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Mass Bias Fractionation Laws for Multi-Collector ICPMS: Assumptions and Their Experimental Verification

Juris Meija,* Lu Yang, Ralph Sturgeon, and Zoltán Mester

Institute for National Measurement Standards, National Research Council Canada, 1200 Montreal Rd., Ottawa, Ontario K1A 0R6, Canada

Although mass bias fractionation correction is among the most studied theoretical aspects of analytical mass spectrometry, several assumptions imbedded in the conventional correction models remain largely untested. Experimental evidence is given herein highlighting parts-per-thousand deviations from the conventional mass bias correction models which can occur with use of multicollector inductively coupled plasma mass spectrometry. Furthermore, current mass spectrometric approaches are not capable of elucidating the fractionation exponent.

Isotope amount ratios determined by mass spectrometry (r) are often biased estimates of their true values (R). Consider a vessel containing equal amounts of hydrogen and deuterium atoms where a small orifice is created and the escaping atoms are observed by counting. The H/D ratio will fall close to $\sqrt{2}$:1 because of the different velocities of the isotopes. This is the basis for Graham's law of effusion, and in the early days of mass spectrometry the measured isotope intensities were corrected to their corresponding true values according to this law. In the case of strontium, where Sr atoms are evaporated from a solid surface, this means that the uncorrected $^{84}Sr/^{88}Sr$ would be $\sqrt{88/84} = 1.023$ times greater than the true ratio[1] (in an oversimplified fashion[2]). The difference between the calculated and true isotope ratios is usually expressed as the mass bias correction coefficient, K_{ij}:

$$R_{ij} = K_{ij} r_{ij} \tag{1}$$

Mass bias fractionation phenomena have been investigated by numerous researchers over several decades.[2−4] To date the most successful have been the semiempirical strategies to quantify this bias. Many functional relationships have been proposed, all with varying degrees of mathematical complexity and veracity.[5] At the core of all of these "laws", however, is a mathematical formulation of the variable separation. Semiempirical formulations of the mass-bias must necessarily be expressed as a combination of two functions: one that is time dependent and mass independent (the fractionation function, f) and other that is time independent and mass dependent (the nuclide mass function, μ). If the fractionation function can be shown to be mass dependent, then the mass-bias fractionation model can produce biased results if assumed otherwise. This was recently shown as the reason for the poor performance of the conventional linear mass-bias model,[6]

$$K_{ij} = 1 + f_{ij} \cdot \mu_{ij} \tag{2}$$

where $\mu_{ij} = m_i - m_j$. Instead of using the linear fractionation law with properly separated variables,[6] it is customary to introduce non-linear fractionation laws, such as the exponential or power law. These, however, are special situations of the generalized power law,[7−9] a product of two functions, one that is mass-independent and another mass-dependent:

$$\ln K_{ij} = f_{ij}(t) \cdot \mu_{ij}(v) \tag{3}$$

Here, $f(t)$ is a mass-independent fractionation function that varies in time and v is a constant that defines the nature of mass bias fractionation:

$$\mu_{ij}(v) = \int_{m_i}^{m_j} m^v \, dm = \frac{m_j^{v+1} - m_i^{v+1}}{v + 1} \tag{4}$$

For example, $v \to -1$ leads to the well-known Russell exponential fractionation law,[10] an expression currently embraced for virtually all isotope ratio determinations.

Regression Method. A major obstacle in validating the mass-bias transfer models is the inherent assumption about the constancy of the fractionation function and the arbitrary values and interpretations of the fractionation exponent. These shortcomings, however, can be circumvented using an approach pioneered by Maréchal et al. a decade ago.[7]

* To whom correspondence should be addressed. E-mail: juris.meija@nrc.ca.

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Table 1. Faraday Cup Configuration Used in This Work

Faraday cup	L4-IC	L4	L3	L2	L1	C	H1	H2	H3	H4	H4-IC
isotope	^{195}Pt	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{203}Tl	^{204}Hg	^{205}Tl	^{206}Pb
cup position, mm		42.059	26.504	16.651	7.282	0.000	6.800	16.500	26.006	35.950	

If two isotope ratios (r_{ij}, r_{kl}) belonging to the same or a different element are monitored simultaneously, from the eq 1 we have the following:

$$\frac{\ln r_{ij} - \ln R_{ij}}{\ln r_{kl} - \ln R_{kl}} = \frac{\ln K_{ij}}{\ln K_{kl}} \tag{5}$$

Rearrangement of this expression leads to a log-linear regression between the measured isotope ratios r_{ij} and r_{kl}.

$$\ln r_{ij} = \ln r_{kl} \cdot \underbrace{\frac{\ln K_{ij}}{\ln K_{kl}}}_{\text{slope, } b} + \underbrace{\ln R_{ij} - \ln R_{kl} \frac{\ln K_{ij}}{\ln K_{kl}}}_{\text{intercept, } a} \tag{6}$$

The slope, b, and intercept, a, of this regression yield the model equation for the regression method:

$$a = \ln R_{ij} - b \ln R_{kl} \tag{7}$$

Further rearrangement of this expression yields the following measurement model equation:

$$R_{ij} = e^a \cdot R_{kl}^b \tag{8}$$

The only prerequisite of the regression model is that a linear relationship between $\ln r_{ij}$ and $\ln r_{kl}$ holds true, which is usually the case. The above semiempirical regression method is now successfully adopted by others to establish the value of R_{ij} from r_{ij}, r_{kl}, and R_{kl}.[8,11−13]

It is known that the regression method comes with its disadvantages, most notably that the high stability of the mass-bias in multicollector ICPMS is directly at odds with the implementation of the regression method as it relies on the presence of short-time variations in the mass-bias. Strategies to overcome these difficulties are discussed in detail elsewhere.[13−15]

In general, correction of the raw isotope ratio data requires an SI-traceable reference isotope ratio in addition to a plausible measurement model (mass-bias correction law). In isotope ratio mass spectrometry, the measurement model is eq 3, and here we summarize the experimental results regarding the assumptions underpinning this model. The central aim of this study is to show that the fractionation function f, as defined in the generalized power law, is mass-dependent. Additionally, we show that the fractionation exponent n or v, where $n = v + 1$, is a dummy variable and that the regression method is immune to all the

shortcomings associated with other models because it does not invoke any of the above variables.

EXPERIMENTAL SECTION

Determination of Mercury Isotope Ratios. Mercury isotope signal intensities were collected with a Thermo Fisher Scientific Neptune multicollector inductively coupled plasma mass spectrometer (Bremen, Germany) equipped with nine Faraday cups and four ion counters. The cup positions were configured at the instrument factory to allow for simultaneous collection of all seven mercury isotopes and both thallium isotopes. Table 1 lists the exact cup positions used in this work. The gain on each Faraday cup was monitored daily to ensure correction for its efficiency. Detector cross-calibration between Faraday cups and ion counters was performed periodically in accordance with the manufacturer's instructions.

A combination of cyclonic and Scott-type spray chambers with a self-aspirating nebulizer (MCN50 Elemental Scientific, Appleton WI, U.S.A.) operating at 50 μL min^{-1} were used for all measurements.

Sample preparation was conducted in a fume hood. Sub-samples of mercury were prepared by serial dilution of NIST SRM 3133 reference material in 2% HCl containing 0.002 M BrCl followed by spiking with thallium standard reference material (NIST SRM 997) yielding mercury and thallium mass fractions of about 100 ng g^{-1}. BrCl reagent was prepared as per U.S. EPA.[16] Intensities of Hg isotopes obtained from a blank solution containing 2% HCl and 0.002 M BrCl were subtracted from those of all samples. Isotope ratio data were calculated following simultaneous collection of all Hg (seven isotopes) and Tl ion beams (two isotopes) in a static measurement sequence. The analyses utilized 5 blocks of 50 integrations (cycles) of 17 s. The duration of each session of measurements was on the order of 10−15 h. Data sets evaluated here were collected between November 2007 and January 2008. Uncertainty propagation of the mass bias corrected isotope ratios was done as described in detail elsewhere.[17,18]

RESULTS AND DISCUSSION

Discussion of the Fractionation Function, *f*. At the core of the mass-bias correction equation is the introduction of a mass-independent non-stationary function $f(t)$. All mass bias models stemming from eq 3 operate under the hypothesis of a constant mass fractionation function. Negation of this hypothesis, in turn, will invalidate these mass bias models.

Interpretation of the mass fractionation function has not been without flaws. Not long ago it was widely held that the value of f is identical for adjacent elements, such as Hg−Tl, Cu−Zn, or

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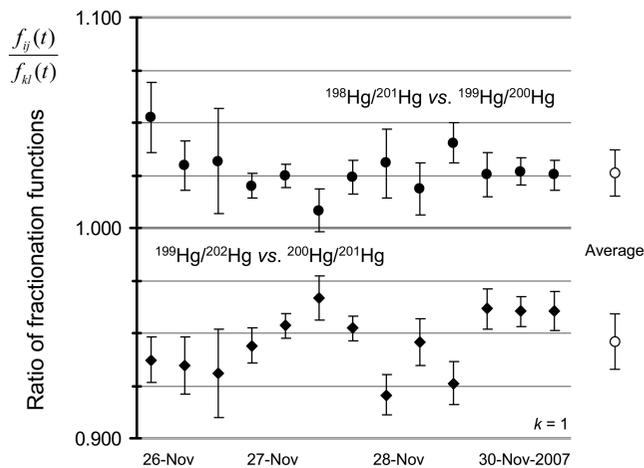
Figure 1. Experimental proof of significant deviations from eq 9 for mercury isotopes. Error bars represent the combined uncertainty ($U = ku$, where $k = 1$).

Pb−Tl. Such an assumption, while known to be only an approximation,[4,9,13,14,19] is still in use today.[6,20−22] According to the current paradigm, the value of the fractionation function f differs between elements. Yet, its value remains widely assumed to be identical for isotopes of a given element, E:
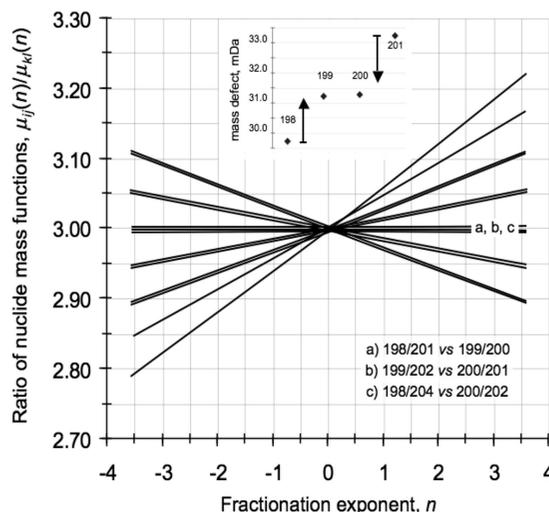
$$\frac{f_{ij}^{E}}{f_{kl}^{E}} \equiv 1 \qquad (9)$$

Although attempts have been made to test the assumptions underlying the proposed isotope fractionation laws,[23,24] the persistence of assumptions regarding the fractionation function have largely limited their success, as shown below.

Experimentally, eq 9 can be evaluated from the observed slopes of the regression method. Combining eqs 3 and 6 leads to the following:

$$\frac{\ln K_{ij}}{\ln K_{kl}} = b = \frac{f_{ij} \cdot \mu_{ij}}{f_{kl} \cdot \mu_{kl}} \qquad (10)$$

Deviations from eq 9 have been sugessted[13] and already noted for neodymium isotopes.[19] Such deviations can lead to Nd isotope ratios that are biased by up to 100 parts-per-million. Herein, we show that an order of magnitude larger bias can occur for mercury isotope ratios.

The ratio of the fractionation functions, determined for various isotope pairs of mercury based on eq 10, is shown in Figure 1. The uncertainty of the correction function ratio is determined solely by that arising from the estimate of the regression slope since the mass-dependent factor $\mu(n)$ is known typically to 1 part-per-million for Hg isotopes. In contrast, the regression slope can be estimated only to within a few parts-per-thousand under good

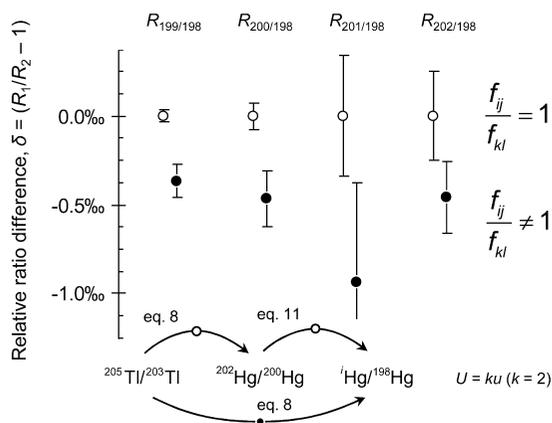(19) Vance, D.; Thirlwall, M. *Chem. Geol.* **2002**, *185*, 227–240.
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Figure 2. Dependence of nuclide mass function ratios on the fractionation exponent (n) for mercury isotopes. Symbols a, b, and c refer to the three approximately parallel lines at about 3.00 on the ordinate, showing strong independence on the fractionation exponent. The inset illustrates the symmetry of the ^{198}Hg, ^{199}Hg, ^{200}Hg, and ^{201}Hg mass defects which results in the mass function independence of the fractionation exponent.

measurement conditions. The precision of the obtained fractionation ratios is, nevertheless, sufficient to discern significant deviations from eq 9.

Note that eq 10 is a function of two unknown variables, namely, the fractionation function f and the exponent n. However, the dependence on the fractionation exponent can be almost completely eliminated using carefully selected isotope pairs such as the ^{202}Hg/^{199}Hg versus ^{201}Hg/^{200}Hg or ^{201}Hg/^{198}Hg versus ^{200}Hg/^{199}Hg since the symmetry of nuclide mass defects in these isotope pairs is particularly favorable. Thus, the value of n has practically no effect on $\mu(n)$ and consequently on f, as shown in Figure 2.

The significance of a measurable departure from eq 9 is that different "corrected" isotope ratios can be obtained depending on whether eq 9 is explicitly assumed or not. In the latter case, R_{ij} is calculated from R_{kl} using eq 6 whereas in the former case K_{ij} is calculated from K_{kl} by combining eqs 3 and 9:

$$\frac{\ln K_{ij}}{\ln K_{kl}} = \frac{\mu_{ij}(n)}{\mu_{kl}(n)} \qquad (11)$$

The difference in "corrected" mercury isotope ratios from these two approaches can be as high as 1%, as shown in Figure 3 for the ^{201}Hg/^{198}Hg ratio. Such bias is comparable to the range of natural variations of mercury isotopes and therefore can pose significant consequences for the interpretation of mercury isotope ratios. Note that the increased uncertainty of the results arising from the regression model does not reflect any shortcomings of the method. Rather, it shows that the uncertainties in conventional mass bias correction models are underestimated by approximately a factor of 3 because of eq 9.

Discussion of the Fractionation Exponent, n. Inherent to all mass bias models stemming from eq 3 is the in-built variable (fractionation exponent) that distinguishes the various mass

Figure 3. Effect of the explicit assumption of equal fractionation functions for all mercury isotopes on the mass bias corrected isotope ratios. Error bars and the reported uncertainties represent the expanded uncertainty ($U = ku$, where $k = 2$). Data were collected between Nov 23, 2007 and Jan 24, 2008 yielding 14 data sets (regressions), each containing 10 measurement results wherein each result is an average of about 1 h data collection. Fractionation exponent $n \to -1$ was used for eq 11.
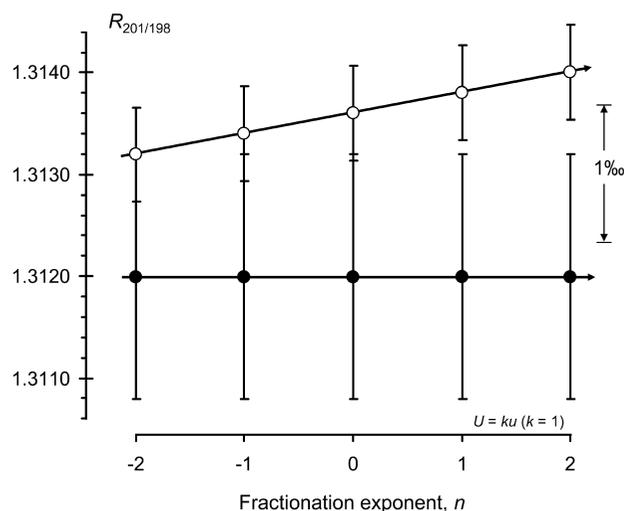
fractionation phenomena. Hence we have linear, exponential, equilibrium, power, and other fractionation models. This variable, in turn, is often used to distinguish between these fractionation models.[4] Consequently, considerable effort has been spent in evaluating the mass-dependence of isotope fractionation.[3,25] In essence, this amounts to extracting the numerical value of the mass bias fractionation exponent, n, from the experimentally determined uncorrected isotope ratios. Besides fundamental insights into the fractionation process, the value of n is important as it affects the values of the mass bias corrected isotope ratios. Proceeding via the mass bias transfer, that is, eq 11, yields mass bias corrected isotope ratios that are explicitly dependent on the fractionation exponent, n:

$$\frac{r_{ij}}{R_{ij}} = \left(\frac{r_{kl}}{R_{kl}}\right)^{\mu_{ij}(n) \cdot f_{ij} / \mu_{kl}(n) \cdot f_{kl}} \qquad (12)$$

This expression is frequently used in mass spectrometry in the form of $K_{ij} = K_{kl}^{\beta}$ where $\beta = \mu_{ij}(n) / \mu_{kl}(n)$ and $f_{ij} = f_{kl}$.[23-25] Note that a priori knowledge of the true isotope ratios R_{ij} and R_{kl} does not contribute to an elucidation of the nature of the fractionation law, that is, the values of n.

Contrary to the conventional mass bias transfer approach based on use of eq 12, the fractionation exponent has no effect on the mass bias corrected isotope ratios, isotope abundances, or atomic weight when the regression method is used.[7,9] Such conclusion is evident from eq 8. Hence, the application of eq 12 is inferior to the regression method for two reasons: first, the explicit assumption has to be made that $f_{ij} = f_{kl}$ and second, eq 12 yields isotope ratios that depend on the fractionation exponent n. This latter aspect is illustrated in Figure 4.

Whereas eqs 10 or 11 cannot be solved for n analytically, numerical solutions are possible. However, the problem of finding n is ill-conditioned since the value of f_{ij}/f_{kl} must be known to calculate the values of n. However, to obtain f, n has to be

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Figure 4. Effect of the fractionation exponent, n, on the mass-bias corrected $^{201}Hg/^{198}Hg$ isotope ratios obtained from: (●) regression method, eq 8 and, (○) mass bias transfer, eq 12. In both cases $R_{kl} = {}^{202}Hg/^{200}Hg = 1.285\ 42(30)$, derived from NIST SRM 997 using $^{205}Tl/^{203}Tl = 2.387\ 14(51)$ via eq 8. Error bars and reported uncertainties represent the expanded uncertainty ($U = ku$, where $k = 1$).

known. While it is true that, in few instances, the ratio of f can be obtained without explicit knowledge of n, as shown in Figures 1−2, the converse is never true. Thus, when f_{ij}/f_{kl} is taken as one for the purpose of estimating the fractionation exponent n, this assumption inevitably results in meaningless values of the fractionation exponent. Both logarithmic, eq 10, and linear, eq 12, coordinate plots of r_{ij} versus r_{kl} have been used to obtain the fractionation exponents.[3,10,23-26] However, conclusions derived from such fitting involve the implicit assumption that $f_{ij}/f_{kl} = 1$. Since such an assumption can be proven incorrect for Hg isotopes (Figure 1), there is no reason to believe it is true for other isotopes. As shown in Figure 5, a particular slope from the ln r_{ij} versus ln r_{kl} does not correspond to a unique value of n.
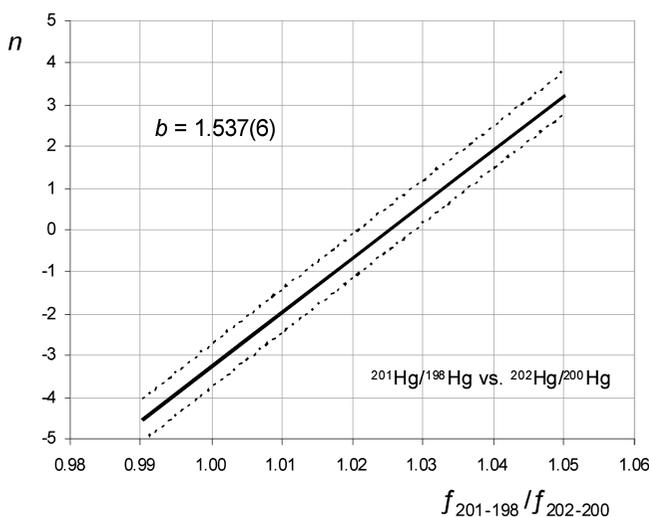
Figure 5. Finding the fractionation exponent n by fitting the experimental data: an ill-conditioned problem. Experimental estimates of the slope (b) can be rationalized using an infinite number of mutually consistent sets of n and f. For example, $n = 0$ and $f = 1.025$ or $n = 1$ and $f = 1.033$. Dotted lines represent the uncertainty bound corresponding to $b = 1.537(6)$.

CONCLUSIONS

Herein we have shown significant departures from conventional mass-bias correction models which assume mass independence of the fractionation function. Consequently, the regression method is the recommended model for mass bias correction because of its independence from the fractionation exponent and fractionation function values. Despite the significant efforts invested in the interpretation of the mass-bias fractionation exponent by others, we show that it is a dummy variable whose unique value cannot be determined as currently practiced. In this light, alternative approaches are required to access this parameter.

APPENDIX

The ion transmission (mass bias) of the isotope of mass m_k is the ratio of the measured and true amount of an isotope, $K_k = n_k/N_k$. Hence, the ratio of two isotope transmissions can be written as follows:

$$\frac{K_i}{K_j} = \frac{n_i/n_j}{N_i/N_j} = \frac{r_{ij}}{R_{ij}} \qquad (13)$$

Although the true functional relation between the K_i and K_j is unknown, it can be approximated using Taylor's theorem which asserts that any sufficiently smooth function can locally be approximated by polynomials. This can be achieved by expanding $\ln K$ as a function of m^n, where n is an arbitrary fractionation exponent:

$$\ln K_i \approx \ln K_j + \frac{\partial \ln K(j)}{1! \cdot \partial m^n}(m_i^n - m_j^n) + \frac{\partial^2 \ln K(j)}{2! \cdot \partial (m^n)^2} \times$$
$$(m_i^n - m_j^n)^2 + \dots \qquad (14)$$

In the conventional form of the generalized power law, the first derivative of the transmission function (evaluated at m_j) is denoted as the fractionation function f_{ij}. Hence, trimming the Taylor expansion to the first-degree gives the familiar generalized power law:

$$\ln K_{ij} = f_{ij} \cdot (m_i^n - m_j^n) \qquad (15)$$

A note has to be made here regarding the higher-order terms in eq 15. If the fractionation function f_{ij} is mass-independent, as postulated in the generalized power law,[8,14] any higher-order derivatives of the f_{ij} with respect to m^n become zero. Therefore, deviations from the first-order Taylor expansion, that is, eq 15, will indicate the mass dependence of the fractionation function. This is the analytical strategy to demonstrate the mass-dependence of f_{ij} followed in this work.

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