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Distillation law and exponential model of isotope fractionation

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ABSTRACT

The exponential law is an empirical model which is used to describe the isotopic fractionation both in instrumental (thermal ionization- and induced coupled plasma-source mass spectrometry) and in natural processes. It is shown that isotopic fractionation which occurs according to this law can be interpreted in terms of a Rayleigh-type distillation process, in which the value of the vapour/residue distribution coefficient for the various isotopes of an element is a natural logarithmic function of the isotope mass:

$$D = D_0 + a \ln\left(\frac{m}{m_0}\right).$$

In this equation, D_0 is the value of the vapour/residue distribution coefficient for a reference mass m_0 and

$$a = \frac{p}{(1+\ln f)},$$

where p is the instantaneous value of the so called "fractionation exponent" (or "fractionation coefficient") of the exponential law, and f is the residual mass fraction of the sample at the same instant.

1. Introduction

Determining the isotopic composition of elements by thermal ionisation- and induced coupled plasma-source mass spectrometry is complicated by instrumental bias. This term is used to mean the effects of some, fundamentally mass-dependent processes which occur in the mass spectrometer source, and which cause the measured values of the isotopic ratios to differ from their true ones. Instrumental bias leads to irreproducibility and reduces accuracy, greatly affecting analytical results.

To solve this problem, three different approaches are generally used for elements which have more than two isotopes. The first (and the simplest) approach consists of assuming a value as the true value of one of the isotopic ratios of the element in analysis. At any instant, the instrumental bias is calculated from the deviation of the measured value of the ratio from the true value, and the values of the other isotopic ratios of the element can be corrected if the isotope fractionation law is known.

This simple technique is called 'internal normalization', and is most frequently used both in thermal ionization- and in plasma-source mass spectrometry for elements which have – or are believed to have – one or more constant isotopic ratios in nature (e.g., Sr, Nd, and Hf) [1,2].

The second method consists of adding to the sample a "tracer" of the same element to be analysed, the isotopic composition of which is strongly enriched in two isotopes (generally the least abundant in nature). Since the tracer has two "spikes", it is usually called a "double spike", and the technique is called the "double spike method" of analysis [3–5].

The extent of instrumental bias is determined from the observed deviation of the double spike isotopic ratio from the true value, after the contribution of the natural element has been removed.

The double spike method was initially designed for analysis of Pb, because this element, due to natural U and Th radioactive decay, has no constant isotopic ratio in nature, but it is nowadays also used to investigate natural variations in the isotopic composition of Fe, Cr, Se and Sr [6–8].

The third approach may be considered as a hybrid between the two previous ones. It consists of adding to the element of which we wish to determine the isotopic composition another element, whose isotopes fall in a mass range which is very close to that of the element under analysis. For example, Zr is added in Sr analysis, and Tl in Pb or Hg analysis [9–11]. Again, instrumental bias is determined from the observed deviation of the measured value of a convenient isotopic ratio of the added element from its true known

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value, assuming that, in the process of ion production, the nuclides of the added element behave like the isotopes of the element in analysis as regards their mass-dependent behaviour.

In all these techniques, besides the value of the reference isotopic ratio of the sample or the added element, it is necessary to know-in practice to assume-the mathematical law for the instrumental isotopic fractionation, which relates the measured values of the isotopic ratios one to the other, and the model of isotopic fractionation which is assumed may be crucial as it may greatly influence the final corrected values.

Since the late 1970s and early 1980s, analytical evidence has shown that an exponential law of fractionation is more suitable than other laws of fractionation (such as the linear and power laws) in describing observed isotopic fractionation in thermal ionization-source mass spectrometry. This was first observed during isotopic analysis of Ca in lunar samples [12], because the relatively high ratio between the mass-span of Ca six isotopes (nominal masses 40 to 48) and its mass amplifies the isotopic fractionation effects. Exponential behaviour was later investigated and confirmed [13], and the exponential law largely substituted the other laws of fractionation in determining the instrumental bias (see also [14,15] for recent confirmation of the exponential law).

At present, Sr, Nd, Pb, Hf, Cr, Fe, Se, Zn and Hg isotopic analysis for geochronology, geochemistry and archeometry, in both thermal ionization- and ICP-source mass spectrometry, are corrected for instrumental bias by the exponential model of isotope fractionation [9,10,16,17], and the importance of this law increases with the applicability of isotopic techniques, and because this model of fractionation is also now used to describe isotopic fractionation in natural processes [7].

More recent confirmation of the exponential law of fractionation in thermal ionization mass spectrometry was given by Cavazzini [14,15]. This author showed that it is possible to ascertain whether the instrumental fractionation does or does not follow the exponential model of fractionation during the run, using a method which can calculate the true isotope ratios of elements formed by at least three isotopes, according to the equation which linearizes the fractionation model.

Linearization consists of assuming that the fractionation factor has the same value for all the isotopic ratios of the element at any instant. This implies that linear distributions occur in x vs. x/y diagrams, where x, y are the measured values of two isotopic ratios of the element at the same instant.

Since calculation of the true values of the isotopic ratios is based on the assumption that instrumental fractionation followed the exponential model of fractionation during the run, and since the true values of the isotopic ratios are fixed, the correctness of the assumption on which the calculation is based is confirmed by the reproducibility, within respective error limits, of the respective true values of the isotopic ratios calculated by all the possible x vs. x/y distributions [15].

In the following, an interpretation is proposed of the exponential law of isotope fractionation in terms of the distillation law [18]. It is shown that an isotopic fractionation process which occurs according to the exponential law can be the result of a Rayleigh-type distillation process in which the distribution coefficient between the vapour phase and the residue phase for the various isotopes of the element is a natural logarithmic function of the isotope mass.

2. Distillation law and exponential model of isotope fractionation

The distillation law [18] can be applied to the mass-dependent evaporation processes of the various isotopes of an element by considering each isotope as a component within the isotopic mixture. That is, each isotope i is characterized by a distribution coefficient D_i – in substance, the ratio between the mass fraction of the isotope in the vapour phase and that in the residue phase in the mass spectrometer source – which value is assumed to depend on isotope mass m_i [15].

Let us consider an element composed of isotopes $i, j, k, \ldots$ with isotopic ratios $r, s, u, \ldots$ According to the distillation law, at a certain instant during the process, mass fraction C_i of isotope i in the residue phase is given by:

$$C_i = C_{i,0} f^{D_i - 1}, \tag{1}$$

where $C_{i,0}$ is the mass fraction of the isotope in the sample on the filament at the beginning of the process ($t = 0$), f is the residue mass fraction of the sample and D_i is the distribution coefficient, which value is assumed to remain constant in time-span t.

In mass spectrometry, the bias at a certain instant between the measured value and the true value of isotopic ratio $r = i/j$ is generally expressed in terms of parameter called *fractionation factor*. We can conveniently define the fractionation factor δ_r as the instantaneous deviation between the measured value of the isotopic ratio (r_m) and the true (initial) value (r_0) per unit of measured value, and per unit of mass difference between the two isotopes which define the ratio:

$$\delta_r = \frac{r_m - r_0}{r_m(m_j - m_i)}, \tag{2}$$

where m_i and m_j, respectively, are the masses of the two isotopes [6,14,15].

Cavazzini [15] has shown that, if instrumental isotopic fractionation follows the distillation law of Eq. (1), the instantaneous value of the fractionation factor Eq. (2) can be written as:

$$\delta_r = \frac{f^{-\xi}}{1 + \xi} - 1, \tag{3}$$

where ξ, which is negative and very small in absolute value ($|\xi| \ll 1$), is the slope of the straight line which passes through the points which represent the two isotopes which define ratio r on the curve which relates the vapour/residue distribution coefficient to the mass of the isotopes.

The fractionation factor values calculated by Eq. (3) are generally different from the respective definition values of Eq. (2). The instantaneous deviation between these values can be calculated by the deviation of the (approximated) value of r_m, which gives Eq. (3), from the true (theoretical) value of r_m, calculated according to the distillation law.

Taking Sr analysis as an example, $^{86}\mathrm{Sr}/^{88}\mathrm{Sr}$ as ratio r, and assuming that ξ has a value of ~ -0.004 – which is typical in Sr analysis on single tungsten filament in thermal ionization mass spectrometry [14,15] – most of the δ_r values calculated by Eq. (3) (in the range of sample residual fraction $f = 0.99$–0.10) are lower than the respective definition values. The instantaneous deviation in the value of r_m is calculated to be from -4.0×10^{-6} (-0.003%, $f = 0.99$) to -9.6×10^{-6} (-0.008%, $f = 0.36$), to 0 ($f = 0.10$) to $+1.2 \times 10^{-5}$ ($+0.012\%$, $f = 0.05$), and the corresponding deviation in δ_r ranges from -0.000017 ($f = 0.99$, -0.4%), to 0 ($f = 0.1$) to $+0.000061$ ($f = 0.05$, $+0.7\%$).

Now, since residual sample fraction $f = 1 - \varphi$, where φ is the fraction of lost (evaporated) sample, and since $0 < \varphi < 1$, power $f^{-\xi} = (1 - \varphi)^{-\xi}$ can be expressed as a binomial Taylor's series as:

$$(1 - \varphi)^{-\xi} = 1 + \xi\varphi + \frac{\xi(1 + \xi)}{2!}\varphi^2 + \frac{\xi(1 + \xi)(2 + \xi)}{3!}\varphi^3 + \cdots \tag{4}$$

Substituting in (3) and after simplification, since ξ is very small in absolute value, the resulting expression may be modified according to the approximation $n+\xi \approx n$ ($n = 1, 2, 3, 4, \ldots$), yielding the following equation for δ_r:

$$\delta_r = -\xi\left(1-\varphi-\frac{\varphi^2}{2}-\frac{\varphi^3}{3}-\frac{\varphi^4}{4}-\cdots\right) = -\xi(1+\ln f), \tag{5}$$

which clearly shows that the instantaneous value of the isotopic ratio coincides with the true value when $\ln f = -1$, i.e., when $f = 1/e \sim 0.368$.

Eq. (5) also calculates fractionation factor values which are lower than the respective values calculated by Eq. (3), and the instantaneous total deviation between δ_r calculated in (5) and the definition value Eq. (2) is calculated to be from -0.000032 ($f = 0.99$), to -0.000048 ($f = 0.36$), to 0 ($f = 0.07$) to $+0.000021$ ($f = 0.05$).

Now, the equation of the exponential law, as written by Russell et al. [12] and Hart and Zindler [13], is:

$$\frac{r_0}{r_m} = \left(\frac{m_j}{m_i}\right)^p, \tag{6}$$

where exponent p changes with time during runs, but at any instant it has the same value for all the isotopic ratios of the element.Since from Eq. (2) δ_r is:

$$\delta_r = \left\{\frac{r_0}{r_m}-1\right\}\frac{1}{m_i-m_j},$$

substituting Eq. (6) we obtain:

$$\delta_r = \left\{\left(\frac{m_j}{m_i}\right)^p-1\right\}\frac{1}{m_i-m_j}. \tag{7}$$

In Eq. (6)

$$\left(\frac{m_j}{m_i}\right)^p = \left(1+\frac{m_j-m_i}{m_i}\right)^p,$$

where m_j-m_i is very small with respect to m_i (for example, m_j-m_i may be approximately 2 whereas m_i, in the case of Sr, is nominally 80-90, and much higher for Nd and Pb), so that $(m_j-m_i)/m_i$ is small and between 0 and 1 in absolute value. Thus, we can again use Taylor's binomial expansion:

$$\left(\frac{m_j}{m_i}\right)^p = 1+p\frac{m_j-m_i}{m_i}+\frac{1}{2}p(p-1)\left(\frac{m_j-m_i}{m_i}\right)^2 + \frac{1}{6}p(p-1)(p-2)\left(\frac{m_j-m_i}{m_i}\right)^3+\cdots$$

Substituting in (7), we obtain:

$$\delta_r = -\frac{p}{m_i}-\frac{1}{2}p(p-1)\frac{m_j-m_i}{m_i{}^2}-\frac{1}{6}p(p-1)(p-2)\frac{(m_j-m_i)^2}{m_i{}^3}-\cdots \tag{8}$$

We now let δ_r (5) = δ_r (8):

$$-\xi(1+\ln f) = -\frac{p}{m_i}-\frac{1}{2}p(p-1)\frac{m_j-m_i}{m_i{}^2} -\frac{1}{6}p(p-1)(p-2)\frac{(m_j-m_i)^2}{m_i{}^3}-\cdots \tag{9}$$

and then let difference m_j-m_i tend to an infinitesimal. In this case, ξ becomes dD/dm on the (m, D) curve, δ_r (8) reduces to – p/m_i, and all the deviations between δ_r (3), δ_r (5) and the definition value (2) tend to an infinitesimal. Thus:

$$\frac{dD}{dm} = \frac{p}{1+\ln f}\frac{1}{m}, \tag{10}$$

where m is now a generic mass on the (m, D) curve.

Due to simultaneous p and $\ln f$ values the tangent to the curve is always negative, and Eq. (10) indicates that its absolute value is inversely proportional to the mass of the isotope.

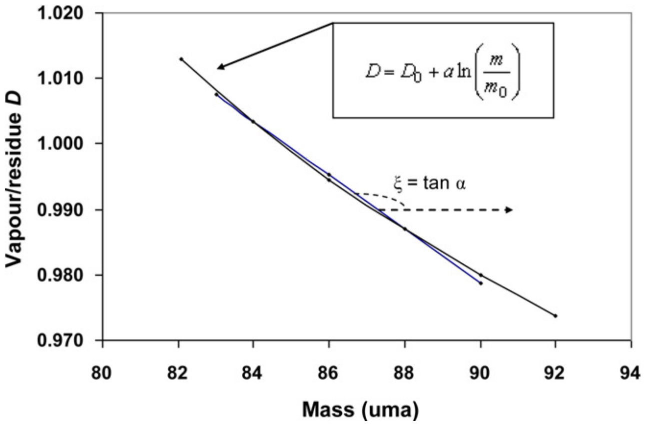

Fig. 1. Relationship between mass and vapour/residue distribution coefficient for isotopes of an element in a Rayleigh-type distillation process which gives rise to exponential isotopic fractionation (Sr isotopes are illustrated as an example). Values m_0 and D_0 are, respectively, mass and value of distribution coefficient for a reference nuclide close to or within range of mass of isotopes of element (see text for further explanation).

Calling a the ratio between the fractionation coefficient and the sum $1+\ln f$ at the same instant, and integrating with a = constant, we obtain the relationship between mass and distribution coefficient as:

$$D = D_0 + a\ln\left(\frac{m}{m_0}\right), \tag{11}$$

where m_0 is the mass of an isotope of the element, or the mass of a convenient nuclide close to or within the mass range of the isotopes of the element, chosen as a reference mass, and D_0 is the respective value of the vapour/residue distribution coefficient.

The relationship between mass and vapour/residue distribution coefficient for the isotopes of an element in a Rayleigh-type distillation process which gives rise to exponential isotopic fractionation is shown in Fig. 1, for the case of strontium isotopes. Due to simultaneous p and $\ln f$ values, the tangent to the curve is always negative.

In Fig. 1, the curvature of the natural logarithmic function has been intentionally exaggerated for reasons of graphics, but the value of ξ approximately conforms to the observed value for Sr isotopes loaded and analysed as in [15].

The form of the curve (11) is stable for a = constant during the run. This occurs when the change in the fractionation exponent is proportional to the relative change in residue mass fraction of the sample, the coefficient of proportionality being a:

$$dp = a\left(\frac{df}{f}\right). \tag{12}$$

If a is not constant, Eq. (10) can be integrated by assuming an average value for parameter a in the range of integration, and Eq. (11) gives an average relationship between mass and distribution coefficient in the range of the residue mass fraction.

3. Conclusions

We have shown that the isotopic fractionation observed to occur according to an exponential law can be interpreted as the result of a Rayleigh-type distillation process, in which the distribution coefficient between the vapour and residue phases is a natural logarithmic function of the mass, or, it is the same, is a linear function of the natural logarithm of the mass.

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