



Reduction of determinate errors in mass bias-corrected isotope ratios measured using a multi-collector plasma mass spectrometer



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ABSTRACT

A nebulizer-centric instrument response function model of the plasma mass spectrometer was combined with a signal drift model, and the result was used to identify the causes of the non-spectroscopic determinate errors remaining in mass bias-corrected Pb isotope ratios (Tl as internal standard) measured using a multi-collector plasma mass spectrometer. Model calculations, confirmed by measurement, show that the detectable time-dependent errors are a result of the combined effect of signal drift and differences in the coordinates of the Pb and Tl response function maxima (horizontal offset effect). If there are no horizontal offsets, then the mass bias-corrected isotope ratios are approximately constant in time.

In the absence of signal drift, the response surface curvature and horizontal offset effects are responsible for proportional errors in the mass bias-corrected isotope ratios. The proportional errors will be different for different analyte isotope ratios and different at every instrument operating point. Consequently, mass bias coefficients calculated using different isotope ratios are not necessarily equal.

The error analysis based on the combined model provides strong justification for recommending a three step correction procedure (mass bias correction, drift correction and a proportional error correction, in that order) for isotope ratio measurements using a multi-collector plasma mass spectrometer.

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1. Introduction

Linear mass bias corrections alone are insufficient to account for all the observed non-spectroscopic determinate errors in elemental analysis by quadrupole plasma mass spectrometry [1]. This was also found to be true of isotope ratios measured using a multi-collector plasma mass spectrometer [2]. Application of the linear mass bias correction was actually a three step procedure: the mass bias correction (using an internal standard), followed by a linear interpolation drift correction of the mass bias-corrected ratios followed by a proportional error correction. The necessity for these additional corrections (drift and proportional error) was never satisfactorily explained because the origins of the errors were poorly understood. Recent developments in modeling response surface effects on signal ratioing [3] and in the signal drift modeling of ion signals and their quotients [4] suggested a combined model may be useful for identifying the causes leading to the necessity for those corrections and for providing justification of their use in analytical isotope ratio plasma mass spectrometry.

Ion signals measured using a plasma mass spectrometer can be considered to be the result of a transform of a steady input signal by an instrument response function and an ion mass-dependent function. In an ideal instrument, there are no ion mass-dependent determinate

errors and the normalized response surfaces of all the ions are coincident and concave downward. The measured isotope ratios are exactly correct at any operating point. Any lack of coincidence among the response surface (differences in the surface curvatures or in the coordinates of the apexes of the response surfaces) will cause a determinate error in an isotope ratio measured at any point, except unless the surfaces happen to intersect. A seemingly small horizontal separation between two response surfaces can cause surprisingly large errors in the quotient of the surfaces (the rational function effect [3]).

Signal drift can be modeled as the orthogonal projection of a time-dependent parametric hardware drift curve (defined in the coordinate axis plane) onto the instrument response surface [4]. That model was useful for explaining the origins of the, at times complex, time-dependent patterns of signal and signal ratio drift in plasma (optical or mass) spectrometry. The optimal calibration strategy may not necessarily involve a mass bias correction; a simple drift interpolation scheme often worked better than the alternatives.

This work combines the response function and signal drift models of the multi-collector plasma mass spectrometer to investigate the origins of drift and proportional errors in the mass bias-corrected isotope ratios of Pb (Tl as the internal standard). The Pb–Tl isotope system was selected for study because it conveniently contains all the response function configurations of interest: normalized response surface curvatures are different for Pb and Tl and the ^{207}Pb and ^{208}Pb level curves are horizontally offset from those of ^{204}Pb , ^{206}Pb , ^{203}Tl and ^{205}Tl [3].

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Model calculations are initially applied to an error analysis, which systematically varies the values of the response function coefficients and documents the resulting errors in the raw and mass bias-corrected ratios. From that error analysis, certain combinations of response function coefficients were identified as producing distinctive isotope ratio drift patterns among the different analyte ratios of an element. Comparison of the model results with the measured drift trends in mass bias-corrected Pb ratios will be used to confirm the basic soundness of the combined response surface and signal drift model. It will then be shown that the multiple correction factors in the instrument calibration are a necessary consequence of the cumulative effects of signal mass bias, signal drift and the signal response surface properties on the measured ion signals.

2. Theory

In plasma spectrometry, measured signals are defined by a multi-dimensional instrument response function $S(x_1, x_2, \dots, x_n)$ (or, for brevity, $S()$), where the x represent pressures, temperatures, voltages, ion mass, ionization potential, geometric factors, etc. $S()$ is assumed to be a concave downward function of the (x_1, x_2, \dots, x_n) possessing a global maximum with no local maxima in the neighborhood of the global maxima. For the purposes of a qualitative analysis, $S()$ can be reduced to the form $S(x_1, x_2)$ and then further simplified by specifying a convenient form for $S(x_1, x_2)$, i.e., a surface which is symmetric about the apex of $S()$. On a nebulizer-centric model of the plasma, level curves of $S()$ are concave downward functions of the nebulizer gas pressure [3,5,6], which are approximately quadratic near the level curve maxima for the multi-collector instrument [3]. In that context, a qualitative study of the multi-collectors' operating characteristics can reasonably begin by defining an ideal instrument response surface as a concave downward paraboloid:

$$S(x_1, x_2) = a_2(x_1 - a_1)^2 + b_2(x_2 - b_1)^2 + k_0 \quad (1)$$

where the constant k_0 is unity; i.e., for each isotope ion i the maximum of $S_i(x_1, x_2)$ is normalized to 1.0 which makes a_2, b_2 normalized curvature coefficients. $S_i(x_1, x_2)$ is symmetric about the apex so the values of the coefficients are related as $(b_1 = a_1) = 0$ and $(b_2 = a_2) < 0$. Then, for this ideal instrument, $S_i()/S_j() = 1.0$ for any (i, j) at any (x_1, x_2) for which $S() > 0$. Later (Section 4), a more realistic model surface will be defined by modifying Eq. (2) to contain cross product terms $(x_1 x_2)$ and by altering the curvature of the x_2 level curves.

The model calculations begin by using for the coefficients of x_1 the least squares fit of quadratic curves to sets of Pb and Tl isotope ion signals measured as a function of the nebulizer gas pressure using a multi-collector plasma mass spectrometer. The errors of mass bias-corrected ratios are then studied by examining the effect of sequentially introducing to the ideal instrument response function a signal mass bias, a change in the response surface curvature and a change in the coordinates of the response surface maximum.

2.1. Changing k_0 to $k_0(m)$

A linear mass bias of the ion signals is represented by a vertical translation of $S()$ so that the constant k_0 in Eq. (1) now becomes the mass bias scaling function $k_0(m) = c_1 m + c_0$ where, for these calculations, $c_1 = 0.004$ (the best case lower limit of the mass bias per amu for a multi-collector spectrometer), $c_0 = 1.0$ and $m = (m_i - m_0)$, where m_0 is the mass of the lightest mass isotope ion being measured and m_i is the mass of an analyte or internal standard ion. Eq. (1) becomes

$$S^*(x_1, x_2, k_0(m)) = a_2(x_1 - a_1)^2 + b_2(x_2 - b_1)^2 + k_0(m) \quad (2)$$

The fractional error, R_{IR} , for an isotope ratio is defined as $R_{IR} = IR_M/IR_T$, where M and T denote the model calculated (or measured) and true

isotope ratios. The general isotope ratio mass bias error function for Eq. (2) is then

$$R_{IR}(m_i, m_j) = S_i^*(x_1, x_2, k_0(m))/S_j^*(x_1, x_2, k_0(m)) \quad (3)$$

The addition of a mass bias scaling function means that for any (i, j) at any (x_1, x_2) , $IR_M \neq IR_T$. Also, for any $((i, j), (k, l))$ pair, $R_{IR}(m_i, m_j) \neq R_{IR}(m_k, m_l)$ at any point (x_1, x_2) . Setting $k_0(m) = \sum a_n m^n$, the polynomial isotope ratio mass bias error function for analytical work is [2]:

$$R_{IR}(m_i, m_j) = \sum_{k=0}^n \left(\sum_{l=0}^n \left(\frac{\alpha_l}{\alpha_k} m_l^l \right) \right)^{-1} m_i^k \quad (4)$$

from which the linear ($n = 1$) mass bias error function is

$$R_{IR}(m_i, m_j) = (m_j + \alpha_0/\alpha_1)^{-1} m_i + (m_j \alpha_1/\alpha_0 + 1)^{-1} \quad (5)$$

A single internal standard isotope ratio is required to obtain the value of the mass bias coefficient α_0/α_1 . Eq. (5) is exact for any analyte-internal standard pair $((i, j), (k, l))$ for all values of (x_1, x_2) . If the internal standard registers no mass bias effect, then the mass bias correction factor is by definition $R_{IR} = 1.0$ for all the analyte ratios.

2.2. Effect of response function curvature

Normalized curvatures of the Pb and Tl nebulizer gas pressure response level curves are identical for isotope ion signals of the same element but differ between elements [3]. Set the curvature coefficients in Eq. (2) to the experimentally determined values $(a_2 = b_2)_{Tl} = -0.0133$ and $(a_2 = b_2)_{Pb} = -0.0131$. The linear mass bias correction is now inexact since the quadratic terms in Eq. (2) are no longer equal for the analyte and internal standard, which invalidates Eqs. (4) and (5). Consequently, there is a proportional error remaining in the mass bias-corrected Pb isotope ratios, which is a different value for each Pb ratio, and the amount of error depends on the location of operating point (x_1, x_2) . This effect also causes values of α_0/α_1 calculated using different (i, j) pairs to be unequal.

In the neighborhood of the response surface maxima, the proportional error values were within $\pm 0.0004\%$ over all Pb ratios ($x_2 = 0, -2 \leq x_1 \leq 2$) and within $\pm 0.004\%$ at operating points where the signals strengths are within 80% of the response surface maxima ($x_2 = -5, -2 \leq x_1 \leq 2$). The difference between the values of a mass bias-corrected ratio as a function of x_1 at any constant x_2 are inconsequential: $\leq 10^{-7}$ at ($x_2 = 0, -2 \leq x_1 \leq 2$) and $\leq 10^{-6}$ at ($x_2 = -5, -2 \leq x_1 \leq 2$). In practice these errors are, typically, undetectable. An x_1 step size of 0.2 was used for the calculations in Sections 2.2 to 2.4.

2.3. Effect of horizontal offsets

The location of the maxima of the nebulizer gas pressure response functions for Pb and Tl isotope ion signals measured using a multi-collector do not coincide (a horizontal offset) [3]. There were no detectable differences among the maxima coordinates of ^{203}Tl , ^{205}Tl , and ^{204}Pb , ^{206}Pb ; however, for ^{207}Pb and ^{208}Pb , there was a small horizontal offset of 0.1 psig. The error in a quotient $S_i()/S_j()$ increases by a factor of ca. 100 when the horizontal offset between two surfaces $S_i()$ and $S_j()$ is increased from 0 to 0.1 ([3]). A mass bias correction for Pb isotope ratios using Tl as an internal standard will not decrease this error, except perhaps by a fortuitous cancellation of errors.

Set $a_1 = b_1 = 0.1$ for ^{207}Pb and ^{208}Pb , the other coefficients retaining their previous values. The calculated mass bias-corrected $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios contained amounts of proportional error which should be experimentally detectable: $\pm 0.25\%$ in the neighborhood of the response surface maxima ($x_2 = 0, -2 \leq x_1 \leq 2$) and

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