\mathbf{i/w}(\mathbf{m})-} \delta_{ST/w(\mathbf{m})}}{\delta_{ST^*/w(\mathbf{m})-} \delta_{ST/w(\mathbf{m})}}$$





 $\mathbf{X} = \mathbf{\delta}_{\mathbf{i}/\mathbf{w}} + \mathbf{1}$

Summarising:

- a) The delta values $\delta_{st/STI(agr)}$ accepted *by agreement* for standards ST and ST* used for normalization are in general affected by unknown systematic error
- b) The value, $\delta_{st,norm}$, obtained on the basis of ST and ST* for a new secondary standard, *st*, is affected by further systematic error: actually $\delta_{st,norm} \hat{\delta}_{st/STI} \neq 0$, where $\hat{\delta}_{st/STI}$ is assumed as the best estimation of $\delta_{st/STI}$
- c) As occurs for the new standard **st**, the value, $\delta_{i,norm}$, obtained on the basis of **ST** and **ST**^{*} for a new substance, *i*, is affected by systematic error: actually $\delta_{i,norm} \hat{\delta}_{i/STI} \neq 0$, where $\hat{\delta}_{i/STI}$ is the best estimation of $\delta_{i/STI}$

d) To avoid the systematic error due to "normalisation" on the calculated $\delta_{i/STI}$ values when considered as referred to STI, we would define a $(\delta_{st/w(m)} + 1)$ vs $(\delta_{st/STI(agr)} + 1)$ regression through several points: O (origin of the $\delta + 1$ coordinates), ST₁, ST₂, ..., ST_n (secondary standards) with increasing delta values, which are certified from the literature.

Thank you very much for your patience



Note. This curve, used to obtain the better estimate, $\hat{\delta}_{i/STI}$, of the true $\delta_{i/STI}$ value without any additional "normalization", would be characterized by prograde variation of slope without any inflection point, and the maximum or minimum values of the function far from the delta interval of interest.

Final consideration

Two-point "normalised" data are appropriate for practical use (e.g.: comparison of isotope data obtained in different laboratories on water, ice, wine, oil, etc.). They, however, *could not* be very appropriate for theoretical use as, for instance, in modelling isotope fractionation.

Actually, *in principle*, the fractionation factor, α_{norm} , defined using the "normalised" values, is dependent not only on temperature, but also on the single $(\delta + 1)$ values assumed during any physical-chemical process;

e.g. for the liquid and gaseous water system at any given temperature, α_{norm} changes as ${}^{2}\delta_{l,norm}$ and ${}^{2}\delta_{v,norm}$ change:

 $\alpha_{\text{norm}} = f(T, {}^{2}\delta_{\text{l,norm}}, {}^{2}\delta_{\text{v,norm}})$