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Letter to the Editors

Comments on the paper by H.A.J. Meijer, R.E.M. Neubert and G.H. Visser: "Cross contamination in dual inlet isotope ratio mass spectrometers" 198(2000) 45–61

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To the Editors:

Before we begin we would like to express our appreciation to the authors of the original article, the study of the effects of cross contamination, and for suggesting methodology for the determination of the cross contamination factor η for improving the precision and accuracy of δ measurements using the dual inlet mass spectrometers. The purpose of this comment is to draw the attention of the authors and the readers of this article to a minor discrepancy in the definition of the quantity η. This does not alter, in any way, the observations and deductions, methodology for the measurement of η, and the interpretation of the results by the authors.

The discrepancy is in Sec. 2.1 and in the appendixes where the theoretical treatment is given. In the above-mentioned section and in Appendix A of the article, it was stated that η is the fraction of the reference sample contaminating the unknown sample and vice versa. The corresponding altered ratios are given by the expressions similar to Eqs. (5) and (6) in Sec. 2.2. The first part of the statement gives the impression that η is the "quantity fraction" of the contaminant in the sample under analysis. The assumption of quantitative mixing does not lead to Eqs. (5) and (6) of Sec. 2.2. In the situation of quantitative mixing, the modified ratios can only be obtained by adding individual contributions of the sample under analysis and the contaminant to the minor and major isotopes in the mixture and then taking their ratios (after the addition). This is also the normal procedure adopted in the isotope dilution analysis for obtaining the isotopic ratio of the mixture when a known quantity of "spike" is added to the sample. Thus, when analyzing a contaminated "sample" [that has a true value of (minor/major) isotope ratio r_s and when it is contaminated with a reference having a true (minor/major) ratio r_r] the fractional concentration of the contaminant in the mixture being f, then, the modified ratio of the mixture r_s^m is given by the following expression:

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$$r_s^m = \frac{[(1-f)r_s/(1+r_s)] + [fr_r/(1+r_r)]}{[(1-f)/(1+r_s)] + [f/(1+r_r)]}$$

Here, the two terms in the numerator represent the contributions to the minor isotope from the unknown sample and the reference sample, respectively; and the two terms in the denominator represent the contributions to the major isotope from the unknown and the reference samples, respectively. In a similar way, when analyzing the reference sample contaminated with a fraction *f*, of the unknown sample, we obtain a similar expression for the modified isotopic ratio given as

$$r_r^m = \frac{[(1-f)r_r/(1+r_r)] + [fr_s/(1+r_s)]}{[(1-f)/(1+r_r)] + [f/(1+r_s)]}$$

From these two measured values of r_s^m and r_r^m, one can deduce the following expression relating $\delta^{\mathrm{TRUE}}=[\{ r_s/r_r \}-1]$ with $\delta^m=[\{ r_s^r/r_r^m \}-1]$.

$$\delta^m = \frac{[1 + r_s + \delta^T(1-f)][1 + 1/r_r + \delta^T(1-f)]}{[1 + r_s + \delta^T f)][1 + 1/r_r + \delta^T f]} - 1$$

However, it may be possible to interpret η not as a quantity fraction, but as that fraction of contaminant which would alter the isotopic ratios as defined by the authors; thus satisfying the relationships [Eqs. (5) and (6) of Sec. 2.2 in the original article)

$$r_r^m = (1-\eta)r_r + \eta r_s$$

$$r_s^m = (1-\eta)r_s + \eta r_r$$

These equations, implicitly assume, that the error in the measured ratio $[r_s^m - r_s]$ is proportional to the true difference in the isotopic ratios of the sample and the reference as given by $[r_s^m - r_s] = -\eta[r_s - r_r]$; η being the constant (or is it a variable?) of proportionality. It is possible to relate the quantity fraction *f* and η, the cross-contamination proportionality factor as defined by the authors, by equating the values of r_s^m and r_r^m as shown previously and as given by Eqs. (5) and (6) in Sec. 2.2

$$\eta = \frac{f(1+r_r)}{[1 + r_s - f(r_s - r_r)]} = \frac{f(1+r_s)}{[1 + r_r + f(r_s - r_r)]}$$

We feel that, it is reasonable to assume, that the quantitative mixing factor *f* remains constant, because the pump down time, waiting time before the data collection, after the sample is let in etc. are held constant during the measurement of δ. However, we do not have sufficient theoretical and logical grounds to assume that error in the measured ratio is proportional to the difference in the isotopic ratios between the sample and the reference. But from the previous expression, when r_r has been selected to be very close to r_r, the term $f(r_s - r_r)$ becomes very small and can be neglected in comparison, with 1, and $(1+r_r)$ is approximately equal to $(1+r_s)$ making η approximately equal to the value of *f*; *f* being the fractional concentration of the contaminant in the sample under the analysis.

Sincerely,

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