An internal normalization technique for unmixing total-spiked mixtures with application to MC-ICP-MS[☆]

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Abstract

Isotopic analyses of a total-spiked sample by multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) are often corrected for mass fractionation by doping the sample with an external tracer element of known isotopic composition and similar mass. However, because of the potential for elemental fractionation on the ICP-MS, internal normalization methods should be used whenever possible. Here, we present a weighted non-linear inversion of the mass spectra of a total-spiked sample, using linear, power, and exponential laws. This method was applied to the calibration of an Osmium tracer solution enriched in ^{190}Os, and the results agree with iterative unmixing algorithms. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Isotope dilution is a widely used method for accurate determination of elemental concentrations. The measured isotopic ratios of spike-sample mixtures must be corrected for mass fractionation in order to obtain accurate isotope dilution calculations and spike unmixing. Whereas, fractionation in normal solutions (e.g., unspiked) can be corrected by normalizing to an isotopic ratio whose value is invariant in nature, there exists no isotopic ratio for direct normalization in spike-normal mixtures because isotopic abundances in the mixture have been altered by adding spiked and unknown amounts of normal solution.

Various approaches have been used to correct for fractionation. In the example where fractionation is linearly dependent on mass, algebraic solutions can be derived (Hofmann, 1971; Moore et al., 1974). Alternatively, an iterative method can be applied to solve for fractionation. In the iterative method, an initial concentration is first calculated for the unknown based on the observed isotopic composition of the isotope dilution mixture. After spike-stripping, an "approximate" theoretical normalizing ratio is calculated, giving rise to a fractionation factor. The fractionation factor is then used to correct the isotopic ratios in the mixture, and spike-unmixing is performed again. The iterative cycle is repeated until the calculated fractionation factors and concentrations converge. In the situation of non-linear fractionation, iterative methods are employed because analytic solutions are lacking.

For MC-ICP-MS analysis, isotopic fractionation can also be corrected by external normalization: for example, Pb, Cu, and Os isotopic ratios are frequently normalized to Tl, Zn, and Ir, respectively (see Hirata, 1996; Marechal et al., 1999; Yin et al., 2001). This approach assumes that the mass fractionation factors for two different elements with similar masses are identical. However, it is becoming increasingly apparent, particularly with highly precise instruments, that elemental discrimination should not be overlooked. One way to overcome this problem is to establish a

correlation between the fractionation factors of the element of interest and the doped element. Yin et al. (2001) demonstrated that the correlation between Ir and Os fractionation factors could be used to correct spike-normal mixtures successfully for mass fractionation. It must be noted, however, that their empirical correlation was established by numerous time-consuming high precision measurements of Ir–Os mixtures by multiple-collector ICP-MS.

As an independent check of this method, we used a weighted least-squares method for internal normalization of spike-normal mixtures. The results of our algorithm were presented in Yin et al. (2001), but the full details were not presented. In this communication, we present our alogrithm along with the source-code for the Fortran program ("SPIKE"). This spike-unmixing algorithm accommodates linear, power, and exponential fractionation laws. While iterative spike-unmixing uses only two isotope ratios (one for peak-stripping and one for fractionation correction), the inversion method allows additional isotope ratios to be incorporated and to be weighted according to their relative errors, thus providing an independent and robust check of the former method.

2. Fractionation "laws"

We consider three fractionation "laws" to account empirically for isotopic fractionation. Following the notation of Wasserburg et al. (1981), we let R_{ij} be the isotopic ratio of isotopes i and j with masses m_i and m_j. We define m_{ij} as $m_i - m_j$, where j is the reference or normalizing isotope. The isotopic reference value is denoted by R_{ij}^N, the measured isotopic ratio by R_{ij}^M, and the corrected ratio by R_{ij}^C.

For the *linear* law, we use the following expression for the corrected ratio:

$$R_{ij}^C = R_{ij}^M (1 + \alpha m_{ij}),\qquad (1a)$$

where the fractionation factor α is determined by

$$\alpha(u, v) = \left(\frac{R_{uv}^N}{R_{uv}^M} - 1 \right) \Big/ m_{uv}\qquad (1b)$$

and u and v represent a particular choice of an isotope pair for normalization.

For the *power* law, the corrected ratio is given by

$$R_{ij}^C = R_{ij}^M (1 + \alpha_p)^{m_{ij}},\qquad (2a)$$

where the fractionation factor is

$$\alpha_p(u, v) = \left(\frac{R_{uv}^N}{R_{uv}^M} \right)^{1/m_{uv}} - 1.\qquad (2b)$$

For the *exponential* law, the corrected ratio is given by

$$R_{ij}^C = R_{ij}^M \left(\frac{m_i}{m_j} \right)^{\beta},\qquad (3a)$$

where

$$\beta = \ln\left(\frac{R_{uv}^N}{R_{uv}^M} \right) \Big/ \ln\left(\frac{m_u}{m_v} \right)\qquad (3b)$$

and the mass fractionation factor $\alpha_E(u, v) = \beta/m_j$.

The power and exponential laws appear to give the best results. Walder et al. (1993) and Hirata (1996) preferred the power law. More recently, Luais et al. (1997) and Marechal et al. (1999) showed that the exponential law produces more precise results. The choice of fractionation law may differ depending upon the type of instrument or specific gas flow dynamics. As such, careful analysis of normal isotopic solutions should be used as a guide.

3. Forward problem

The two parameters that we wish to obtain in isotope dilution calculations are the fractionation factor (Eqs. (1b), (2b) or (3b)) and the mole fraction of a particular isotope in the spike and normal solutions, denoted as A^{Sp} and A^N. A set of mass–balance equations relating the fractionation-corrected isotopic ratios of the mixture to the spike and normal solutions can thus be written

$$(R_{ij}^C)_{Mix} = A_j^{Sp}(R_{ij}^C)_{Sp} + A_j^N(R_{ij}^C)_N,\qquad (4a)$$

where $(R_{ij}^C)_{Mix}$, $(R_{ij}^C)_{Sp}$, and $(R_{ij}^C)_N$ represent, respectively, the fractionation-*corrected* isotopic ratios of the mixture, spike, and normal solutions, and A_j^{Sp} and A_j^N represent the mole fraction of the normalizing isotope. Since $A_j^{Sp} + A_j^{No} = 1$, Eq. (4a) can be rewritten as

$$(R_{ij}^C)_{Mix} = A_j^{Sp}(R_{ij}^C)_{Sp} + (1 - A_j^{Sp})(R_{ij}^C)_N.\qquad (4b)$$

Substituting Eqs. (1a), (2a) and (3a) into the mass–balance Eq. (4b) and rearranging so that the unknown parameters are on the right-hand side, we get the following expressions for the linear, power, and exponential laws:

Linear :

$$\frac{(R_{ij}^C)_N}{(R_{ij}^M)_{Mix}} = 1 + \alpha(m_{ij}) - A_j^{Sp}\frac{(R_{ij}^C)_{Sp} - (R_{ij}^C)_N}{(R_{ij}^M)_{Mix}},\qquad (5a)$$

Power :

$$\frac{(R_{ij}^C)_N}{(R_{ij}^M)_{Mix}} = (1 + \alpha)^{m_{ij}} - A_j^{Sp}\frac{(R_{ij}^C)_{Sp} - (R_{ij}^C)_N}{(R_{ij}^M)_{Mix}},\qquad (5b)$$

Exponential :

$$\frac{(R_{ij}^C)_N}{(R_{ij}^M)_{Mix}} = \left(\frac{m_i}{m_j} \right)^{\beta} - A_j^{Sp}\frac{(R_{ij}^C)_{Sp} - (R_{ij}^C)_N}{(R_{ij}^M)_{Mix}},\qquad (5c)$$

where $(R_{ij}^M)_{Mix}$ represents the measured isotopic ratio of the spike-normal mixture. For a given fractionation law,

Eqs. (5a)–(5c) represents a system of equations with two unknown parameters, A_j^{Sp} and α (or β in Eq. (5c)). For an element with at least three non-radiogenic isotopes there exists at least two equations, and thus the system of equations can be solved.

Eqs. (5a)–(5c) are in the form of a forward problem,

$$\mathbf{d} = \mathbf{g}[\mathbf{p}], \tag{6}$$

where $\mathbf{g}[\mathbf{p}]$ is a function of parameters $\mathbf{p}$, and $\mathbf{d}$ represents the predicted values of the observables. For example, if Eq. (5c) is used, then $\mathbf{d} = (R_{ij}^C)_N/(R_{ij}^M)_{Mix}$ and $\mathbf{g}$ is a function of $\mathbf{p} = (\beta, A^{Sp})$. Because we wish to extract the parameter vector, $\mathbf{p}$, the forward problems, as represented by Eqs. (5a)–(5c), must be inverted.

4. Generalized inversion

In Eqs. (5b) and (5c), the parameter vector $\mathbf{p}$ cannot be factored out of the function $\mathbf{g}$ due to the non-linearity of the problem. Iteration is thus needed to solve for $\mathbf{p}$. The inversion represents $\mathbf{g}$ at iteration step $k + 1$ by the first-order Taylor series around the set of parameters determined at step k

$$g_n^{k+1} \approx g_n^k + \sum_n G_{nm}^k (p_m^{k+1} - p_m^k), \tag{7}$$

where

$$G_{nm}^k = \left. \frac{\partial g_n}{\partial p_m} \right|_{p^k}. \tag{8}$$

$\mathbf{G}^k$ is an $N \times M$ matrix, N is the number of data $\mathbf{d}$ ($n = 1, 2, \ldots, N$), and M is the number of parameters $\mathbf{p}$ ($m = 1, 2, \ldots, M$). We define the misfit function at step k by the quadratic

$$S_k = \tfrac{1}{2}\{(\mathbf{d}^{obs} - \mathbf{g}_k)^{\mathrm{T}} \mathbf{C}_d^{-1} (\mathbf{d}^{obs} - \mathbf{g}_k)$$
$$+ (\mathbf{p}^{initial} - \mathbf{p}_k)^{\mathrm{T}} \mathbf{C}_p^{-1} (\mathbf{p}^{initial} - \mathbf{p}_k)\}, \tag{9}$$

where $\mathbf{p}^{initial}$ represents an initial guess of parameter values, and $\mathbf{C}_d$ and $\mathbf{C}_p$ represent the covariance matrices for the data and the parameters, respectively. $\mathbf{C}_d$ is determined from analytical precision and is used to weight (or normalize) the data according to their uncertainties. The data are assumed to be free of systematic error (independent of each other) such that $\mathbf{C}_d$ is diagonal. $\mathbf{C}_p$ represents only an estimate of the covariance, and it is assumed that the parameters are independent of each other so that $\mathbf{C}_p$ is also a diagonal matrix. Note that the first term in Eq. (9) without the weighting factor is equivalent to the least-squares approach used by Albarede (1995) for peak-stripping. The least-squares approach requires us to minimize the misfit at step $k + 1$

$$\frac{\partial S_{k+1}}{\partial \mathbf{p}} = \frac{\partial S_k}{\partial \mathbf{p}} + \frac{\partial}{\partial \mathbf{p}} \left[\left(\frac{\partial S}{\partial \mathbf{p}} \right)_k^{\mathrm{T}} (\mathbf{p}_{k+1} - \mathbf{p}_k) \right] = 0. \tag{10}$$

Following the derivation presented in Lee (1999), we obtain the iteration algorithm (also known as the Gauss–Newton method)

$$\mathbf{p}_{k+1} = \mathbf{p}_k + \mathbf{C}_{p'k}\{\mathbf{G}_k^{\mathrm{T}} \mathbf{C}_d^{-1}(\mathbf{d}^{obs} - \mathbf{g}_k)$$
$$+ \mathbf{C}_p^{-1}(\mathbf{p}^{initial} - \mathbf{p}_k)\}, \tag{11a}$$

$$\mathbf{C}_{p'k}^{-1} = \mathbf{C}_p^{-1} + \mathbf{G}_k^{\mathrm{T}} \mathbf{C}_d^{-1} \mathbf{G}_k. \tag{11b}$$

The latter is equivalent to the covariance matrix $\mathbf{C}_{p'}$ of post-processed parameters for linear problems. The diagonal nature of $\mathbf{C}_p$ ensures that Eq. (11b) is invertible. The off-diagonal entries of $\mathbf{C}_{p'}$ indicate whether the computed parameters are cross-correlated.

This algorithm is implemented by a Fortran program ("SPIKE"), which is available from the IAMG server. Accurate and precise knowledge of the spike composition is required. Iteration (for each set of $\mathbf{p}^{initial}$) is continued until $\partial S_{k+1}/\partial \mathbf{p} \leq 0.00001$. The initial values for the parameters are updated until the root mean square $\sqrt{\sum_{n=1}^{N} (g_n^k - d_n^{obs})^2/(N-M)}$ is minimized (<0.0001). We find that for any reasonable estimate of the initial parameters, the algorithm rapidly converges within 10–15 steps for all three fractionation laws.

5. Application to the calibration of Os spike

We applied this method towards the calibration of an osmium spike HOST (Harvard Osmium Tracer) against two gravimetrically prepared Os standards. Mass spectrometry details and accompanying data are presented in Yin et al. (2000). Analyses were conducted on a Micromass Isoprobe multiple-collector (MC) ICP-MS. Solution was introduced by a conventional glass spray chamber and Meinhard nebulizer. All solutions were doped with normal Ir (Plasmachem standard) for external normalization. Analysis of normal Os solutions showed that internal normalization according to the exponential law gave the best precision and accuracy. The exponential law was therefore adopted. By analyzing Os–Ir solutions over a period of several days and varying gas flow, Yin et al. (2000) showed that the mass fractionation factor of Os and Ir were not identical, but that their mass fractionation factors were highly correlated. The following empirical relationship was derived: $\beta^{Os} = 0.8717\beta^{Ir} - 0.15175$ ($R^2 = 0.99898$), where β^{Os} and β^{Ir} refer to the exponential fractionation factor normalized to $^{192}Os/^{188}Os = 3.08261$ and $^{193}Ir/^{191}Ir = 1.682992$ (Walczyk and Heumann, 1993). Although changing the normalization values can change the intercept of this equation, the slope (0.8717) cannot be changed. The non-unity of the slope indicates that Ir and Os fractionate differently, and therefore, Ir cannot simply be used to make external corrections for Os

fractionation. However, Ir can be used provided the Ir fractionation factor is corrected according to this empirical correlation (which may need to be established at the beginning of each day).

Yin et al. (2001) showed a comparison between spike concentrations determined by internal and external normalization. Inversion results agree with those determined using the empirical Os–Ir correlation to within ~ 0.5‰ (analytical precision is 0.4‰, this value being limited by handling error and is discussed at length in Yin et al.). However, there is a systematic bias towards higher values (1‰) if Ir, only, is used for external normalization. The agreement between the internal normalization technique and the empirical Os–Ir correlation indicates that the latter is valid (to within error), even if the correlation was established by combining data from different runs with variable gas flow dynamics.

6. Conclusions

The inversion technique described here provides a method for highly accurate determination of elemental concentrations by isotope dilution using internal normalization and simultaneous peak-stripping (provided there are no isobaric interferences). This technique can be used to double-check external normalization methods. More importantly, it can be used to verify "internal normalizations" based on empirical correlation between the mass fractionation factors of the element of interest and of the doped element used for external normalization on ICP-MS measurements.

Acknowledgements

Appendix

The executable Fortran program is called "SPIKE." The program allows the use of a preexisting input file (.INP) or a new input file to be entered. Four isotopes are used, yielding 3 isotope ratios. The program first asks the user to specify the isotopes in the numerator and the isotope in the denominator (e.g., the reference isotope). For the calibration of the Os spike, ^{190}Os is used as the reference isotope. The user is then asked to specify the values of each isotopic ratio for the standard (normal isotopic composition) and the spike, e.g. ^{188}Os/^{190}Os, ^{189}Os/^{190}Os, and ^{192}Os/^{190}Os. Afterwards, the measured values of each ratio for the spike-normal mixture are entered, as well as the measured standard deviation. After choosing the appropriate fractionation law (linear, power, exponential), the user makes an initial guess of A_j^{Sp} and β, as well as an initial guess of their respective errors. The program allows the initial guesses to be manipulated to minimize the residual error. The results are tabulated in the output file. The set of initial guesses yielding values of A_j^{Sp} and β with the lowest residuals are summarized by the program in the output file. Comparison of the inversion technique with spike-normal unmixing by the iterative approach (as discussed in the introduction) yields agreement to within 0.3‰. It is important to note that this inversion technique, as any spike-unmixing technique, assumes that there are no isobaric intereferences during the measurement.

Below is an example of an input file "MIX11-1.INP" for Osmium spike-normal mixtures. ^{190}Os is used as the reference mass because it is the enriched isotope in the spiked solution. Standard 1, 2, and 3 represent the normal ^{188}Os/^{190}Os, ^{189}Os/^{190}Os, and ^{192}Os/^{190}Os ratios ("Low at mass#" = 188, "Mid at mass#" = 189, "High at mass#" = 192), and Spike 1, 2, and 3 represent the respective spike ratios (all of which must be known independently). "Measuremt" 1, 2, and 3 represent the measured ^{188}Os/^{190}Os, ^{189}Os/^{190}Os, and ^{192}Os/^{190}Os of the spike-normal mixture and "Stn dev" 1, 2, and 3, represent initial guesses of the analytical precision of the mixture ratios. This input file can be modified for other elements of interest, such as Nd and Hf.

```
OS MIX 11 RUN           1 MIX11-1.INP
  Ref at mass#          Low at mass#   Mid at mass#   High at mass#
  .1900000D+03         .1880000D+03   .1890000D+03   .1920000D+03
   Standard 1            Spike 1        Standard 2     Spike 2        Standard 3    Spike 3
  .5040270D+00         .4754000D-02   .6147810D+00   .6481000D-02   .1553719D+01   .1033400D-01
   Measuremt 1           Stn dev 1      Measuremt 2    Stn dev 2      Measuremt 3   Stn dev 3
  .5058800D-01         .5000000D-05   .6293900D-01   .1400000D-04   .1580740D+00   .3300000D-04
OS MIX 11 RUN           1 MIX11-1.INP
       EXPONENTIAL LAW
```

A summary of the results is given below in the output file MIX11-1y.OUT. This summary file reports the initial guesses and the inverted estimates of A and β ("BETA"). The covariance matrix and the cross-correlations are also given. The estimated parameters are then used to recalculate the measured ratios, from which a measure of the misfit can be determined. In general, the initial guess should be based on an estimate of the fractionation factor (estimated from an unspiked sample) and A (based on a rough estimate of the sample's concentration). If these are not known, the inversion is robust enough that convergence nearly always occurs even if the initial guess is significantly off. In such cases, it is worth taking the calculated results from the output file and entering these numbers back into "SPIKE" to get a better residual. A residual of $< 10^{-5}$ is considered sufficiently small.

```
OS MIX 11 RUN 1 MIX11-1.INP


     S U M M A R Y: Set 11 of 12 trial sets has the least rms
  Initially guessed parameters
     Exponential       BETA =-.1830000D+01 +/- .1000000D+00
                         A = .9000000D+00 +/- .3000000D+00
  Finally calculated parameters
     Exponential       BETA =-.1830353D+01 +/- .7344144D-01
                         A = .9062146D+00 +/-.9736471D-04
                    Alpha =-.9633438D-02 +/-.3865339D-03
  Covariance
                                    .539D-02  .366D-05
                                    .366D-05  .948D-08
  Cross Correlation= .7152186D+00
  Resolution ONEness= .6787012D+00
                                    .461D+00  .406D-04
                                    .366D-03  .100D+01
Calculated    Ratio 1,   Ratio 2,   Ratio 3: .5058811D-01  .6293703D-01  .1580748D+00
Measured          1         2         3: .5058800D-01  .6293900D-01  .1580740D+00
Calculated-Measured=                      .1137748D-06  -.1965600D-05  .7956891D-06
          Mist rms=.2123594D-05
```

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