

15.4 Application of Isotope Dilution in Geochemistry

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15.4.1 Introduction

A multitude of methods for concentration measurements in geological, environmental, and extra-terrestrial samples are available (see [Chapters 15.9–15.23](#)). The most commonly applied methods are x-ray fluorescence (XRF), electron probe micro analysis (EPMA), instrumental neutron activation analysis (INAA), secondary ion mass spectrometry (SIMS), and inductively coupled plasma mass spectrometry (ICPMS). The method employed generally depends on the elements of interest, the available amount of sample, as well as the available instrumentation and its technical specifications, such as sensitivity, mass resolution, and stability. Whenever element concentrations with ultimate accuracy and precision are required, as, for example, in geochronology, isotope dilution (ID) is the method of choice (see [Chapters 1.11, 1.12, 4.8, 4.10, and 14.1](#)). For an ID analysis, a known quantity of an element having a nonnatural isotope composition (IC), the so-called spike, is added to a known quantity of the sample. By measuring the IC of the spike-sample mixture with mass spectrometry, it is possible to calculate the concentration of the element of interest in the sample ([Figure 1](#)). In principle, ID can be applied to any element comprising at least two naturally occurring isotopes, irrespective of the kind of sample to be analyzed, that is, solid, liquid, or gas.

After the US Atomic Energy Commission first supplied isolated stable isotopes of many elements in 1946, ID became a widely applied tool for concentration determinations in a wide range of samples in the natural sciences (e.g., [Heumann, 1986; Inghram, 1954](#)). Isotope dilution was first applied to geological problems in the 1950s (e.g., [Inghram et al., 1950; Marshall and Hess, 1960; Reynolds, 1950; Wasserburg and Hayden, 1955; Webster, 1960](#)). In geochronology, for example, ID can minimize uncertainties on the calculated ages of rocks, which critically depend on the uncertainties of the determined parent

and daughter element concentrations. Moreover, for many geological applications, it is becoming increasingly important to resolve percent-level differences in concentration (e.g., [Baker et al., 2002; Evensen et al., 1978; Hofmann and White, 1983; Jochum et al., 1983, 1988, 2011; Münker et al., 2000; Nakamura, 1974; Pfänder et al., 2007; Stracke et al., 2012; Weyer et al., 2002; Willbold and Jochum, 2005; Willbold and Stracke, 2006](#); see [Chapters 2.2, 3.1, and 4.1](#)). For these reasons, we review here the basic principles of ID, its strengths and weaknesses, and its applicability to geological problems.

15.4.2 Applications of Isotope Dilution

Isotope dilution has two principal applications in the earth and planetary sciences:

- (1) to determine accurate and precise element concentrations, and
- (2) to distinguish between mass fractionation that occurs before the equilibration of the spike-sample mixture and afterward (the so-called double-spike techniques).

15.4.2.1 Determination of Accurate and Precise Element Concentrations

To determine the concentration of an element by ID, a known quantity of spike is added to a known quantity of the sample. By measuring the IC of the spike-sample mixture, and knowing the IC of the sample and spike, the concentration of the element of interest can be calculated ([Figure 1](#)). ID can therefore be applied to determine the concentration of any element having at least two naturally occurring isotopes in any sample. In general, the mono-isotopic elements (F, Na, Al, P, Sc, Mn,

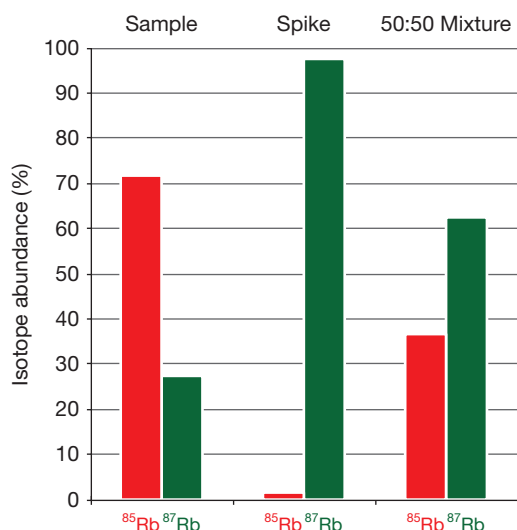


Figure 1 A schematic diagram showing the basic principle of isotope dilution for the example of Rb. A known quantity of a Rb spike consisting of 98% ⁸⁷Rb and 2% ⁸⁵Rb is mixed with the sample whose Rb consists of 72.17% ⁸⁵Rb and 27.83% ⁸⁷Rb. By measuring the isotope composition of the spike–sample mixture, the Rb concentration in the sample can be calculated given that the isotopic compositions of the sample and spike are known.

Co, As, Y, Nb, Rh, Pr, Tb, Ho, Tm, Au, Bi) cannot be directly measured with this method. Some mono-isotopic elements however, such as Be, I, Cs, Th, and Pa, can be analyzed by ID using a spike consisting of a synthetic radioisotope. For example, a ²³³Pa spike can be used in the case of natural ²³¹Pa, or a ²²⁹Th spike in the case of natural ²³²Th.

An ID analysis typically involves the following steps:

- (1) Weighing the desired or necessary amount of sample.
- (2) Adding a known amount of spike, usually by means of weighing, in either dissolved or solid form.
- (3) Equilibration and homogenization of the sample–spike mixture. For solid samples, this step usually involves the dissolution of the solid sample.
- (4) Chemical separation of the element(s) to be analyzed. This step may be omitted if subsequent isotope ratio (IC) measurements do not require the chemical purification of the elements to be analyzed (e.g., Stracke et al., 2012; Willbold and Jochum, 2005).
- (5) Measurement of the isotopic composition of the sample–spike mixtures for the element(s) of interest on a mass spectrometer.
- (6) Calculation of the concentration using the known amounts and isotopic compositions of the sample and spike, and the measured isotopic composition of the sample–spike mixture.

The main advantage of ID over other methods (e.g., XRF, INAA, EPMA, SIMS, IPMS) is that the concentration of an element does not depend on the calibration of the method relative to an external reference material. Rather, the concentration is directly determined from the masses of sample and spike, and the measured ICs of the sample, spike, and sample–spike mixture. Hence, ID is a primary method of analysis (De Bièvre, 1993; Moody and Epstein, 1991; Pin and Le Fèvre, 2002) that is directly traceable to SI units (Lamberty et al.,

1994) and considered superior to comparative methods (e.g., XRF, INAA, EPMA, SIMS, ICPMS; Pin and Le Fèvre, 2002). Another advantage of ID over most other methods (e.g., XRF, INAA, ICPMS) is that it only relies on the measurement of ICs. Once complete homogenization of the spike and samples has been achieved, quantitative recovery of the element is not required. However, quantitative recovery is often attempted to maximize the ion signals during IC measurements. In principle, highly accurate and precise element concentrations can be determined, even for elements occurring at exceedingly low concentrations, such as the femtogram quantities of Pa in volcanic rocks (e.g., Bourdon et al., 1999; Goldstein et al., 1993; Koornneef et al., 2010; Pickett and Murrell, 1997; Regelous et al., 2004).

The major disadvantage of ID is its destructive nature, that is, it generally requires dissolution of the sample so that complete homogenization with the spike may be achieved. Furthermore, spiking often precludes the analysis of other elements on the same sample aliquot. Moreover, mono-isotopic elements (Be, F, Na, Al, P, Sc, Mn, Co, As, Y, Nb, Rh, I, Cs, Pr, Tb, Ho, Tm, Au, Bi) can only be analyzed by ID using a radioisotope spike (see discussion above), which may not be practical.

15.4.2.2 ‘Double Spiking’ for IC Measurements

For IC measurements by mass spectrometry, the addition of two spike isotopes and analyses of four or more isotopes of an element can help distinguish the isotope fractionation that occurs before the equilibration of the spike–sample mixture from any isotope fractionation that occurs afterward. This so-called double-spike technique is used to separate natural isotope fractionations from those induced by chemical processing and analytical measurements. Alternatively, the addition of two spike isotopes may enable mass fractionation corrections to be made for elements that do not have enough stable non-radiogenic isotopes available for internal normalization, such as Pb (Compston and Oversby, 1969; Galer, 1999). Owing to the increasing impact of natural stable isotope fractionation on earth and planetary science research that has been sparked by analytical advances in mass spectrometry, there has been renewed interest in applying this well-established method. Double-spike techniques are particularly useful for correcting for instrumental mass fractionation and for quantifying natural stable isotope variations for elements ranging from Ca to U (e.g., DePaolo, 2004; Stirling et al., 2007).

15.4.3 Principles of Isotope Dilution

15.4.3.1 Derivation of the Principal ID Equation

From the ratio of a spike isotope (A) to a reference isotope (B) of the same element in the sample–spike mixture, the concentration of an element in a given sample is calculated by means of mass balance:

$$\begin{aligned}
 A_{\text{mix}} &= A_{\text{sa}} + A_{\text{sp}} \\
 B_{\text{mix}} &= B_{\text{sa}} + B_{\text{sp}} \\
 \left(\frac{A}{B}\right)_{\text{mix}} &= \frac{A_{\text{sa}} + A_{\text{sp}}}{B_{\text{sa}} + B_{\text{sp}}}
 \end{aligned}$$

where A and B refer to the number of atoms of the spike and reference isotope, respectively. The isotope enriched in the spike is A (e.g., ^{84}Sr for Sr), B is the reference isotope of the measured ratio (e.g., for ^{86}Sr for Sr), and A/B is the measured ratio (e.g., for Sr : $A/B = ^{84}\text{Sr}/^{86}\text{Sr}$). Subscripts mix, sa, and sp refer to the sample–spike mixture, the sample, and the spike, respectively.

By rearranging, an equation relating the proportion of B in the sample and added spike to the isotopic compositions of the sample, spike, and mixture can be derived:

$$\begin{aligned} \left(\frac{A}{B}\right)_{\text{mix}} &= \frac{A_{\text{sa}} + A_{\text{sp}}}{B_{\text{sa}} + B_{\text{sp}}} = \frac{\left(\frac{A}{B}\right)_{\text{sa}} B_{\text{sa}} + \left(\frac{A}{B}\right)_{\text{sp}} B_{\text{sp}}}{B_{\text{sa}} + B_{\text{sp}}} \\ \left(\frac{A}{B}\right)_{\text{mix}} B_{\text{sa}} + \left(\frac{A}{B}\right)_{\text{mix}} B_{\text{sp}} &= \left(\frac{A}{B}\right)_{\text{sa}} B_{\text{sa}} + \left(\frac{A}{B}\right)_{\text{sp}} B_{\text{sp}} \\ B_{\text{sp}} \left[\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}} \right] &= B_{\text{sa}} \left[\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}} \right] \\ \frac{B_{\text{sa}}}{B_{\text{sp}}} &= \frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}} \quad [1] \end{aligned}$$

B_{sa} and B_{sp} refer to the number of atoms of the reference isotope B in the sample (B_{sa} , e.g., $^{86}\text{Sr}_{\text{sa}}$), and the spike (B_{sp} , e.g., $^{86}\text{Sr}_{\text{sp}}$). Hence,

$$\begin{aligned} B_{\text{sa}} &= \frac{\text{weight}_{\text{sa}} \text{conc}_{\text{sa}} ab(B_{\text{sa}}) N_A}{\text{atwt}(\text{element}_{\text{sa}})} \\ B_{\text{sp}} &= \frac{\text{weight}_{\text{sp}} \text{conc}_{\text{sp}} ab(B_{\text{sp}}) N_A}{\text{atwt}(\text{element}_{\text{sp}})} \end{aligned}$$

where weight corresponds to the sample (sa) and spike (sp) weight, conc to the concentration of the element (g g^{-1}) in the sample and spike, $ab(B)$ to the abundance of reference isotope B in the sample and spike, and $\text{atwt}(\text{element})$ to the atomic weight of the element of interest in the sample and spike. N_A is Avogadro's number, which cancels out on the left-hand side of the ID equation (i.e., eqn [1]; $B_{\text{sa}}/B_{\text{sp}}$; e.g., $^{86}\text{Sr}_{\text{sa}}/^{86}\text{Sr}_{\text{sp}}$).

Substitution into eqn [1] results in:

$$\frac{B_{\text{sa}}}{B_{\text{sp}}} = \frac{\text{weight}_{\text{sa}} \text{conc}_{\text{sa}} ab(B_{\text{sa}}) \text{atwt}(\text{element}_{\text{sp}})}{\text{weight}_{\text{sp}} \text{conc}_{\text{sp}} ab(B_{\text{sp}}) \text{atwt}(\text{element}_{\text{sa}})} = \frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}}$$

rearranging:

$$\text{conc}_{\text{sa}} = \frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}} \frac{\text{weight}_{\text{sp}} \text{conc}_{\text{sp}} ab(B_{\text{sp}}) \text{atwt}(\text{element}_{\text{sa}})}{\text{weight}_{\text{sa}} ab(B_{\text{sa}}) \text{atwt}(\text{element}_{\text{sp}})} \quad [2]$$

Hence the concentration of an element in a sample can be calculated with the measured IC of the sample–spike mixture, the known IC and atomic weight of the spike and sample, the measured sample and spike weight, and the concentration of the spike. The natural, IUPAC ('International Union of Pure and Applied Chemistry')-recommended values of the atomic weights of the elements, $\text{atwt}(\text{element}_{\text{sa}})$, are given by Wieser and Coplen (2011). The atomic weight of the spike can be calculated

using the measured isotope ratios of the spike and the IUPAC-recommended atomic weights of the individual isotopes (Wieser and Coplen, 2011). In most cases, the natural IUPAC-recommended isotopic composition can be used for $(A/B)_{\text{sa}}$, and abundance of isotopes, $ab(B_{\text{sa}})$ (Berglund and Wieser, 2011), unless the IC used for the calculation varies significantly in nature, as, for example, for Sr and Pb . For such elements, calculating isotopic abundances from the actual measured ICs gives more accurate results than the IUPAC-recommended values.

For the example of Sr , eqn [2] becomes:

$$\begin{aligned} \text{Sr}_{\text{sa}} (\mu\text{g g}^{-1}) &= \frac{\left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{mix}} - \left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{sp}}}{0.05649 - \left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{mix}}} \\ &\quad \frac{\text{weight}_{\text{sp}} (\text{g}) \text{conc}_{\text{sp}} (\mu\text{g g}^{-1}) ab(^{86}\text{Sr}_{\text{sp}}) \times 87.62 (\text{g mol}^{-1})}{\text{weight}_{\text{sa}} (\text{g}) \times 0.09860 \times \text{atwt}(\text{Sr}_{\text{sp}})} \end{aligned}$$

Note that eqn [2] can be recast in terms of the abundance of the spike isotope by using

$$ab(B_{\text{sp}}) = \frac{ab(A_{\text{sp}})}{\left(\frac{A}{B}\right)_{\text{sp}}}$$

and substituting into eqn [2]:

$$\begin{aligned} \text{conc}_{\text{sa}} (\mu\text{g g}^{-1}) &= \frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left[\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}\right] \left(\frac{A}{B}\right)_{\text{sp}}} \\ &\quad \frac{\text{weight}_{\text{sp}} (\text{g}) \text{conc}_{\text{sp}} (\mu\text{g g}^{-1}) ab(A_{\text{sp}}) \text{atwt}(\text{element}_{\text{sa}})}{\text{weight}_{\text{sa}} (\text{g}) ab(B_{\text{sa}}) \text{atwt}(\text{element}_{\text{sp}})} \end{aligned}$$

For the example of Sr :

$$\begin{aligned} \text{Sr}_{\text{sa}} [\mu\text{g g}^{-1}] &= \frac{\left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{mix}} - \left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{sp}}}{\left[0.05649 - \left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{mix}}\right] \left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{sp}}} \\ &\quad \frac{\text{weight}_{\text{sp}} (\text{g}) \text{conc}_{\text{sp}} (\mu\text{g g}^{-1}) ab(^{84}\text{Sr}_{\text{sp}}) \times 87.62 (\text{g mol}^{-1})}{\text{weight}_{\text{sa}} (\text{g}) \times 0.09860 \times \text{atwt}(\text{Sr}_{\text{sp}})} \end{aligned}$$

In the case that A_{sp} is a nonnatural radioisotope, for example, ^{233}Pa or ^{229}Th , $A_{\text{sa}} = (A/B)_{\text{sa}} = 0$ in eqn [1].

Hence:

$$\begin{aligned} \frac{B_{\text{sa}}}{B_{\text{sp}}} &= \frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{0 - \left(\frac{A}{B}\right)_{\text{mix}}} = \frac{\left(\frac{A}{B}\right)_{\text{sp}} - \left(\frac{A}{B}\right)_{\text{mix}}}{\left(\frac{A}{B}\right)_{\text{mix}}} \\ B_{\text{sa}} &= \left[\frac{\left(\frac{A}{B}\right)_{\text{sp}} - \left(\frac{A}{B}\right)_{\text{mix}}}{\left(\frac{A}{B}\right)_{\text{mix}}} \right] B_{\text{sp}} \\ B_{\text{sa}} &= \left[\left(\frac{A}{B}\right)_{\text{sp}} \left(\frac{B}{A}\right)_{\text{mix}} - 1 \right] B_{\text{sp}} \end{aligned}$$

Thus,

$$\text{conc}_{\text{sa}} (\mu\text{g g}^{-1}) = \frac{\left[\left(\frac{A}{B} \right)_{\text{sp}} \left(\frac{B}{A} \right)_{\text{mix}} - 1 \right] \text{weight}_{\text{sp}} (\text{g}) \text{conc}_{\text{sp}} (\mu\text{g g}^{-1}) \text{ab}(B_{\text{sp}}) \text{atwt}(\text{element}_{\text{sa}})}{\text{weight}_{\text{sa}} (\text{g}) \text{ab}(B_{\text{sa}}) \text{atwt}(\text{element}_{\text{sp}})}$$

Substituting

$$\text{ab}(B_{\text{sp}}) = \frac{\text{ab}(A_{\text{sp}})}{\left(\frac{A}{B} \right)_{\text{sp}}}$$

$$\text{conc}_{\text{sa}} (\mu\text{g g}^{-1}) = \frac{\left[\left(\frac{B}{A} \right)_{\text{mix}} - \left(\frac{B}{A} \right)_{\text{sp}} \right] \text{weight}_{\text{sp}} (\text{g}) \text{conc}_{\text{sp}} (\mu\text{g g}^{-1}) \text{ab}(A_{\text{sp}}) \text{atwt}(\text{element}_{\text{sa}})}{\text{weight}_{\text{sa}} (\text{g}) \text{ab}(B_{\text{sa}}) \text{atwt}(\text{element}_{\text{sp}})}$$

15.4.3.2 Criteria for Spiking Samples

For appreciating what criteria are crucial for selecting which spike isotope to use, and in what proportion to the investigated sample, recall the definition of a 'spike': A spike is an element with nonnatural IC that is highly enriched in an isotope (usually one that has low abundance in nature). Spikes are produced e.g., by electromagnetic separation (calutron), neutron bombardment in nuclear reactors, and by bombardment of target materials with high-energy (~100 MeV) charged particles. Elements that are highly enriched in a single isotope are expensive and available only from a few suppliers, including Oak Ridge National Laboratory, USA, and Cambridge Isotope Laboratories, Inc., USA. The different suppliers offer different elements at variable degrees of isotopic enrichment, and the availability and price of spikes vary.

Two principal criteria for selection of the spike isotope are simply its availability and pricing. Also, one does not want to unnecessarily consume a valuable and rare spike such as ^{84}Sr . The selection of the spike must also consider the spike-sample ratio to be measured. Measurement of very small or large isotope ratios is often subject to larger inherent measurement uncertainties than measurement of ICs of about 1, that is, ion beams having similar intensity, and hence similar counting statistics and response of the collectors. The measured uncertainty of the spike-sample ratio directly scales with the ultimate precision of the calculated concentration. It is therefore important to select an appropriate type and amount of spike to minimize uncertainty on the final concentration determinations.

15.4.3.3 The Optimum Spike-Sample Ratio

It can be shown that the uncertainty on an element concentration, determined by ID, is minimized at a certain ratio of the spike-sample mixture $(A/B)_{\text{mix}}$. This so-called optimum IC of the spike-sample mixture, $\left(\frac{A}{B} \right)_{\text{mix}}^{\text{opt}}$, is given by the geometric mean of the spike and sample ICs (e.g., Webster, 1960; see derivation in the Appendix A):

$$\left(\frac{A}{B} \right)_{\text{mix}}^{\text{opt}} = \sqrt{\left(\frac{A}{B} \right)_{\text{sa}} \left(\frac{A}{B} \right)_{\text{sp}}} \quad [3]$$

For optimally spiked samples, the uncertainty of the determined element concentration is equal to the measurement uncertainty on the ratio $\left(\frac{A}{B} \right)_{\text{mix}}^{\text{opt}} \times F_{\text{min}}$, the error magnification factor at the optimum IC of the spike-sample mixture:

$$F_{\text{min}} = \frac{\left| \left(\frac{A}{B} \right)_{\text{sa}} - \left(\frac{A}{B} \right)_{\text{sp}} \right|}{\left(\sqrt{\left(\frac{A}{B} \right)_{\text{sa}}} - \sqrt{\left(\frac{A}{B} \right)_{\text{sp}}} \right)^2}$$

For all other spike-sample mixtures, the uncertainty of the element concentration is equal to the measurement uncertainty on the ratio $(A/B)_{\text{mix}}$ multiplied by F , the error magnification factor:

$$F = \frac{\left| \left(\frac{A}{B} \right)_{\text{mix}} \left[\left(\frac{A}{B} \right)_{\text{sa}} - \left(\frac{A}{B} \right)_{\text{sp}} \right] \right|}{\left[\left(\frac{A}{B} \right)_{\text{sa}} - \left(\frac{A}{B} \right)_{\text{mix}} \right] \left[\left(\frac{A}{B} \right)_{\text{mix}} - \left(\frac{A}{B} \right)_{\text{sp}} \right]}$$

For the derivation of the above equations according to Webster (1960), see Appendix A.

From the above equations, and corresponding Figures 2 and 3, it becomes obvious that the optimum IC of the spike-sample mixture and the corresponding minimum error magnification factor (F_{min}) are both a function of the purity of the spike, specifically the value of $(A/B)_{\text{sp}}$. As the spike becomes purer, the optimum IC of the spike-sample mixture increases,

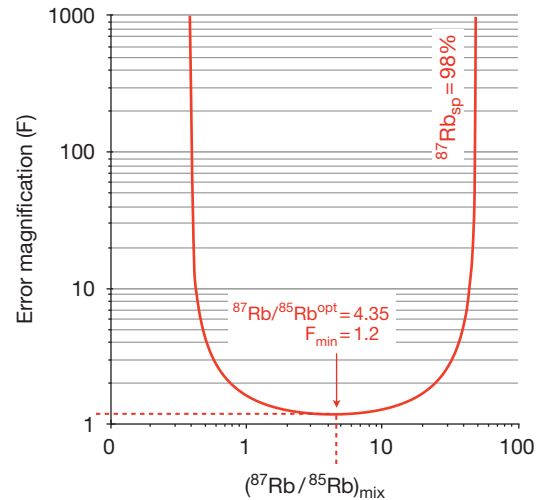


Figure 2 Diagram showing the error magnification as a function of the isotope ratio of the spike-sample mixture. Calculations assume that a Rb spike consisting of 98% ^{87}Rb and 2% ^{85}Rb is mixed with natural Rb from the sample ($^{85}\text{Rb} = 72.17\%$ and $^{87}\text{Rb} = 27.83\%$). The minimum error magnification factor of 1.2 is observed for a spike-sample mixture having $^{87}\text{Rb}/^{85}\text{Rb} = 4.35$. Thus, the lowest uncertainty attainable with the isotope dilution method is 1.2 times the uncertainty of the mass spectrometric measurement of $^{87}\text{Rb}/^{85}\text{Rb}$.

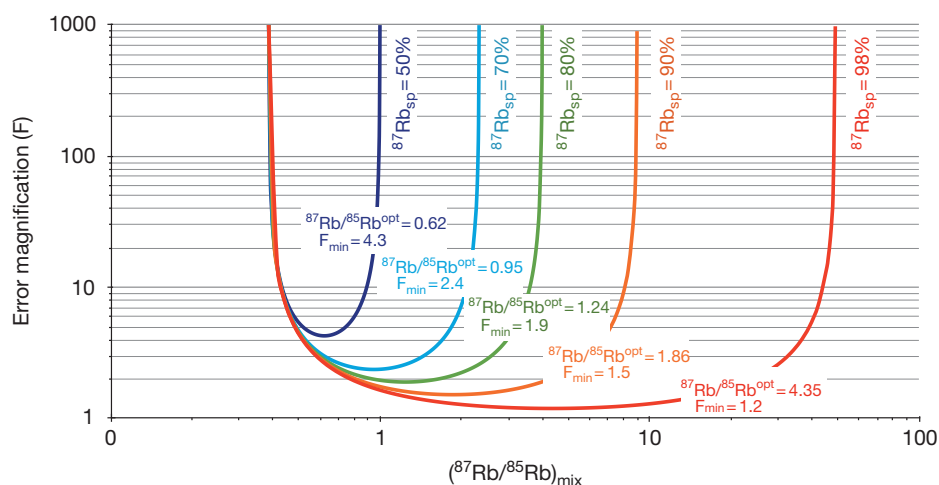


Figure 3 Diagram showing the error magnification as a function of the isotope ratio of the spike-sample mixture for Rb spikes of different composition. Enrichment of ^{87}Rb in the spike is indicated for each curve, in addition to the optimum $^{87}\text{Rb}/^{85}\text{Rb}$ and minimum error magnification factor (F_{\min}). See further discussion in the text.

and the minimum error magnification factor (F_{\min}) decreases. Hence, purer spikes principally allow more precise concentration determinations for optimum ICs of the spike-sample mixture. Another interesting property shown in **Figure 3** is that the range of ICs of the spike-sample mixture having close-to-minimum error magnification increases with increasing spike purity, that is, increasing $(A/B)_{\text{sp}}$. In other words, purer spikes provide the user with more flexibility for spiking samples because the precision of the measured spike-sample ratios is less dependent on accurately estimating the sample concentration before measurement, and valuable spikes can be saved by using less-than-optimum ICs of the spike-sample mixture.

15.4.3.4 Sources of Uncertainty in ID Measurements

Modern mass spectrometers readily permit many isotope ratios to be determined to a precision of better than 0.01%. Thus, the above equations show that ID is a highly accurate and precise technique for measuring concentrations. Mass spectrometric measurement errors on the final spike-sample mixture can, for example, result from poor counting statistics (low signal-to-noise ratios), potential nonlinearity of the detector system, and poor detection limits. However, the accuracy and precision of sample concentrations determined by ID also depend on a number of additional factors. These include uncertainties associated with the terms in eqn [2], such as errors in weighing (sample and spike weight), spike calibration (concentration, IC, and atomic weight of the spike), and those attached to the IUPAC-recommended natural atomic weights of the elements and their isotopic composition (Berglund and Wieser, 2011; Wieser and Coplen, 2011).

From the aforementioned factors alone, propagation of the estimated (or measured) uncertainties on each term of eqn [2] (see **Chapter 15.2**) shows that precision and accuracy of ID concentrations should be on the order of 0.1–0.6%, depending on the actual uncertainties in **Table 1**. For each input variable, we assume that the sum of systematic errors is much smaller than the measurement uncertainty, that is, the values are accurate within their stated precisions. For simplicity, we have neglected the small uncertainties in the atomic weights of

Table 1 Parameters entering eqn [2] with estimated or measured uncertainties for the hypothetical example of a Sr isotope dilution analysis

Parameter in eqn [2]	Absolute value	Relative uncertainty	Absolute uncertainty
weight _{sa} (g)	0.0500	0.2%	0.0001
weight _{sp} (g)	0.1000	0.1%	0.0001
conc _{sp} ($\mu\text{g g}^{-1}$)	10.00	0.2%	0.02
ab ($^{86}\text{Sr}_{\text{sa}}$) ^a	0.0985995	0.001%	0.0000099
ab ($^{86}\text{Sr}_{\text{sp}}$)	0.0005899	0.15%	0.0000009
atwt (Sr_{sa}) ^a	87.6167	0.01%	0.0088
atwt (Sr_{sp})	83.9165	0.01%	0.0084
$^{84}\text{Sr}/^{86}\text{Sr}_{\text{sa}}$	0.05649	0.05%	0.000028
$^{84}\text{Sr}/^{86}\text{Sr}_{\text{sp}}$	1693.1	0.15%	2.5
$^{84}\text{Sr}/^{86}\text{Sr}_{\text{mix}}$	1.0875	0.01%	0.0001

^aBecause of the highly variable abundance of the radiogenic isotope ^{87}Sr among natural samples, $\text{ab}(^{86}\text{Sr}_{\text{sa}})$ and $\text{atwt}(\text{Sr}_{\text{sa}})$ should be calculated using the sample's own isotopic composition rather than relying on the average natural values. This applies as well to other elements that may contain significant contributions from radiogenic isotopes such as Pb, Hf, and Nd.

individual isotopes, as well as correlations among A/B , atomic weight of the element, and abundance of B . The uncertainty of the procedural blank would also propagate into the uncertainty of ID concentration measurements, but we assume here that the analyst has taken measures to reduce blanks to insignificant levels.

An important observation from **Tables 1** and **2** is that the propagated relative uncertainty on the final calculated Sr concentration is several times larger – a factor of 37 in this example – than the relative uncertainty on the measured $^{84}\text{Sr}/^{86}\text{Sr}$ in the spike-sample mixture $(A/B)_{\text{mix}}$. For ideally spiked samples, most of the uncertainty stems from weighing errors, as well as the uncertainty on $(A/B)_{\text{sp}}$ and thus the abundance of B_{sp} . Hence, improving the precision of the measured IC of the spiked sample, $(A/B)_{\text{mix}}$, by prolonging the measurement time would not necessarily improve the precision of measured concentrations.

The parameters in eqn [2] are not the only sources of uncertainty in an ID analysis. Additional errors derive from sample

Table 2 Propagated uncertainties on terms in eqn [2]

Term in eqn [2]	Absolute value	Propagated relative uncertainty	Propagated absolute uncertainty
$\frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}}$	1641.3	0.2%	2.7
$\frac{\text{weight}_{\text{sp}}(\text{g})}{\text{weight}_{\text{sa}}(\text{g})}$	2.000	0.22%	0.0045
$\text{conc}_{\text{sp}}(\mu\text{g g}^{-1})$	10.00	0.2%	0.02
$\frac{ab(B_{\text{sp}})}{ab(B_{\text{sa}})}$	0.005983	0.15%	0.000009
$\frac{\text{atwt}(\text{element}_{\text{sa}})}{\text{atwt}(\text{element}_{\text{sp}})}$	1.04409	0.014%	0.00015
$\text{conc Sr}_{\text{sa}}(\mu\text{g g}^{-1})$	205.1	0.37%	0.8

digestion and subsequent sample processing, for example, sample loss during processing, incomplete sample digestion (see [Chapter 15.5](#)), lack of spike-sample equilibration, isotope fractionation of the sample caused by incomplete recovery during ion exchange chromatography (see [Chapter 15.7](#)), and inherent sample heterogeneity. Finally, inaccurate measurement of the ICs caused, for example, by isobaric interferences, or inappropriate instrumental mass bias correction (see detailed discussion in [Section 15.4.4.3](#)), can introduce errors that have not been included in the error propagation example shown above.

Especially when comparing ID data from different laboratories, it is these latter sources of error that usually dominate over uncertainties arising from mass spectrometry. Comparing ID data between different laboratories is further complicated when only an aliquot of the investigated sample is spiked, as opposed to spiking the entire sample before digestion ('total spiking'). Aliquoting of samples is often done when the natural, unspiked IC of the sample is to be determined in addition to the ID concentration on the same digested sample solution. Especially in situations when a large amount of sample is required to achieve the required precision on the IC analyses, often a much smaller sample aliquot is taken for the ID determination. This approach is motivated either by saving spike or by otherwise being unable to accurately measure the totally spiked sample's natural IC because the spike is not pure enough or there are less than two stable, non radiogenic reference isotopes available in the element of interest (see more detailed 'spike stripping' discussion in [Section 15.4.4.3](#)). Aliquots of samples are taken after sample digestion by removing part of the bulk sample solution. Hence the accuracy and precision involved depend on the completeness of digestion and dissolution: If the sample is not in perfect solution, that is, if any undigested sample or newly formed precipitates are present, then aliquoting may produce solution splits that have unequal proportions of liquid and solid(s). These splits could differ with respect to element concentrations, element ratios, or isotopic ratios, thereby decoupling the IC and ID results. In geochronology, for example, such decoupling causes analytical scatter on isochron plots, adversely affecting the accuracy and precision of dates. Another disadvantage of aliquoting is that the extra steps involved for weighing the aliquot and remaining sample introduce additional weighing errors.

Similar to all other methods of concentration determination, ID can also be compromised by contamination during any step

of the procedure. Strictly speaking, one has to assure that the analyzed material derives entirely from the sample, and not from extraneous sources such as the environment, the reagents, and labware (e.g., vials, pipettes). This can be achieved by analyzing different amounts of sample and testing for consistency or by duplicating the entire procedure without sample, that is, performing a so-called blank measurement. The former possibility is clearly cumbersome and time consuming. The blank measurement is therefore usually the method of choice. Note that the amount of contamination (the 'blank') is calculated with a slightly modified version of eqn [2]:

$$\text{blank}(\text{pg}) = 10^6 \frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}} \frac{\text{weight}_{\text{sp}}(\text{g}) \text{conc}_{\text{sp}}(\mu\text{g g}^{-1}) ab(B_{\text{sp}}) \text{atwt}(\text{element}_{\text{sa}})}{ab(B_{\text{sa}}) \text{atwt}(\text{element}_{\text{sp}})}$$

where subscript sa in this case refers to the 'blank.' The blank is the total amount of the element that mixed with the spike during the procedure. It is expressed as a mass rather than a concentration as in eqn [2] because there is no sample weight in the case of a blank measurement.

When measuring the concentrations of several samples relative to each other using the same spike, several errors affect all samples in the same manner, for example, errors in $(A/B)_{\text{sp}}$ and thus $ab(B_{\text{sp}})$, conc_{sp} , $(A/B)_{\text{sa}}$ and $\text{atwt}(\text{element}_{\text{sp}})$. Hence, a somewhat better precision than quoted above can be achieved. For example, an error in the conc_{sp} will affect the concentrations of all samples in the same sense, that is, the error is systematic and not random. For this reason, spike calibration uncertainties are often not propagated into the overall uncertainty for geochronological applications such as isochron diagrams or U–Pb concordia plots (see [Chapter 4.10](#)), where it is important to measure the scatter among data points or around a regression line to determine the uncertainty of an age. Once the age and uncertainty are determined, the additional systematic errors must be taken into account when comparing the resulting age to one determined using a different spike (e.g., performed by a different lab or using a different isotopic system altogether). A similar line of reasoning applies when comparing ID concentrations reported by two different laboratories: their results may differ more than can be explained by their reported analytical precisions if systematic errors are neglected.

15.4.4 Applying Isotope Dilution

15.4.4.1 Preparation and Calibration of Spikes

The accuracy and precision of concentrations calculated by ID depend critically on accuracy and precision of the concentration and isotopic composition of the spike ([Tables 1 and 2](#); see discussion in [Section 15.4.3.4](#)). Spikes, purchased in solid or dissolved form from one of the suppliers of enriched isotopes (e.g., Oak Ridge National Laboratory, USA, and Cambridge Isotope Laboratories, Inc., USA), must therefore be carefully calibrated against gravimetric concentration and isotopic standards. For the metal elements, this often entails preparing a high concentration standard solution, for example, 1000 ($\mu\text{g g}^{-1}$), by dissolving about a gram of a pure metal or metal compound (e.g., an oxide or salt) in about a liter of an

appropriate acid. Typically, the metal used has a natural isotopic composition. The large amounts of metal and solution allow precise weighing, whereas accuracy is ensured by cross-calibration of the balances with a range of standard weights. This procedure results in gravimetric standard solutions having accurately and precisely known concentrations. For a metal weight of 1.0000 ± 0.0001 g, dissolved to a final solution of 1000.0 ± 0.1 g, the uncertainty on the final concentration of 0.001 g g^{-1} is $\pm 1.4 \times 10^{-7} \text{ g g}^{-1}$ ($1000 \pm 0.14 \text{ } \mu\text{g g}^{-1}$) or 0.014% (see [Chapter 15.2](#)). To avoid wasting valuable spike during the calibration process, the concentrated standard solution is usually diluted further, resulting in additional weighing errors. An aliquot of this dilute standard solution is then mixed with an appropriate amount of spike, taking care that both aliquots are large enough (>0.1 g) to be weighed very precisely, and that the resulting spike-sample mixture is nearly optimal (using the criteria and formulae in [Section 15.4.3.3](#)). Although an additional dilution step results in a slightly larger uncertainty, it avoids the much larger precision loss that would be encountered when weighing only tens of mg of an evaporating liquid. The final concentration of the spike is then calculated by ‘reverse’ ID, that is, by solving eqn [2] for the concentration of the spike (conc_{sp}), using the gravimetrically determined concentration of the standard solution (conc_{sa}), and the isotopic compositions of the natural standard and the spike, as verified by mass spectrometric measurement.

Determination of the accurate isotopic composition of spikes by mass spectrometry is generally not straightforward because of their nonnatural IC, which precludes the usual internal correction for instrumental mass bias. This issue can be resolved by the use of sample-standard bracketing, that is, by assuming that the mass bias during analysis of the spike solution is equal to the mean mass bias of natural standards analyzed before and after the spike. This method can, in principle, be applied to both multi-collector ICPMS (MC-ICPMS) and thermal ionization mass spectrometry (TIMS). Alternatively, spikes measured by MC-ICPMS can be doped with a second element having a known (usually natural) IC and similar mass bias behavior to that of the spike element. Ideally, the second element should not produce any isobaric interferences on the spike element. During the measurement, the mass bias factor measured for the second element is used to correct the spike composition for mass bias. This method has been applied, for example, in recent high-precision Rb ID measurements, where Zr was used as the mass bias reference (e.g., [Nebel et al., 2011](#); [Waight et al., 2002](#)). Another difficulty arising during measurement of spike ICs is that the measured intensity of the spike isotope ideally dwarfs that of the other isotopes, so a high dynamic range is often required for the precise measurement of the complete isotopic composition.

For the aforementioned spike calibration method, solutions prepared from ultrapure (e.g., 99.99%) metal ingots are preferred. Such ingots can be weighed precisely and gravimetric solutions derived from them can be analyzed by (MC-) ICPMS or other methods to verify that the contribution of nonvolatile contaminants to the metal mass was indeed less than 0.01%. Some metals however, such as the alkalis, react violently when placed into aqueous solutions. The resulting material loss via splattering or aerosol escape precludes the use of such elements in metallic form to produce calibration solutions. Rather, salts or oxides of such elements can be employed instead. However, the stoichiometry of the salt has to be assumed or determined, and any adsorbed water must be driven off before weighing.

Stoichiometry assumptions and the effectiveness of the dehydration procedure may be tested by comparing multiple spike calibrations performed using different salts of the same element (e.g., [Nebel et al., 2011](#)).

It is tempting to forgo the effort of producing calibration solutions and simply use commercially available, certified element solutions designed as standards for ICPMS or atomic absorption spectrometry. Even though it is possible to check for impurities as mentioned above, one still has to trust the accuracy of the certified concentration. The analysis certificates may be traceable, that is, either the solution derives from a unique batch of well-characterized standard or it has been calibrated against such a standard. However, the authors’ experience shows that certified solutions can still deviate significantly from their stated concentrations. For applications requiring the highest accuracy, we therefore recommend that analysts produce their own standard solutions for spike calibration, or cross-check certified solutions against gravimetrically prepared solutions. All standard (and spike) solutions should be stored in inert, acid-resistant bottles, and contain appropriate acids to minimize adsorption of the element(s) of interest onto the vessel walls. We also recommend calibrating spikes as soon as possible after production of the standard solution(s), i.e., before changes in the concentration of the latter occur due to water loss (evaporation) or element loss (adsorption, precipitation).

15.4.4.2 Mixed Spikes Versus Single Spikes

For some applications, most notably geochronology, it is essential to be capable of measuring an element ratio at high accuracy and precision over a period of many years. The x-axes of isochron plots, for example, $^{176}\text{Lu}/^{177}\text{Hf}$, $^{147}\text{Sm}/^{144}\text{Nd}$, and $^{87}\text{Rb}/^{86}\text{Sr}$, are essentially proportional to the ratios of the respective elements. One method of measuring the denominator and numerator concentrations would be to weigh in two separate spikes, for example, a ^{149}Sm spike and a ^{150}Nd spike, for a Sm–Nd isochron point. The disadvantage is that any nonsystematic (i.e., random) error component from the separate spike weighings will not cancel. Furthermore, if the Sm spike bottle is impermeable whereas the Nd spike bottle slowly loses evaporated water, the Nd spike will eventually become more concentrated. A sample measured after such spike ‘aging’ will yield an apparent Nd concentration that is too low and thus a Sm/Nd value that is too high. For the sake of long-term- and inter laboratory reproducibility of results, a mixed spike can be employed. A single spike solution containing both parent and daughter elements of a given geochronometer is made. In this way, any evaporative losses or error on the single spike weighing results in the same systematic errors for both elements. These errors cancel in the ratio of these elements. Even if the spike evaporates by a few percent over the years, the absolute concentrations of the elements will be affected, but their concentration ratio will remain constant. This strong advantage comes at a price: because the element ratio is fixed in a given spike, it is seldom possible to simultaneously achieve optimal spike-to-sample ratios for both elements in a large range of unknowns. Thus, to avoid error magnification on the resulting element ratio for different materials, a series of spikes that cover a range of element ratios is produced. For the Lu–Hf system, for example, separate low-, medium-, and high-Lu/Hf spikes can be employed in the analysis of zircon, whole

rocks, and garnet, respectively. In summary, single-element spikes or a suite of several mixed spikes allow a wide range of chemically diverse samples to be measured at near-optimal spike-to-sample ratios for both elements. Mixed spikes provide the additional advantages of smaller uncertainties on measured element ratios, and long-term reproducibility even if the spikes become more concentrated over time.

A set of mixed spikes that cover a range in element ratios can be calibrated with a set of gravimetric standards that also range in element ratio, such that for all spikes, calibrations are performed near the optimal spike-sample ratio for both elements simultaneously. If the spikes are pure enough with respect to the spike isotope, it is often possible to replicate the calibration of each spike with standards having the 'next best' element ratios. In this way, all spike calibrations can be tied in to a single, internally consistent set of mixed element gravimetric standards.

The same recommendations made above for producing single-element standard and spike solutions apply to producing mixed element standards and spikes. Special care must be taken to ensure that all of the included elements are stable in the final acid matrix of the standard or spike. This is especially the case for chemically different pairs such as Lu (a rare earth element) and Hf (a high field strength element). For example, mixing a Lu-bearing HCl stock solution with a Hf-bearing HF solution results in milky white precipitates – presumably Lu fluorides – if the final concentration of HF is too high. Such precipitates would most likely fractionate Lu from Hf, rendering the solution useless as a Lu/Hf standard.

Owing to the chemical variability among rocks and minerals, such mixed spikes are often limited to element pairs (in geochronology) or small suites of elements (trace element geochemistry). For most geochronological applications, isobaric interferences (e.g., ^{176}Lu on ^{176}Hf , ^{144}Sm on ^{144}Nd , and ^{87}Rb on ^{87}Sr) require separation of the elements by ion exchange chemistry and separate mass spectrometric analysis. Modern ICPMS methods allow the simultaneous measurement of ID concentrations for several elements in a sample with only minimal chemical separation (Baker et al., 2002), or even without one (Stracke et al., 2012; Willbold and Jochum, 2005).

15.4.4.3 Simultaneous IC and ID: 'Spike Stripping'

For some applications, it is desirable to measure the element's natural isotopic composition concurrently with the ID measurement using totally spiked samples rather than separate aliquots. This is particularly the case for Sm–Nd, Lu–Hf, and Rb–Sr geochronology, where IC and ID aliquots taken from an imperfect (i.e., precipitate-bearing) solution may have parent–daughter element ratios differing from that of the bulk sample (as discussed in Section 15.4.3.4, but here assuming that the sample has been completely dissolved at some stage and that the post-digestion precipitates and solution have identical ICs after correcting for any mass-dependent fractionation). Such an effect would decouple the x and y coordinates of isochrons, producing analytical scatter. This problem can be avoided by spiking the entire sample before digestion. Because spikes have very unnatural ICs, deconvolution of the resulting data is necessary to recover the true mass bias factor, the ID concentration, and the IC of the sample. This approach requires that the element in question has at least three isotopes whose relative abundances are constant among all natural samples. One of these has to be the isotope in which the spike is enriched, and the other two are

the numerator and denominator of the ratio used for the instrumental mass bias correction. We can thus define two isotope ratios having a common denominator:

$$A/B = (\text{spike isotope A})/(\text{reference isotope B})$$

$$C/B = (\text{mass bias monitor isotope C})/(\text{reference isotope B})$$

We are often interested in a fourth isotope that is radiogenic, thus we define a third ratio:

$$D/B = (\text{radiogenic isotope D})/(\text{reference isotope B})$$

The subscripts mix, sa, and sp will be used to refer to the sample–spike mixture, the sample, and the spike, respectively (Table 3).

In Figure 4, points 'Sa' and 'Sp' denote the ICs of the natural sample and the spike, that is, $\text{Sa} = \{(C/B)_{\text{sa}}, (A/B)_{\text{sa}}\}$ and $\text{Sp} = \{(C/B)_{\text{sp}}, (A/B)_{\text{sp}}\}$. Because the x - and y -axis ratios have the same denominator isotope (B), mixtures of sample and spike lie along a straight line between Sa and Sp. In our example, the point ' M_{true} ' represents the true isotopic composition of the spike-sample mixture, that is, $\{(C/B)_{\text{mix}}, (A/B)_{\text{mix}}\}$. During the mass spectrometric measurement, the sample will become progressively fractionated as the sample evaporates (TIMS), or will be subject to a relatively large but constant instrumental mass bias (MC-ICPMS). The resulting measured IC is denoted ' M_{biased} '. If the mass spectrometer makes an online correction for mass bias, a natural isotopic composition is generally assumed. However, this assumption is clearly false in our example, where $(C/B)_{\text{mix}} > (C/B)_{\text{sa}}$ because of an unnaturally high $(C/B)_{\text{sp}}$ (Figure 4). The instrument thus overcorrects for mass bias, resulting in point ' $M_{\text{over corr.}}$ ' whose C/B value is too low, resulting in an A/B value that is also too low, that is, $(A/B)_{\text{over corr.}} < (A/B)_{\text{mix}}$ and $(C/B)_{\text{over corr.}} < (C/B)_{\text{mix}}$. Using $(A/B)_{\text{over corr.}}$ in eqn [2] would result in an erroneously low spike-to-sample ratio and thus erroneously high element concentration for the sample. This creates an additional problem when the spike contribution is later subtracted ('stripped') from the mixture to yield the sample IC: Not enough spike would be stripped, resulting in errors in the measured sample IC if the

Table 3 Commonly used isotopes and isotope ratios used for simultaneous IC and ID analyses

Isotopes	Hf	Nd	Sm	Sr
Spike isotope (A)	180	150	149	84
Reference isotope (B)	177	144	152	86
Mass bias monitor (C)	179	146	147	88
Radiogenic isotope (D)	176	143	–	87
<i>Isotope ratios</i>				
A/B	180/177	150/144	149/152	84/86
C/B	179/177	146/144	147/152	88/86
D/B	176/177	143/144	–	87/86

Note that although Sm ICs are not needed for Sm–Nd chronology, the use of spike stripping allows a more accurate mass bias correction to be applied and can thus improve the accuracy and precision of Sm concentration determinations: For elements such as Sm, Sr, Nd, and Hf, which have more than two stable, nonradiogenic isotopes, precise ID analyses can be made by applying an internal mass bias correction, that is, using A/B and C/B . For elements having only two isotopes, an external mass bias correction must be applied using a similarly fractionating element (e.g., correcting Lu mass bias with naturally occurring Yb or admixed Er in MC-ICPMS analyses; Blichert-Toft et al., 2002; Lapan et al., 2004), or by measuring the C/B of standards interspersed with samples and assuming that mass bias is consistent between analyses (e.g., TIMS analyses of Pb).

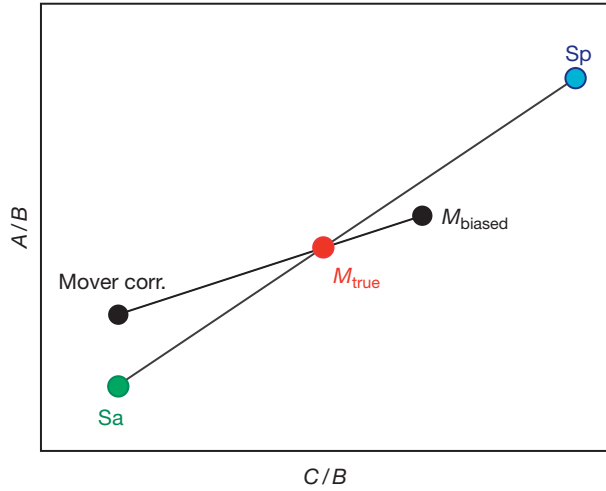


Figure 4 Schematic diagram (not to scale) showing the principle of correcting spiked samples for mass bias. Sa = natural sample, Sp = spike, M_{true} = true composition of spike-sample mixture, M_{biased} = measured, mass-biased composition of the spiked sample, $M_{\text{over corr.}}$ = spiked sample overcorrected for mass bias by instrument when $(C/B)_{\text{mix}}$ is assumed to be natural, that is, $(C/B)_{\text{over corr.}} = (C/B)_{\text{sa}}$. Note that the mixing line Sa–Sp is a straight line, whereas $M_{\text{over corr.}} - M_{\text{true}} - M_{\text{biased}}$ is a mass fractionation curve defined by the exponential mass fractionation law (e.g., Russell et al., 1978; Wasserburg et al., 1981). Note: the actual arrangement of points and slopes of trends depends on the isotopic system and spike being used.

spike is impure (e.g., contains significant amounts of isotopes other than A and $(D/B)_{\text{spike}}$ differs substantially from $(D/B)_{\text{sa}}$).

The true IC of the spiked sample, ' M_{true} ' can be calculated from the intersection between the mixing line Sa–Sp and the exponential mass bias curve that passes through ' M_{biased} '. The Sa–Sp mixing line can be defined as:

$$\left(\frac{A}{B}\right) = m \left(\frac{C}{B}\right) + b \quad [4]$$

where m and b are the slope and intercept of the mixing line Sa–Sp, respectively:

$$m = \frac{\left(\frac{A}{B}\right)_{\text{sp}} - \left(\frac{A}{B}\right)_{\text{sa}}}{\left(\frac{C}{B}\right)_{\text{sp}} - \left(\frac{C}{B}\right)_{\text{sa}}}$$

$$b = \left(\frac{A}{B}\right)_{\text{sa}} - m \left(\frac{C}{B}\right)_{\text{sa}}$$

The relationship between the true spiked sample composition, $M_{\text{true}} = \{(C/B)_{\text{mix}}, (A/B)_{\text{mix}}\}$, and that of the mass-biased sample, $M_{\text{biased}} = \{(C/B)_{\text{biased}}, (A/B)_{\text{biased}}\}$, can be described with the exponential mass fractionation law (e.g., Russell et al., 1978; Wasserburg et al., 1981):

$$\left(\frac{A}{B}\right)_{\text{mix}} = \left(\frac{A}{B}\right)_{\text{biased}} \left[\frac{\text{atwt}(A)}{\text{atwt}(B)} \right]^{\beta}$$

$$\left(\frac{C}{B}\right)_{\text{mix}} = \left(\frac{C}{B}\right)_{\text{biased}} \left[\frac{\text{atwt}(C)}{\text{atwt}(B)} \right]^{\beta}$$

Here, 'atwt(isotope)' refers to the exact mass of the isotope in question, and β is the exponential mass bias factor (e.g., Wasserburg et al., 1981).

Rearranging yields:

$$\beta = \frac{\ln \left[\frac{(A/B)_{\text{mix}}}{(A/B)_{\text{biased}}} \right]}{\ln \left[\frac{\text{atwt}(A)}{\text{atwt}(B)} \right]} = \frac{\ln \left[\frac{(C/B)_{\text{mix}}}{(C/B)_{\text{biased}}} \right]}{\ln \left[\frac{\text{atwt}(C)}{\text{atwt}(B)} \right]}$$

$$\ln (A/B)_{\text{mix}} - \ln (A/B)_{\text{biased}} = \ln \left[\frac{(C/B)_{\text{mix}}}{(C/B)_{\text{biased}}} \right] \frac{\ln \left[\frac{\text{atwt}(A)}{\text{atwt}(B)} \right]}{\ln \left[\frac{\text{atwt}(C)}{\text{atwt}(B)} \right]}$$

$$\ln (A/B)_{\text{mix}} = \ln (A/B)_{\text{biased}} + k \ln \left[\frac{(C/B)_{\text{mix}}}{(C/B)_{\text{biased}}} \right]$$

$$\text{where } k = \frac{\ln \left[\frac{\text{atwt}(A)}{\text{atwt}(B)} \right]}{\ln \left[\frac{\text{atwt}(C)}{\text{atwt}(B)} \right]}$$

Taking the exponent of both sides yields

$$\left(\frac{A}{B}\right)_{\text{mix}} = \left(\frac{A}{B}\right)_{\text{biased}} \left[\frac{(C/B)_{\text{mix}}}{(C/B)_{\text{biased}}} \right]^k \quad [5]$$

The composition of ' M_{true} ' that is, $\{(C/B)_{\text{mix}}, (A/B)_{\text{mix}}\}$, can now be found by iteration of eqs [4] and [5], which can be conveniently combined into a single equation:

$$\left(\frac{C}{B}\right)_n = \frac{\left(\frac{A}{B}\right)_0 \left(\frac{(C/B)_{n-1}}{(C/B)_0}\right)^k - b}{m} \quad [6]$$

where the subscript '0' denotes the measured (mass biased) isotope ratios, and the subscript 'n' is the iteration number, starting with $n = 1$. For the first iteration, the subscript ' $n - 1$ ' has a value 0, so $(C/B)_{\text{biased}}$ is used. Iteration is repeated until $(C/B)_n$ no longer changes significantly, which usually is the case after only a few steps. Once $(C/B)_n$ has converged to the true $(C/B)_{\text{mix}}$, the corresponding $(A/B)_{\text{mix}}$ can be retrieved using eqn [4]. Note that the overcorrected $(C/B)_{\text{over corr.}}$ that is, $(C/B)_{\text{sa}}$, and $(A/B)_{\text{over corr.}}$ could also be used for $(C/B)_0$ and $(A/B)_0$ in eqns [5] and [6]. This essentially 'undoes' the over-correction applied by the instrument. Other accurate mass bias 'laws,' such as the 'generalized power law' (e.g., Wombacher and Rehkämper, 2003), may also be adapted for the data deconvolution starting from M_{biased} (Figure 4).

A word of caution regarding data reduction: The mass bias curve should not be approximated by a straight line for MC-ICPMS analyses. Although deriving M by solving for intersection of this line with Sa–Sp would be straightforward (Figure 4), it would produce inaccurate results at high mass bias values. This should be taken into account when adapting older TIMS data reduction software to MC-ICPMS applications.

At this point, the true value of $(A/B)_{\text{mix}}$ is known and data reduction is complete if only an ID analysis with internal mass bias correction is required: This value, inserted into a slightly modified version of eqn [2], yields the blank-corrected concentration in ppm of the element in the sample:

$$\text{conc}_{\text{sa}} (\mu\text{g g}^{-1}) = \frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}} \frac{\text{weight}_{\text{sp}} (\text{g}) \text{conc}_{\text{sp}} (\mu\text{g g}^{-1}) \text{ab}(B_{\text{sp}}) \text{atwt}(\text{element}_{\text{sa}})}{\text{weight}_{\text{sa}} (\text{g}) \text{ab}(B_{\text{sa}}) \text{atwt}(\text{element}_{\text{sp}})} - \frac{\text{blank}(\text{pg})}{10^6 \text{weight}_{\text{sa}} (\text{g})}$$

If, however, one also needs to recover the natural IC from a totally spiked sample, the contribution of the spike must be stripped away (Figure 5). Using $(C/B)_{\text{mix}}$ the true mass bias factor for the analysis can now be calculated:

$$\beta_{\text{mix}} = \frac{\ln \left[\frac{(C/B)_{\text{mix}}}{(C/B)_{\text{biased}}} \right]}{\left[\frac{\text{atwt}(C)}{\text{atwt}(B)} \right]}$$

Now, the radiogenic ratio $(D/B)_{\text{mix}}$ corrected for the true degree of mass bias is calculated:

$$\left(\frac{D}{B} \right)_{\text{mix}} = \left(\frac{D}{B} \right)_{\text{biased}} \left[\frac{\text{atwt}(D)}{\text{atwt}(B)} \right]^{\beta_{\text{mix}}}$$

Any other remaining isotope ratios may be also corrected for mass bias in similar fashion. The calculation of β_{mix} also allows a consistency check between the mass bias of samples and that of standards. Large differences may indicate uncorrected interferences, matrix element effects, or, in the case of solution MC-ICPMS, different sample solution viscosities.

Once all ICs have been properly corrected for mass bias, the effects of the spike may be ‘stripped’ from the analysis so that the sample IC may be retrieved. First, $B_{\text{sp}}/B_{\text{mix}}$ is calculated using the $B_{\text{sa}}/B_{\text{sp}}$ resulting from inserting the mass bias corrected $(A/B)_{\text{mix}}$ into eqn [1]:

$$\begin{aligned} \frac{B_{\text{mix}}}{B_{\text{sp}}} &= \frac{B_{\text{sa}}}{B_{\text{sp}}} + \frac{B_{\text{sp}}}{B_{\text{sp}}} = \frac{B_{\text{sa}}}{B_{\text{sp}}} + 1 \\ \frac{B_{\text{sp}}}{B_{\text{mix}}} &= \frac{1}{\left(\frac{B_{\text{sa}}}{B_{\text{sp}}} \right)_{\text{eqn}[1]} + 1} \end{aligned} \quad [7]$$

The spike contribution to each measured isotope ratio is calculated as:

$$\frac{\text{Isotope}_{\text{sp}}}{B_{\text{mix}}} = \left(\frac{B_{\text{sp}}}{B_{\text{mix}}}_{\text{eqn}[7]} \right) \left(\frac{\text{Isotope}}{B} \right)_{\text{sp}}$$

Then, the sample (plus blank, ‘bl’) contribution to each ratio is calculated:

$$\frac{\text{Isotope}_{\text{sa+bl}}}{B_{\text{mix}}} = \left(\frac{\text{Isotope}}{B} \right)_{\text{mix}} - \frac{\text{Isotope}_{\text{sp}}}{B_{\text{mix}}}$$

The IC of the sample (plus blank) can now be calculated for all isotopes of the element:

$$\left(\frac{\text{Isotope}}{B} \right)_{\text{sa+bl}} = \frac{\left(\frac{\text{Isotope}_{\text{sa+bl}}}{B_{\text{mix}}} \right)}{\left(\frac{B_{\text{sa+bl}}}{B_{\text{mix}}} \right)}$$

With the isotopic composition of the sample (plus blank) in hand, the number of moles of each isotope can be calculated using the weight of spike added, the spike concentration, and the sample-to-spike ratio derived from eqn [1]. To correct for the blank, its mass is first converted into moles of each isotope. These amounts are then subtracted from the corresponding sample (plus blank) moles for each isotope before calculating the blank-corrected IC and abundances. Finally, the atomic weight of the element is calculated by summing the mass contributions of all isotopes:

$$\text{atwt}(\text{element}) = \sum \text{ab}(\text{isotope}) \times \text{atwt}(\text{isotope}) \quad [8]$$

The sum of moles for all isotopes times their respective atomic weights gives the number of grams of the element in

the sample. This mass, multiplied by 10^6 and divided by the sample weight in grams, gives the $\mu\text{g per g}$ concentration of the element of interest (Figure 5).

There are certain conditions to meet and cautions to heed when performing simultaneous IC and ID measurements: First, note that the ideal spike-to-sample ratio to use for combined IC-ID analyses is generally much lower than the optimal value for a pure ID measurement (Section 15.4.3.3) because the errors introduced on $(D/B)_{\text{mix}}$ by the spike-stripping method employed here increase with spike-sample ratio. On the other hand, the ID errors will be sharply magnified (Figures 2 and 3; Section 15.4.3.3) if the spike-sample ratio is too low. Thus, the ideal ratio will be a compromise that satisfies both ID and IC requirements. For this reason, the spikes should be as pure as possible with respect to the spike isotope. Pure spikes allow a wider range of spike-to-sample ratios to be used without introducing unreasonably large uncertainties on either the natural IC or the ID. Some spikes, for example ^{183}W , are not pure enough to allow combined IC and ID analyses at the required precision. For such applications, the fully dissolved sample must be split into unspiked IC and spiked ID aliquots. By weighing these aliquots, the amount of the element of interest in the IC aliquot can be calculated. Note, however, that the amounts of acid in the aliquots as well as the exact chemical processing procedure for the IC and ID fractions often differ. Thus, the IC and ID aliquots often accumulate different amounts of blank. The blanks of both IC and ID process paths may be determined by carrying out an unspiked digestion, and then spiking both aliquots when the solution is split. The resulting ID blank is used to adjust the number of moles of the element in ID analyses of unknowns. This corrected number of moles is then multiplied by the mass ratio of the IC and ID aliquots to determine how many moles of the sample element are in the IC cut. The measured IC can now be corrected for the blank contribution of the IC process path as described above.

15.4.5 Double and Triple Spiking

The double- or triple-spiking technique is an extension of the single-spike technique described above. It uses two independent measured ratios to calculate two unknown variables: the spike-sample mixing proportions and the degree of mass fractionation. For the double-spike technique, the fractionation is partitioned into that which occurs naturally (i.e., before spike and sample are mixed) and the fractionation of the spiked mixture caused by the analytical procedure. To uniquely separate the three unknown variables – the spike-sample mixing proportions, the degree of mass fractionation between the sample and standard, and the fractionation induced by the measurement – three simultaneous equations can be derived and solved, given three independent inputs (Dodson, 1963, 1970). The measurement of four isotopes, that is, three isotope ratios, can provide the three independent inputs required to uniquely solve the equations. Because the equations are non-linear, the mathematical inversion, termed here deconvolution, is done iteratively (Siebert et al., 2001), using, for example, computer programs such as MATLAB (Rudge et al., 2009). For samples having isotopic anomalies, such as Sr enriched in

Data reduction scheme for mass-bias corrected ID measurements and combined IC-ID measurements on totally spiked samples:

Mass-bias corrected ID measurements

Solve for M_{true} , i.e., $\{(C/B)_{\text{mix}}, (A/B)_{\text{mix}}\}$:

Using either $M_{\text{biased}} = \{(C/B)_{\text{biased}}, (A/B)_{\text{biased}}\}$ or $M_{\text{biased}} = \{(C/B)_{\text{over corr}}, (A/B)_{\text{over corr}}\}$,

iterate Eq. 6 to find the true, mass bias corrected $(C/B)_{\text{mix}}$.
Recover the true, mass bias corrected $(A/B)_{\text{mix}}$ using Eq. 4.

If only a mass bias corrected ID concentration is required, it can now be calculated with a modified version of Eq. 2:

$$\text{conc}_{\text{sa}} [\mu\text{g g}^{-1}] = \frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}} \frac{\text{weight}_{\text{sp}} [\text{g}] \text{conc}_{\text{sp}} [\mu\text{g g}^{-1}] \text{ab}(B_{\text{sp}}) \text{atwt}(\text{element}_{\text{sa}})}{\text{weight}_{\text{sa}} [\text{g}] \text{ab}(B_{\text{sa}}) \text{atwt}(\text{element}_{\text{sp}})} - \frac{\text{blank} [\mu\text{g}]}{10^6 \text{weight}_{\text{sa}} [\text{g}]}$$

Continue data reduction for combined IC-ID measurements on totally spiked samples :

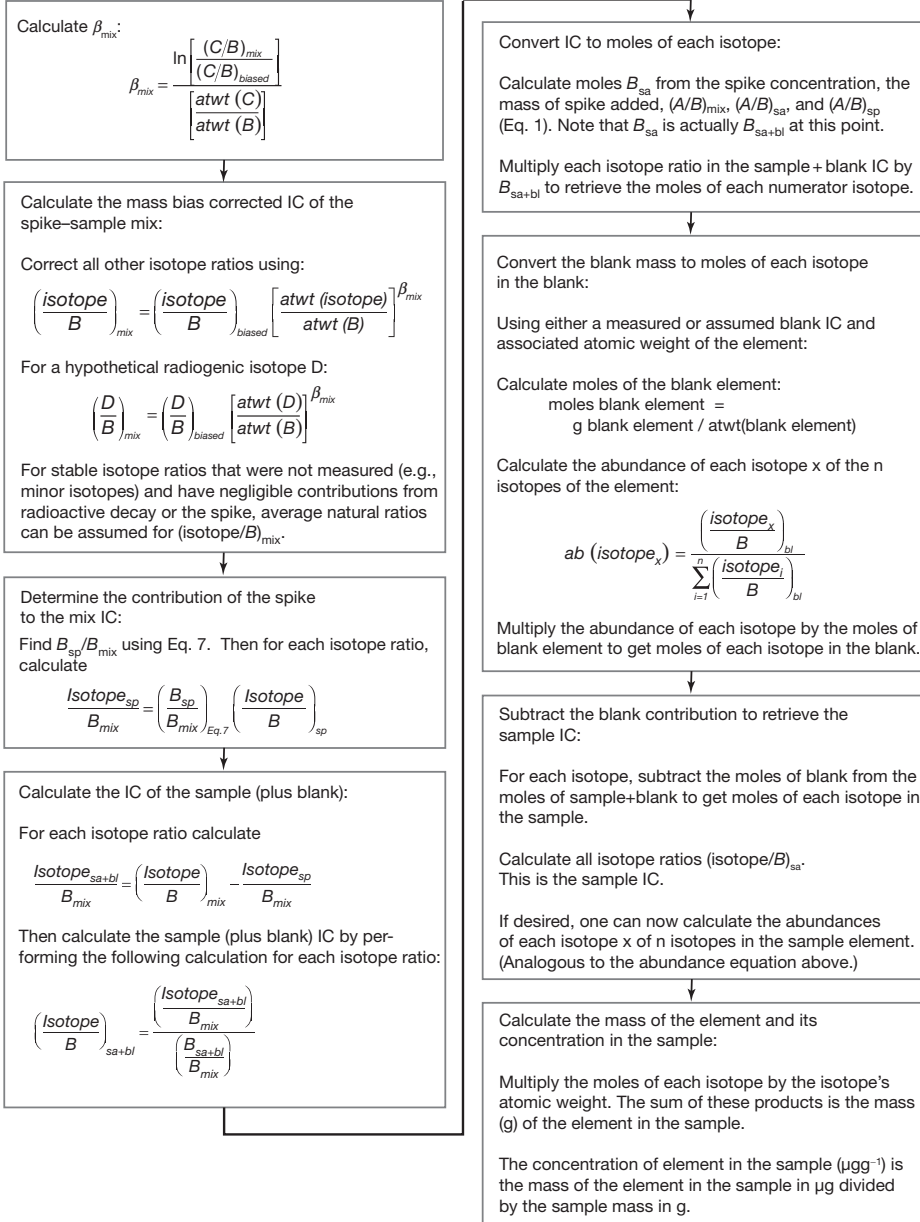


Figure 5 Flow chart showing the main steps involved in the data reduction scheme for mass bias corrected ID measurements and combined IC-ID measurements on totally spiked samples, including 'spike stripping' (for detailed description of the method, see [Section 15.4.4.3](#)).

radiogenic ^{87}Sr from the decay of ^{87}Rb , the double-spike technique requires separate unspiked and spiked analyses to determine the size of the isotope anomaly prior to calculation of stable isotope fractionation from the spiked analyses in a similar manner to the spike stripping discussed above. For elements such as Pb, application of the double-spike technique does not aim to quantify stable isotope variations of a sample from a standard, but only those arising from instrumental fractionation during an unspiked analysis. The double-spike deconvolution then quantifies the instrumental fractionation of the spiked and unspiked analyses (Compston and Oversby, 1969).

It is insightful to consider how the double-spike technique works by considering a three-dimensional space defined by four isotope abundances (Galer, 1999), as shown in Figure 6. By rotating this figure, it is possible to view directly along the mixing line between the standard and spike (Figure 6(b)). For the double-spike technique to work, the fractionation line through natural samples and standards (β_{nat}) must lie on a trajectory crossing the mixing line, whilst the fractionation line

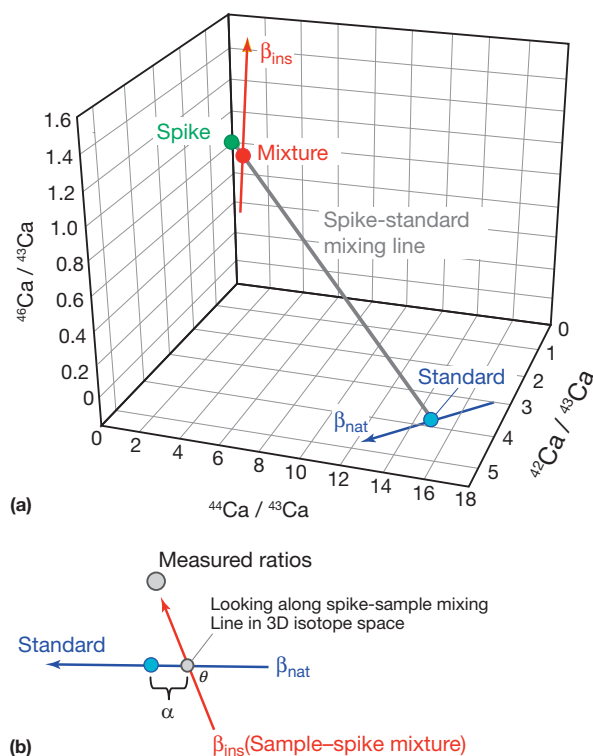


Figure 6 (a) An example of a 3D isotope space defined here by ^{42}Ca – ^{43}Ca – ^{44}Ca – ^{46}Ca , with a ^{43}Ca – ^{46}Ca double spike. Also shown are the trajectories of the curved mass-dependent fractionation lines for natural samples and standards (β_{nat}) and a spike–standard mixed composition (β_{ins}). The mixture indicated along the gray standard–sample mixing line is a X:1 spike–standard molar ratio. (b) A schematic representation of the 3D isotope space rotated to look directly along the gray spike–sample mixing line, with the two trajectories (separated by an angle, θ) of mass-dependent fractionation curves for a spike–standard mixed composition (β_{ins}) and natural samples and standards (β_{nat}), as shown in (a). In panel (b), the measured ratio, i.e., the gray circle, can be projected back along a trajectory (β_{ins}) onto that of β_{nat} , and the mass fractionation between the sample and standard (α) determined.

of a spiked mixture should lie on a different trajectory (β_{ins}). Any measured combination of ratios can then be described by a linear combination of these two trajectories from the mixing line, and thus the extent of natural (β_{nat}) and analytical fractionation (β_{ins}) can be quantified. For Pb, an unspiked measurement is used to determine the ‘natural fractionation’ that is then used in the determination of instrumental fractionation within the ‘spiked analysis.’ If the two trajectories, β_{ins} and β_{nat} , are more orthogonal, the separation of the two fractionations along the two trajectories is less error prone. We can thus visualize why some double spikes and the mixing proportion between double spikes and samples may be better suited than others for minimizing ‘error magnification’ (Galer, 1999). Error magnification during deconvolution is not due to the algorithms themselves because the double-spike equations can be solved exactly. Rather, the magnification stems from the translation of the associated and correlated errors of the input values into the errors on the unknown values being determined.

The choices of which two isotopes to enrich for the double spike, and which additional two isotopes are used in the deconvolution are often numerous, and there is considerable ambiguity in which isotopes should be chosen. Furthermore, the determination of stable isotope variations for elements with many isotopes also leads to ambiguity in the notation that should be used to report any stable isotope variations. By convention, relative isotope variations should be reported in δ -notation, which is a relative deviation of an IC from an internationally recognized standard, with the denominator being the lightest stable isotope. Because stable isotope variations are small, δ is typically given in per mil (‰). For stable isotope variations determined by the double-spike technique, the δ -values could be reported for any of the ratios of the heavier measured isotopes to that of the lightest, although some authors suggest that only the ratio of the two nonspiked isotopes should be considered. However, because the double-spike technique assumes only mass-dependent fractionation, any δ -value, and its corresponding error, scale almost with the mass difference between of the two isotopes used to define the δ -values (John, 2012; Rudge et al., 2009), for example, $\delta^{56}\text{Fe}/^{54}\text{Fe}/2 = \delta^{57}\text{Fe}/^{54}\text{Fe}/3 = \delta^{58}\text{Fe}/^{54}\text{Fe}/4 = \delta^{57}\text{Fe}/^{56}\text{Fe}$.

It is important to consider that mathematically mass fractionation is described by a single mass-dependent law (or a curved vector in the 3-D space defined by the 4 isotopes; the vector is straight in log-ratio space). However, both instrumental fractionation and stable isotope variations can be described by several different laws (Young et al., 2002), and so we must consider which laws to apply to avoid imparting systematic bias. Instrumental mass fractionation is now typically described by an exponential mass fractionation law (Russell et al., 1978; Wasserburg et al., 1981), rather than a linear law (Eugster et al., 1969) or power law used in earlier studies (see Albarède et al., 2004). This amendment reflects the increased precision obtainable and the need to correct for larger fractionations (such as those induced by MC-ICPMS compared to TIMS). Hence, the potential bias induced by poorly describing the fractionation process is a function of these three points, which will vary between applications. Stable isotope variations may be induced both from kinetic and equilibrium fractionation processes, and these distinct processes may induce subtly distinct fractionation patterns. However, published algorithms

ignore such subtlety, which would require the addition of another variable and measurement of another isotope to quantify the suitability of each law. Given the current precision, and the relatively small degree of fractionation in nature (for Ca and heavier elements), ignoring the differences between kinetic and equilibrium fractionation laws seems justified.

Considering a known standard and spike IC, the transformation or correction of measured ratios into a spike-sample mixing proportion and stable IC is, as outlined above, relatively straightforward, although mathematically laborious. Numerous authors have detailed their procedures for solving the double spike equations (Dodson, 1963, 1970; Eugster et al., 1969; Hamelin et al., 1985; John, 2012; Powell et al., 1998; Rudge et al., 2009; Siebert et al., 2001). The deconvolution is not a significant source of error, or a limit on the application of the double-spike technique, given an appropriate double-spike composition and appropriate approximation for the mass fractionation. However, the different algorithms handle error propagation differently (e.g., Dodson, 1969; Galer, 1999; John, 2012; Rudge et al., 2009), which leads to confusion about the precision and accuracy obtainable for different double-spike compositions, or rather what the optimal double-spike composition may be. Such differences are compounded by the determination of the double-spike composition, or 'calibration' of the double spikes, such that many researchers regard the calibration as a major obstacle to the successful application of the double-spike technique. However, the calibration is comparatively straightforward and can be achieved by inverting the deconvolution (Dodson, 1970) to find the spike composition which, when mixed with the standard in various proportions, always results in reproducing the IC of the standard.

Because the double-spike composition is typically determined by inverting the deconvolution with a range of spike-standard mixtures, it follows that any determined IC is relative to the standard. Alternatively, if the composition of the two spikes is known absolutely and the spikes are mixed gravimetrically, it is potentially possible to know the true spike composition, and thereby redefine the IC of the standard in absolute terms (Richter et al., 2010). However, there are four important caveats in considering the IC as 'absolute': (i) the composition of either spike may only be known relative to a standard, (ii) spike compositions can be strongly effected by any blank contribution, which is difficult to quantify or neglect, (iii) the gravimetric mixing of the two spike compositions will be a major source of error, and, most importantly, (iv) there must be traceability to international standards. Hence, we should generally consider the calculated isotopic compositions and estimated precision as relative, rather than absolute.

It has recently been argued that the error propagation through the deconvolution is independent of which of the four isotopes is used as the denominator in the three ICs (Mel'nikov, 2005; Rudge et al., 2009). Because the angle between the two vectors, shown in Figure 6(b) (θ), depends upon the isotope space, or rather which isotope is used as the denominator, the angle between the two vectors shown cannot be considered to directly reflect the error magnification of the double-spike technique. Rather, it has been suggested that the optimal, theoretical, double-spike composition can be assessed by propagating the errors associated with measuring the ion-beam intensities through the deconvolution (see more detailed discussions in

John, 2012; Rudge et al., 2009). Note, however, that the exact optimal double-spike composition is not unique, because it depends upon the choice of parameter to be minimized. For example, the optimal spike calculated to minimize the error of the natural stable isotope fractionation factor varies with the assumed ion beam intensities and may differ from the optimal spike calculated to minimize the uncertainty of an isotopic ratio.

From the published 'toolbox' by Rudge et al. (2009), the comparative choice of various double spikes and spike-sample mixing proportions can be found, although the theoretical optima and the maximal precision obtainable are also a function of the analysis conditions, including ion beam intensities, blank contributions, period and number of measurement integrations, etc. In practice, the precision and accuracy of the double-spike technique, and the optimal choice of spikes, are limited by the ability to measure ion beams without interferences or systematic biases being introduced. Hence, various practical constraints often determine the optimal double-spike composition, or the choice of isotopes used in the deconvolution. The most suitable double-spike composition may depend upon: (a) avoiding an isotope for which isobaric interferences may exist, (b) maximizing the range of spike-sample ratios for which precision remains appropriate, (c) the availability or purity of a particular spike, (d) optimizing for either high or low spike-sample ratio for samples with limited or abundant quantity, respectively, (e) avoiding the use of odd and even mass isotopes together if nuclear-spin isotope fractionation effects may exist, or (f) limiting the range of mass to that which is appropriate for the mass spectrometer. Optimal spikes of a particular element, as determined by Rudge et al. (2009), are often based on the inversion of the largest range of mass, with the two spikes on the isotopes that are least abundant in nature. Calculations of the theoretical precision of stable isotope variations show that spike purity has little effect on the obtainable precision (Russell, 1971) and that the range of double-spike compositions and spike-sample ratios can vary within a factor two from the optimal values (i.e., those that result in the highest precision; Figure 7). These large ranges allow the two spikes to be mixed inexactly and allow the double spike to be used over large ranges in sample quantity or concentration without much loss in precision.

With such accessibility to estimating appropriate spike compositions and methods for calibrating spikes, application of the 'double spike' technique is expected to surge in the near future, especially in conjunction with ICPMS. One of the first elements for which the double-spike technique was used for the determination of stable isotope variations with MC-ICPMS was molybdenum (Siebert et al., 2001). Since then, stable Mo isotope variations, determined by double spike, have been applied in many subsequent studies (e.g., Archer and Vance, 2008; Arnold et al., 2004; Burkhardt et al., 2011; Scheiderich et al., 2010; Siebert et al., 2003). Recently, a number of studies reported stable isotope measurement using a U double spike (Brennecka et al., 2010a,b; Stirling et al., 2007; Weyer et al., 2008).

Despite the potential of double-spike techniques to further enhance analytical precision and accuracy, some problems remain. For the heavier divalent cations, Sr and Ca, for example the application of the double-spike technique to determine stable isotope variations has resulted in variable precision

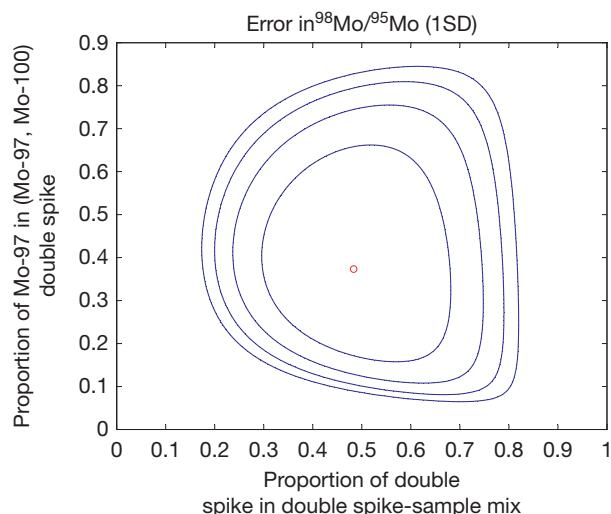


Figure 7 A contour plot of the relative theoretical errors of determining the stable isotope variations of $^{98}\text{Mo}/^{95}\text{Mo}$ using ^{97}Mo – ^{100}Mo spikes available from Oak Ridge National Laboratory, USA, with varying proportions of the two spikes and natural samples. The optimum is marked by a red circle, and the blue contours shown are for errors at +12.5%, +25%, +37.5, and +50% of the optimal error. Created using the Double Spike Toolbox (Rudge et al., 2009), in MATLAB using the command `errorcurve2d('Mo','real',[97 100],[95 97 98 100],[98 95],0,0,100,0.5,5)`.

(Fantle and Bullen, 2009; Heuser et al., 2002; Hindshaw et al., 2011; Krabbenhöft et al., 2009). Whereas the precision of the double-spike analyses for Sr is close to the theoretical limits imposed by counting statistics of the ion beams, the precision for Ca is typically a factor of four worse, despite the similar analytical technique (TIMS). The relatively poor precision for Ca may be explained by at least five different problems related to the TIMS technique that could induce systematic biases that are difficult to correct: (1) there may be mixing of fractionated Ca reservoirs during measurement (Fantle and Bullen, 2009; Russell et al., 1978), (2) there may be evaporation of CaO, which fractionates differently, (3) the large mass dispersion of the ion beams may be problematic (Holmden, 2005), (4) the large ion beam of ^{40}Ca may induce problems such as secondary ions or degrading Faraday cup efficiencies, and (5) isobaric interferences resulting from the ionization of molecules such as MgO. Unfortunately, it would appear that the mass bias correction estimated from the deconvolution may not always adequately describe the mass fractionation that occurs during the measurement routine, as detailed by Fantle and Bullen (2009). However, slight technical difficulties in some instances should not deter the widespread adoption of double-spike techniques to enhance precision and accuracy of stable isotope variations.

15.4.6 Conclusions

Isotope dilution as a primary, SI-traceable method of element analysis is both accurate and precise, even for ultra-trace level concentrations, and thus considered superior to comparative methods that rely on calibration against external reference materials. The two most significant limitations of ID are (1) that the technique is not applicable to most mono-isotopic elements and (2) that the technique is destructive, i.e., it

requires dissolution of the sample and homogenization with the spike, often preventing analyses of other elements on the same sample aliquot. In general, however, trace element analyses that are both accurate and precise to within a few tenths of percent are readily achievable for a wide range of elements. Furthermore, double-spike techniques allow not only the determination of the spike-sample mixing proportions but also the degree of isotopic mass fractionation that occurs both naturally (before spike-sample mixing), and during subsequent processing and measurement. Stable isotope fractionations can be determined accurately and precisely with the double-spike technique, even in cases such as Pb, where the degree of fractionation arising from analysis can be determined and corrected for although none of the Pb isotope ratios are constant in nature. Hence ID is a versatile tool and the method of choice whenever both highly accurate and precise element concentrations and ICs are required in the earth and planetary sciences, as well as the environmental and nuclear sciences.

Appendix A

Derivation of the equations in Section 15.4.3.3 ('the optimum ratio of the sample-spike mixture') according to Webster (1960).

Equation [1] can be written as:

$$B_{\text{sa}} = \left[\frac{\left(\frac{A}{B}\right)_{\text{mix}} - \left(\frac{A}{B}\right)_{\text{sp}}}{\left(\frac{A}{B}\right)_{\text{sa}} - \left(\frac{A}{B}\right)_{\text{mix}}} \right] B_{\text{sp}}; \quad B_{\text{sa}} = \left[\frac{M - \text{Sp}}{\text{Sa} - M} \right] B_{\text{sp}}$$

with

$$M = \left(\frac{A}{B}\right)_{\text{mix}}; \quad \text{Sp} = \left(\frac{A}{B}\right)_{\text{sp}}; \quad \text{Sa} = \left(\frac{A}{B}\right)_{\text{sa}}$$

Assuming Sp, Sa, B_{sa} , and B_{sp} are well known, that is, constant, the relative error on B_{sa} ($\Delta B_{\text{sa}}/B_{\text{sa}}$) corresponds to the relative error on M ($\Delta M/M$) times a factor F , the error magnification factor.

$$\frac{\Delta B_{\text{sa}}}{B_{\text{sa}}} = F \frac{\Delta M}{M}$$

Hence, F is defined as:

$$F = \frac{\Delta B_{\text{sa}}/B_{\text{sa}}}{\Delta M/M}$$

We can write:

$$\lim_{\Delta M \rightarrow 0} \frac{\Delta B_{\text{sa}}}{\Delta M} = \frac{dB_{\text{sa}}}{dM} = \frac{\text{Sa} - \text{Sp}}{(\text{Sa} - M)^2} B_{\text{sp}}$$

Because

$$\begin{aligned} \frac{\Delta B_{\text{sa}}}{\Delta M} &= F \frac{B_{\text{sa}}}{M} \\ \frac{\Delta B_{\text{sa}}}{\Delta M} &= F \frac{B_{\text{sa}}}{M} = \frac{\text{Sa} - \text{Sp}}{(\text{Sa} - M)^2} B_{\text{sp}} \quad \text{or} \\ F &= M \frac{\text{Sa} - \text{Sp}}{(\text{Sa} - M)^2} \frac{B_{\text{sp}}}{B_{\text{sa}}} \end{aligned}$$

with

$$B_{sa} = \left[\frac{M - Sp}{Sa - M} \right] B_{sp}$$

F can then be expressed as:

$$F = M \frac{(Sa - Sp)}{(Sa - M)(M - Sp)}; \text{ or in unabbreviated terms:}$$

$$F = \left| \frac{\left(\frac{A}{B} \right)_{\text{Mix}} \left[\left(\frac{A}{B} \right)_{Sa} - \left(\frac{A}{B} \right)_{Sp} \right]}{\left[\left(\frac{A}{B} \right)_{Sa} - \left(\frac{A}{B} \right)_{\text{Mix}} \right] \left[\left(\frac{A}{B} \right)_{\text{Mix}} - \left(\frac{A}{B} \right)_{Sp} \right]} \right|$$

The error magnification factor F becomes minimum if $dF/dM = 0$:

$$\frac{dF}{dM} = (Sa - Sp) \frac{M^2 - SaSp}{(Sa - M)^2 (M - Sp)^2} = 0$$

Hence, F becomes minimum for: $M^2 - SaSp = 0$

The sample-spike mixture (M) for which error magnification is minimum therefore is:

$M = \sqrt{SaSp}$; or in unabbreviated terms:

$$\left(\frac{A}{B} \right)_{\text{Mix}}^{\text{opt}} = \sqrt{\left(\frac{A}{B} \right)_{Sa} \left(\frac{A}{B} \right)_{Sp}}$$

Substituting

$$M = \sqrt{SaSp}$$

into

$F = M \frac{(Sa - Sp)}{(Sa - M)(M - Sp)}$ yields the minimum error magnification factor F_{\min} :

$$\begin{aligned} F_{\min} &= \sqrt{SaSp} \frac{(Sa - Sp)}{(Sa - \sqrt{SaSp})(\sqrt{SaSp} - Sp)} \\ &= \sqrt{SaSp} \frac{(Sa - Sp)}{(Sa\sqrt{SaSp} - 2SaSp + Sp\sqrt{SaSp})} \\ F_{\min} &= \frac{(Sa - Sp)}{(Sa - 2\sqrt{SaSp} + Sp)} = \frac{(Sa - Sp)}{(\sqrt{Sa} - \sqrt{Sp})^2} \end{aligned}$$

or in unabbreviated terms:

$$F_{\min} = \frac{\left| \left(\frac{A}{B} \right)_{sa} - \left(\frac{A}{B} \right)_{sp} \right|}{\left(\sqrt{\left(\frac{A}{B} \right)_{sa}} - \sqrt{\left(\frac{A}{B} \right)_{sp}} \right)^2}$$

Acknowledgment

During our graduate studies, we all essentially reinvented the wheel by deriving many of the equations and methods described here. Of course, most of this information can be found in the early works on isotope dilution and in numerous textbooks. However, it seemed that no single source explained the practical application of isotope dilution and spike-stripping from A to Z. We have therefore attempted to

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