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LETTER

Direct correction for mass fractionation of spiked isotopic ratios from dynamic multicollector measurements

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It is shown that two internal reference isotopic ratios of an element permit direct and exact power law correction for mass fractionation of its isotopically spiked ratios from dynamic multicollector measurements. Applications of this method to spike calibration and a few elements of geochronological interest are discussed.

INTRODUCTION

Multicollector thermal ionization mass spectrometers have come into wide use because of two of their significant advantages over the time-honoured single collector machines. Simultaneous measurement of two or more isotopes of an element eliminates errors due to beam fluctuations and time interpolation for beam drift. Secondly, since a much greater proportion of the available ion currents is collected, analysis time for a given statistical precision is significantly reduced. Also effects of amplifier decay constants are negligible in multicollection, as much longer delay times are affordable after any field adjustments or shifts during an analysis. All these features of multicollection are very favourable for small sample analysis that is becoming the trend in modern isotopic research in earth and planetary sciences. The development of high performance multicollectors spurred by the limitations of single collection in thermal ionization mass spectrometers was very handy for the recently developed plasma source sector mass spectrometers to cope with inherent fluctuations of ion beams from an inductively coupled plasma (ICP) ion source (Walder and Freedman, 1992; Halliday *et al.*, 1998).

Multicollection has been used in either static or dynamic modes. In static multicollection (SMC) magnetic field is fixed and isotopes of interest are measured in as many individual collectors that are positioned appropriately. Hence the ratios of measured isotopes require that the gain- and cup efficiency factors of the individual collectors be accurately calibrated and remain stable within the uncertainty of this calibration during the course of a measurement. In dynamic multicollection (DMC) static multicollection of a subset of the desired number of isotopes is combined with magnet field switching to include all the isotopes in such a way to cancel out inter-collector gain factors and to some extent ion collection efficiencies in ratio calculations. Ludwig (1997) has shown that the time efficiency of dynamic analyses is similar to that of static in most cases. Also if the number of collectors is small (2 or 3) as in older instruments, DMC is the only option.

In both SMC and DMC, correction for mass fractionation of isotopes in the thermal or plasma

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ionization process of unspiked (natural) elements is by normalizing to one accepted constant isotopic ratio (e.g., ^{86}Sr/^{88}Sr = 0.1194 for Sr) as in single collection (Thirlwall, 1991). For isotopically spiked elements as in isotope dilution analysis, mass fractionation correction in SMC is again by normalizing to the one accepted ratio in the natural element after subtracting iteratively or algebraically a small spike contribution to it. For single collector measurements, Boelrijk (1968) showed how spiked ratios can be directly corrected for linear mass fractionation, if the element in question has two internal reference ratios for normalization (e.g., ^{84}Sr/^{86}Sr in addition to ^{88}Sr/^{86}Sr).

Despite its advantages over SMC (Ludwig, 1997), no procedure for direct mass fractionation correction of spiked isotopes of an element from DMC measurements is generally known. Wendt and Haase (1998) have recently described a procedure to indirectly correct spiked ratios from DMC measurements. The procedure reported here uses dynamic multicollector measurements in conjuction with two internal reference ratios of an element to not only directly correct all its spiked isotopic ratios for mass fractionation but also monitor the varying fractionation according to power law during an analysis. The significant advantages of this method over that of Wendt and Haase (1998) and its applications to spike calibration and analysis of Sr, Nd and Sm are discussed.

METHOD

The method can be more easily followed if applied to a specific element like Sr and DMC routine using just 3 cups. Table 1 shows the matrix of peak height measurements in a mixture of natural (sample) Sr and a highly enriched ^{84}Sr spike (tracer). One single cycle (scan) shown consists of simultaneous measurements of three isotopes of Sr in the low mass (l), axial (a) and high mass (h) collectors, respectively with three sequential magnetic field shifts to cover all the four isotopes of Sr. Baselines are measured before and after each block of typically 10 such cycles. 84, 86 etc. are net peak heights of the respective Sr isotopes. $(84/86)_1$ is then the apparent ratio of these two isotopes measured in the low and high mass collectors in the first field setting. All these ratios (4 in all) are to be corrected for mass fractionation in the ion source and inter-collector gain differences at the detector end, assuming ion collection efficiencies of and ion transmission to the three collectors are 100%. If f_p is the mass fractionation factor per unit mass difference according to power law (Russell *et al.*, 1978), and $(1 + g_l)$ and $(1 + g_h)$ are the gain factors of the low and high mass collectors, respectively relative to the axial collector, the corrected ratios in the mixture (m) are given by

Table 1. One cycle of three sequential measurements in a dynamic triple collector routine for Sr isotopes

Field position	Collectors		
Measurement	low (l)	axial (a)	high (h)
1	84	—	86
2	—	86	87
3	86	87	88

$$(84/86)_m = (84/86)_1\,(1 + g_l)\,(1 + g_h)^{-1}\,(1 + f_p)^{-2} \tag{1}$$

$$(87/86)_m = (87/86)_2\,(1 + g_h)\,(1 + f_p) \tag{2}$$

$$= (87/86)_3\,(1 + g_l)^{-1}\,(1 + f_p) \tag{3}$$

$$(88/86)_m = (88/86)_3\,(1 + g_l)^{-1}\,(1 + g_h)\,(1 + f_p)^2. \tag{4}$$

Setting $(1 + g_l)^{-1}(1 + g_h)(1 + f_p)^2 = x$ gives

$$(84/86)_m = (84/86)_1\cdot x^{-1} \tag{5}$$

$$(87/86)_m = [(87/86)_2\,(87/86)_3]^{1/2}\cdot x^{1/2} \tag{6}$$

$$(88/86)_m = (88/86)_3\cdot x. \tag{7}$$

The identity relation between the true (corrected) ratios of 84, 87 and 88 relative to 86 in the sample (s), spike (t) and mixture (m) is given by the isotope dilution equation (Webster, 1960; Boelrijk, 1968) as

$$[{}^{86}N_s/{}^{86}N_t] = [(84/86)_t - (84/86)_m]/[(84/86)_m - (84/86)_s] \tag{8}$$

$$= [(87/86)_t - (87/86)_m]/[(87/86)_m - (87/86)_s] \tag{9}$$

$$= [(88/86)_t - (88/86)_m]/[(88/86)_m - (88/86)_s] \tag{10}$$

where ${}^{86}N_s$ and ${}^{86}N_t$ are the number of moles of ^{86}Sr in the sample and spike portions, respectively of the mixture. Substitution of $(84/86)_m$ and $(88/86)_m$ from Eqs. (5) and (7) into the right hand side expressions of Eqs. (8) and (10), cross multiplication, multiplication throughout by x and rearrangement of the terms lead to the quadratic equation, $ax^2 + bx + c = 0$, where

$$a = (88/86)_3\ [(84/86)_t - (84/86)_s]$$

$$b = [(88/86)_t\ (84/86)_s - (84/86)_t\ (88/86)_s]$$

$$c = (84/86)_1\ [(88/86)_s - (88/86)_t].$$

The expressions within the square brackets above remain unchanged for any mixture of sample Sr and given spike, as the terms involved are all known. Using the apparent $(88/86)_3$ and $(84/86)_1$ ratios of each scan or their averages for a block of several such scans in a mass spectrometer run, the quadratic equation can be solved for its two roots. For a spike highly enriched in ^{84}Sr, the positive root close to unity will be the obvious choice for x, which can then be used in Eqs. (5), (6) and (7) to calculate the corrected $(84/86)_m$, $(87/86)_m$ and $(88/86)_m$ ratios directly and immediately after each scan. Since intercollector gain factors will be quite stable during an analysis, the variation in x will accurately track changing mass fractionation with time. The grand means of these ratios from several blocks of data can finally yield the desired sample ratios from the usual sample – spike unmixing equation as

$$(87/86)_s = (87/86)_m - [(87/86)_t - (87/86)_m]\ [(84/86)_m - (84/86)_s]/[(84/86)_t - (84/86)_m]$$

$$(88/86)_s = (88/86)_m - [(88/86)_t - (88/86)_m]\ [(84/86)_m - (84/86)_s]/[(84/86)_t - (84/86)_m].$$

The closeness of agreement of the derived $(88/86)_s$ with the accepted value of 8.37521 used in fact as one of the two normalizing ratios will serve as a check on the appropriateness of the power law of mass fractionation to characterize the actual fractionation in the ion source.

The correction factor x has so far included only terms for inter-collector gain differences (mainly electronics related) and mass fractionation in the ion source. But it can as well include additional terms for small differences in intercollector ion collection efficiencies as $(1 + e_l)$ and $(1 + e_h)$ and ion transmission as $(1 + T_l)$ and $(1 + T_h)$. Due to the symmetry of the DMC routine used, the method will once again give a quadratic equation in x whose solution will now combine corrections also for unequal cup efficiencies and ion transmissions. So the excellent long term external precision and accuracy realizable with DMC on unspiked elements should also be realisable on spiked elements.

While this method provides exact power law correction, it can also accommodate correction according to exponential law (Russell *et al.*, 1978) with a small algebraic approximation. Applying exponential mass fractionation correction to the present choice of isotopic ratios, Eqs. (1) to (3) will change to

$$(84/86)_m = (84/86)_1(1+g_l)(1+g_h)^{-1}[84/86]^{86f_e} \tag{11}$$

$$(87/86)_m^2 = (87/86)_2 (87/86)_3 (1+g_l)^{-1} (1+g_h) [87/86]^{2\times 86 f_e} \tag{12}$$

$$(88/86)_m = (88/86)_3 (1+g_l)^{-1} (1+g_h) [88/86]^{86 f_e} \tag{13}$$

where f_e is the exponential fractionation factor per unit mass difference and the ratios within square brackets are those of corresponding isotopic masses. Since

$$[84/86]^{86 f_e} = [1-2/86]^{86 f_e} \simeq [1+2/86]^{-86 f_e}$$

and

$$[87/86]^{2\times 86 f_e} = [1+1/86]^{2\times 86 f_e} \simeq [1+2/86]^{86 f_e}.$$

Equations (11) to (13) above will be mathematically analogous to Eqs. (5), (6) and (7), namely

$$(84/86)_m = (84/86)_1 \cdot x^{-1}$$

$$(87/86)_m{}^2 = (87/86)_2\ (87/86)_3 \cdot x$$

$$(88/86)_m = (88/86)_3 \cdot x,$$

where $x = (1 + g_l)^{-1}\ (1 + g_h)\ (1+2/86)^{86 f_e}$. The rest of the procedure is the same as given earlier leading to a quadratic equation in x, whose positive root close to unity will contain the correction for exponential mass fractionation.

DISCUSSION

In the above method the relevant root (x) of the quadratic equation is a direct correction factor for instrumental biases (mass fractionation and differences in intercollector gains and cup efficiencies) on measured spiked Sr ratios. In the method of Wendt and Haase (1998) the relevant root (x) of the quadratic equation is the fraction of ^{86}Sr from a highly enriched ^{84}Sr spike in the sample + spike mixture and hence has to be subsequently used in the usual sample – spike mixing equation to calculate corrected spiked isotope ratios. This particular choice for x is unsatisfactory for three main reasons. Firstly, x being necessarily very small (x << 1) in optimally spiked mixtures, it cannot be computed accurately and precisely enough from measured ratios in each scan or even block of scans. So the authors themselves recommend calculating a mean x at the very end of a run for retrospective calculation of corrected ratios in each scan. Secondly, the error in the mean value of x is propagated through the sample – spike mixing equation into the total error of the corrected ratios. Thirdly and more importantly, the analyst will have no idea of the magnitude and variability of mass fractionation during or even after a run, which is a serious drawback.

To determine the mass fractionation during an analysis, Wendt and Haase have had to use the static multicollector data from the large array of dynamic seven collector measurements after correcting them for intercollector gain differences. This step undoes the very advantage of DMC namely cancellation of intercollector gain and cup efficiency factors in ratio calculations. The authors claim that this combination of DMC and SMC data provides five independent ^{87}Sr/^{86}Sr ratios from each scan on a 7 or 5 collector array of cups instead of just two ratios from DMC and 3 from SMC alone. This claim is not valid, as only three independent ^{87}Sr/^{86}Sr ratios are available in each scan. To use SMC data, one needs a minimum of five collectors, whereas one needs a minimum of only three collectors in the present method. With a five collector DMC routine, the present method will give two independent corrected ^{87}Sr/^{86}Sr ratios in each scan besides closely tracking changing mass fractionation during an analysis. Other advantages of the present method are its capability to accommodate exponential correction for mass fractionation with a small algebraic approximation and its close similarity to DMC measurement of unspiked isotopic ratios.

The two reference ratio formulation outlined above can of course be used for direct correction for mass fractionation of spiked isotopic ratios in static analyses also. However, it is best suited to realize the inherent advantages of DMC over SMC even on spiked samples.

APPLICATIONS

Spike (tracer) calibration

Any error in the isotopic composition of tracers used in isotope dilution analysis propagates into an error in the determination of sample isotopic composition as a result of subtraction of tracer contribution from the sample-tracer mixture data. The main error in the tracer composition is due to mass fractionation which cannot be easily corrected in the absence of an internal reference ratio. For this reason isotopic results from spiked analyses rarely have accuracy and precision comparable to unspiked analyses, even if samples could be optimally spiked to minimize propagation of error in the spike composition to unknown sample compositions.

Algebraic solution (Hofmann, 1971) for correction of mass fractionation in isotopic tracers of a variety of elements has been based on determining a critical mixture of a normal standard and tracer to define their mixing line and using its intersection with the mass fractionation trajectory of the tracer, that is assumed to be linear. Besides the problem of unfavourable intersection angles (Roddick *et al.*, 1992), uncertainties in spike calibration can arise from the unrealistic assumption of linear mass fractionation. Also this procedure is quite tedious.

Since two internal reference ratios in a normal standard can directly correct isotopic data of its mixture with a tracer according to the more realistic power law and, in favourable cases, exponential law, they can in principle facilitate accurate and precise determination of the tracer composition. In the example of Sr above, one way could be to start with a mass fractionated isotopic composition of a Sr tracer and measure apparent $(84/86)_1$, $(88/86)_3$ ratios for its mixture with a normal Sr standard. Substituting incrementally and systematically adjusted values of the tracer composition according to power law in the coefficients a, b and c of the quadratic equation, one can quickly compute a tracer composition that yields spike corrected standard ratios $(87/86)_s$ and $(88/86)_s$ closest to their known values (0.71025 and 8.37521, respectively in the case of SRM 987 Sr standard). This can be checked with the results from other mixtures of the standard and tracer.

Table 2. One cycle of dynamic triple collector routine for selected Nd and Sm isotopes

Field position Measurement	Collectors low (l)	 axial (a)	 high (h)
Nd			
1	142	143	144
2	143	144	145
3	144	145	146
Sm			
1	—	147	148
2	147	148	149
3	148	149	150

Spiked Sm and Nd analysis

Fortunately several other elements used in geocosmochronological studies have two or more internal reference ratios that can be used for direct correction of spiked ratios for mass fractionation according to power law or even exponential law for heavy elements. For example, DMC routines with 3 collectors for Nd and Sm are given in Table 2 and briefly discussed below.

The DMC routine for Nd is similar to that for Sr with the desired isotopic ratio (143/144) and (145/144) measured twice in each scan. The tracer used is ^{146}Nd. ^{150}Nd tracer used by some labs is not suitable for a 3 collector routine. Either (142/144), (146/144) or (145/144), (146/144) can be used as the two reference ratios. The latter pair may be preferable, as ^{142}Nd could be subject to isobaric interference from ^{142}Ce due to incomplete chemical separation prior to mass spectrometry. The latter pair gives the corrected spiked ratios as

$$(142/144)_m = (142/144)_1 \cdot x^{-2}$$

$$(143/144)_m = [(143/144)_1\ (143/144)_2]^{1/2} \cdot x^{-1}$$

$$(145/144)_m = [(145/144)_2\ (145/144)_3]^{1/2} \cdot x$$

$$(146/144)_m = (146/144)_3 \cdot x^2$$

where $x^2 = (1 + g_l)^{-1}(1 + g_h)(1 + f_p)^2$. Substitution for $(145/144)_m$ and $(146/144)_m$ in the corresponding identity relation of the isotope dilution equation will lead to a quadratic equation in x as before with its three coefficients being

$$a = (146/144)_3\ [(145/144)_t - (145/144)_s]$$

$$b = (145/144)_0\ [(146/144)_s - (146/144)_t]$$

$$c = [(146/144)_t\ (145/144)_s - (145/144)_t\ (146/144)_s]$$

where $(145/144)_0 = [(145/144)_2\ (145/144)_3]^{1/2}$. Note that coefficients b and c above are mathematically equivalent to c and b, respectively in the Sr case. The real root close to unity can then be used to calculate $(142/144)_m$, $(143/144)_m$ and $(145/144)_m$ that are least affected by the spike addition. Sample spike unmixing equation will then yield the desired radiogenic isotopic ratio $(143/144)_s$ with $(142/144)_s$ and $(145/144)_s$ serving as a check on the accuracy of power law correction. Exponential correction can be implemented, if desired, using the following algebraic approximation.

$$(1+g_l)^{-1}(1+g_h)[146/144]^{144f_e} = (1+g_l)^{-1}(1+g_h)[1+2/144]^{144f_e} = x^2$$

$$(1+g_l)^{-1}(1+g_h)[145/144]^{2\times 144f_e} \simeq (1+g_l)^{-1}(1+g_h)[1+2/144]^{144f_e} = x^2$$

$$(1+g_l)(1+g_h)^{-1}[143/144]^{2\times 144f_e} \simeq (1+g_l)(1+g_h)^{-1}[1+2/144]^{-144f_e} = x^{-2}.$$

For samarium analysis, (147/148) and (149/148) are taken as the two internal reference ratios. With ^{147}Sm as the enriched tracer isotope, the DMC routine in Table 2 is very efficient in measuring the spiked ratio twice in each scan. They can be corrected for mass fractionation by the relevant root of the quadratic equation in x in which

$$x = [(1 + g_l)^{-1}(1 + g_h)(1 + f)^2]^{1/2}$$

$$a = (149/148)_0\ [(147/148)_s - (147/148)_t]$$

$$b = [(147/148)_t\ (149/148)_s - (147/148)_t\ (147/148)_s]$$

$$c = (147/148)_0\ [(149/148)_t - (149/148)_s]$$

where $(149/148)_0 = [(149/148)_2\ (149/148)_3]^{1/2}$ and $(147/148)_0 = [(147/148)_1\ (147/148)_2]^{1/2}$. While $(147/148)_m$ can be used for deriving ^{147}Sm concentration in the sample portion of the mixture, $(149/148)_m$ and $(150/148)_m$ after correction for a small spike contribution can serve as check on the validity of the fractionation correction. Correction after exponential law is exactly as in Nd case.

Although the procedure outlined here is not directly amenable to the measurement of oxide species with high precision, it may be useful for some oxide species, especially Os in which relatively less precision (0.1%) is acceptable.

CONCLUSIONS

A simple computational procedure is given for direct power law correction for mass fractionation of spiked isotopic ratios of an element from dynamic multicollector measurements using two internal normalizing ratios. Besides tracking any variation of mass fractionation during an analysis, it can realize the inherent advantages of DMC over SMC in the analysis of unspiked elements also for spiked elements.

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