

Reprint from

RECENT ADVANCES
IN DOPING ANALYSIS
(11)

W. Schänzer
H. Geyer
A. Gotzmann
U. Mareck
(Editors)

Sport und Buch Strauß, Köln, 2003

U. FLENKER, W. SCHÄNZER:
Expression of Differences in Isotopic Composition
In: W. Schänzer, H. Geyer, A. Gotzmann, U. Mareck (eds.) Recent advances in doping
analysis (11). Sport und Buch Strauß, Köln, (2003) 179-182

Expression of Differences in Isotopic Composition

Institute of Biochemistry, German Sports University Cologne

1 Introduction

The δ -notation generally is used to express isotopic composition. This scale relates the isotope ratio of some material of interest to an internationally accepted standard rather than telling absolute ratios. The latter is difficult, if not impossible. By introducing a sign the δ -notation immediately clarifies whether one deals with “more” or with “less” of the rarer (and usually heavier) isotope species relative to the standard. Finally isotope researchers prefer to multiply their results by 1000, because variation of isotope ratios numerically usually happens in the third or fourth digit. To sum it up, δ -values translate isotope ratios for humans.

However the use of this scale is not entirely unproblematic. This especially applies when not a single isotope ratio is regarded but rather differences between several compounds are of interest. Problems arise from the fact that the δ -scale is not suited for some usual mathematical operations. In the following it will be shown why this is the case and how these problems can be circumvent.

2 Theory

The δ -value of a compound “A” is defined as

$$\delta_A := \left(\frac{R_A}{R_{STD}} - 1 \right) \cdot 10^3 \quad (1)$$

where R_A is the isotope ratio of the compound and R_{STD} is the isotope ratio of a standard. When differences of the isotope ratios of two compounds “A” and “B” are to be expressed,

it is useful to think of this difference as of a ratio of ratios. Hence we first may want to rewrite the δ -value in terms of an isotope ratio:

$$R_A = R_{\text{STD}} \cdot \left(\frac{\delta_A}{10^3} + 1 \right) \quad (2)$$

The isotope ratio of compound "B" is calculated identically and for the ratio of ratios we obtain:

$$\frac{R_A}{R_B} = \frac{R_{\text{STD}} \cdot (\delta_A/10^3 + 1)}{R_{\text{STD}} \cdot (\delta_B/10^3 + 1)} \quad (3)$$

$$= \frac{\delta_A + 10^3}{\delta_B + 10^3} \quad (4)$$

It can be seen, that the ratio of the standard does not matter as long as it is the same for both compounds. For convenience we may want to express the difference on the δ -scale instead of using the raw ratio. So R_A/R_B may be treated as if R_A is related to a standard with R_B . This is known as the $\Delta\delta$ -notation. We define:

$$\Delta\delta_{A/B} := \left(\frac{R_A}{R_B} - 1 \right) \cdot 10^3 \quad (5)$$

Putting in (4) gives

$$\Delta\delta_{A/B} = \left(\frac{\delta_A + 10^3}{\delta_B + 10^3} - 1 \right) \cdot 10^3 \quad (6)$$

$$= \frac{(\delta_A - \delta_B) \cdot 10^3}{\delta_B + 10^3}. \quad (7)$$

(7) can be rewritten as

$$\Delta\delta_{A/B} = \frac{\delta_A - \delta_B}{1 + \delta_B/10^3} \quad (8)$$

which is not significantly simpler, but illustrates an important fact: $1 + \delta_B/10^3$ usually is sufficiently close to 1.0 and hence:

$$\Delta\delta_{A/B} \approx \delta_A - \delta_B \quad (9)$$

Looking closer at (8) and at (4) we will notice another interesting property: Whereas the numerator in (8) just changes its sign when R_A and R_B are exchanged in (4), the denominator changes its value. The somewhat surprising conclusion is that it makes a

difference whether “A” is compared to “B” or whether “B” is compared to “A”. We have to keep in mind that the δ -scale is just a comfortable method to express very small **ratios**. Therefore $\Delta\delta_{B/A}$ has to be regarded as an expression for the **reciprocal** of $\Delta\delta_{A/B}$. Because of the approximation of the denominator these effects however can be neglected and therefore:

$$\Delta\delta_{A/B} \approx -1 \cdot \Delta\delta_{B/A} \quad (10)$$

Some authors have used the ratio of δ -values to express differences in isotopic composition. To clarify what this parameter really does express it will be illustrative to use the definition (1) and perform the division explicitly:

$$\frac{\delta_A}{\delta_B} = \frac{(R_A/R_{STD} - 1) \cdot 10^3}{(R_B/R_{STD} - 1) \cdot 10^3} \quad (11)$$

$$= \frac{R_A - R_{STD}}{R_B - R_{STD}} \quad (12)$$

This term is not particularly useful for two reasons:

1. In contrast to (8) and to (4) R_{STD} is not eliminated.
2. δ_A/δ_B depends on the absolute values of R_A , R_B and R_{STD} rather than on possible differences between R_A and R_B .

Although this should be clear without rewriting δ_A/δ_B as (12) it is worth while pointing out that things become especially weird when at least one of the ratios of “A” and “B” is close to R_{STD} . A part of the ratio may become zero and consequently the ratio may evaluate to zero or to ∞ .

To put it simple: The δ -scale does not allow for division just as the Celsius temperature scale does not. 20°C is **not** twice as warm as 10°C , simply because the zero point has been arbitrarily chosen. For the same reason other parameters obtained by division are not meaningful. For example the coefficient of variation does not make much sense because it is mostly dependent on the absolute δ -values and not on the true precision of the work.

Similar problems will occur – if to a lesser extent – when identical samples are measured on different machines with probably different calibrations of the working standard.

3 Example

We want to compare two compounds “C” and “D” the $\delta^{13}\text{C}_{\text{PDB}}$ -values of which are -22.0‰ and -26.0‰ respectively. Putting these values into (8) gives $(-22.0+26.0)/(1-26.0/10^3) = 4.106776 \approx 4.1\text{‰}$. With respect to the precision of a typical GC/C/IRMS system we are justified to say that “C” is isotopically 4‰ heavier than “D”. *Vice versa* we obtain $(-26.0 + 22.0)/(1 - 22.0/10^3) = -4.089980\text{‰}$ which can be approximated to the same absolute value as above. Nonetheless the latter point illustrates that order does matter on the δ -scale: “C” is 4.106776‰ heavier than “D”, but “D” is only 4.089980‰ lighter than “C”. The reason is that $R_{\text{A}}/R_{\text{B}} = 1.004107$ but $R_{\text{B}}/R_{\text{A}} = 0.99591$ calculated according to (4). The two $\Delta\delta^{13}\text{C}$ -values refer to an ratio and its reciprocal respectively. It also illustrates that addition and subtraction are not trivial on the δ -scale. For most practical purposes the approximation from (8) will be sufficient anyway.

The ratio $\delta_{\text{C}}/\delta_{\text{D}}$ from the values above is 0.8461538 . Approximately the same difference in isotopic composition would be present if we compared two compounds with $\delta^{13}\text{C}_{\text{PDB}}$ -values of -12‰ and -16‰ ($+4.065041 \approx +4\text{‰}$). In contrast $\delta_{\text{C}}/\delta_{\text{D}}$ drops to 0.75 . This clearly illustrates that ratios of δ -values do not provide meaningful information with respect to differences of isotope ratios. For values of -4‰ and -8‰ the ratio already becomes 0.5 and for values of 0‰ and -4‰ apparently no difference in isotopic composition is present.

At the same time a precision of $\pm 0.2\text{‰}$ would result in a coefficient of variation of 0.9% for a measured value of -22‰ and in 1.7% for -12‰ .

4 Conclusions

- Basic mathematical operations are not allowed on the δ -scale.
- The $\Delta\delta$ -notation is a good approximation with respect to addition and subtraction.
- Division and multiplication are not meaningful on the δ -scale due to the arbitrary zero point.