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Rayleigh's distillation law and linear hypothesis of isotope fractionation in thermal ionization mass spectrometry

Giancarlo Cavazzini*

Laboratorio di Geocronologia, C.N.R. Istituto di Geoscienze e Georisorse, Via Matteotti 30, 35137 Padova, Italy

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ABSTRACT

The relationship which exists between Rayleigh's distillation law and linear models of instrumental isotopic fractionation in thermal ionization mass spectrometry is shown. If the process of isotope fractionation in the mass spectrometer source occurs in terms of a Rayleigh's distillation, and, within the range of mass of isotopes of the element, the vapor/residue distribution coefficient is a linear function of mass with a slope which is sufficiently small in absolute value, then the linear hypothesis of isotope fractionation is fulfilled.

The model shows that the fractionation factor per amu, defined as the instantaneous difference between the measured and true values of the isotope ratio, per unit of measured/true value and per unit of mass difference between the two isotopes which define the ratio, can be interpreted as a function of two parameters: the residual mass fraction of the sample on the filament, and the rate of change of the distribution coefficient with mass. These two parameters can be calculated and, in particular, the value of the residual mass fraction of the sample when the measured values of the isotopic ratios coincide with the actual values can be calculated as a function of the rate of change with mass of the distribution coefficient.

A linear model of instrumental isotopic fractionation can be derived from the exponential hypothesis of fractionation, which can be also interpreted in terms of a Rayleigh's distillation process, but where mass is an exponential function of the distribution coefficient.

Experimental results of instrumental isotopic fractionation (up to 1% amu^{-1}) of strontium in NIST standard reference material 987, loaded as a nitrate on a single tungsten filament, can be interpreted in terms of the linear models of isotope fractionation (and therefore of Rayleigh's distillation law) within experimental error. They show: (i) changes in the vapor/residue distribution coefficient with mass in the range -0.006 to -0.004 amu^{-1}; (ii) approximately constant rates of sample consumption in the range of residual mass fraction from ~1 to ~0.3–0.25, which are between 0.05 and 0.13% min^{-1}; (iii) values of the residual mass fraction of the sample, when the measured values of the isotopic ratios coincide with the true ones, between 0.3668 and 0.3671, which correspond to sample consumption of 63.3%.

Since the linear hypothesis of fractionation is fulfilled, the values of isotopic ratios of strontium in the standard material can be determined. The global weighted averages of the weighted averages of the results obtained in eleven runs in which ^{86}Sr, ^{87}Sr and ^{88}Sr peaks were sampled are as follows: $^{86}\mathrm{Sr}/^{88}\mathrm{Sr} = 0.119445 \pm 0.000053$, $^{87}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.71016 \pm 0.00019$, and $^{87}\mathrm{Sr}/^{88}\mathrm{Sr} = 0.084826 \pm 0.000040$.

1. Introduction

In thermal ionization-source mass spectrometry of solid elements, the sample evaporates from a heated filament. Since the rate of evaporation of each isotope does not only depend on its respective abundance but also on mass, this process causes isotope fractionation in the sample, and the measured values of the isotope ratios progressively change with time.

This effect cannot be totally controlled and reproduced, and the accuracy of results is greatly limited, so that in laboratory routine a calculation procedure is commonly adopted for some elements (e.g., Sr and Nd), in which the measured values of the isotope ratios are corrected according to the calculated shift of one of them from the value which is assumed to be true for the sample. This correction procedure is known as 'normalization', the corrected isotope ratios are said to be 'normalized to' the 'true' value, and the calculation is not based only on the assumption of one value for one of the isotopic ratios of the element, but also on the assumption of a model for the isotope instrumental fractionation which occurred during run in the mass spectrometer.

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* Tel.: +39 049 827 2002; fax: +39 049 827 2010.
E-mail address: giancarlo.cavazzini@igg.cnr.it.

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In the literature, four different models – which are called ‘laws’ – have been proposed to describe the process of isotope fractionation which occurs in a sample when it evaporates from a heated metal surface. They are respectively known as Rayleigh’s law [1–4], Power law [3–6] and Exponential law [3,4]. A Linear law can be also derived, by series expansion and truncation to the first-order term in the power-law equation [3,4,7–9], and other ‘linear’ approximations have also been proposed in the same way starting from Rayleigh’s, power- and exponential-law equations [3,5,9–14]. In substance, the measured isotope ratios can be normalized according to somewhat different schemes of calculation.

The linear hypothesis of fractionation substantially consists of assuming the value of a parameter, the fractionation factor per amu, to be independent of the isotope ratio. The fractionation factor per amu is often defined as the instantaneous difference between the measured and true values of the isotope ratio, per unit of measured/true value and per unit of mass difference between the isotopes which define the ratio [3–5,7–14]. Therefore, calling F the fractionation factor, and $x, y, z, \ldots$ the various isotope ratios of an element, the linear hypothesis of fractionation is expressed by

$$F_x = F_y = F_z = \cdots$$

This assumption was widely used in the 1960–1980s to normalize the measured values of isotope ratios for instrumental fractionation, and it can of course still be used, if fractionation is not extensive [3,4]. It is also commonly used in isotope dilution analysis calculation schemes [5–11,15–18], and [14] has shown that the values of the isotopic ratios of an element with at least three isotopes can be obtained if instrumental fractionation follows the linear hypothesis during run in the mass spectrometer.

Despite this extensive use, however, approaching to ‘linear behaviors’ of descriptions of the process of evaporation in terms of accepted physical models has not been sufficiently discussed and investigated.

Nevertheless, a demonstration of the plausibility of the linear hypothesis according to accepted physical models would certainly produce new interesting and valuable insights, as it would necessarily imply interpreting the fractionation factor from a physical point of view.

Habfast [13] investigated the problem of evaporation of isotopes from a hot filament by combining Rayleigh’s diffusion law [19] with Langmuir’s law of evaporation in a vacuum [20], showing the relationship which exists between the Rayleigh–Langmuir equation and the exponential model of Russel et al. [3], and the possibility of obtaining a ‘linearized Rayleigh’s law’ [13, Eq. (13)].

Following a similar line of approach, in this paper we interpret the process of evaporation of isotopes in terms of Rayleigh’s distillation law (RDL) [21]. In this model, the isotopes of the element are considered as being different component elements within the sample mixture, each characterized by a different value of a vapor/residue distribution coefficient.

In the first part, we show that if the process of isotope fractionation in the sample during run in the mass spectrometer follows the RDL and if in the range of mass of the isotopes of the element the relationship between the vapor/residue distribution coefficient and mass is linear with a slope which is sufficiently small in absolute value, then the linear hypothesis is quite closely fulfilled. The mathematical treatment shows: (1) the physical meaning which may be assigned to the parameter fractionation factor per unit of atomic mass; (2) the possibility to estimate (a) the rate of change with mass of the vapor/residue distribution coefficient of the isotopes of the element, and (b) at any instant, the mass of sample on the filament in terms of the residual fraction of the initial amount. In the second part, experimental results of isotope fractionation of strontium samples evaporating from single tungsten filaments, which within the limit of error may be interpreted as following the linear hypothesis of fractionation, are used to illustrate these aspects.

2. Theory

Let us apply Rayleigh’s distillation law [21] to the process of fractionation of isotopes during evaporation from a hot filament. At a certain instant, the concentration of isotope i of the element in the sample (residue) on the filament may be written as:

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

where f is the mass fraction of residual sample on the filament and D_i is the distribution coefficient of the isotope between the vapor phase and the phase on the filament, which is assumed to be constant during the process.

At any instant, f is the same for all the isotopes of the element, so that the i/j concentration ratio in the residue at a certain instant is

$$\frac{C_i}{C_j} = \left(\frac{C_{i,0}}{C_{j,0}}\right) f^{D_i - D_j} \tag{2}$$

The i/j concentration ratio is proportional to the isotopic ratio. Thus, we can write:

$$x = x_0 f^{D_i - D_j} \tag{3}$$

where x, x_0 are the instantaneous and initial (true) i/j isotope ratios in the sample, respectively.

The rates of evaporation of the isotopes do not depend only on their respective abundances but also on their distribution coefficients and, at any instant, the value of i/j isotope ratio in vapor phase, x_v, is related to x according to the equation:

$$x_v = \left(\frac{D_i}{D_j}\right) x \tag{4}$$

Assuming no mass discrimination during ionization and extracting ions from the source of the mass spectrometer, then $x_m = x_v$, where x_m is the measured i/j isotope ratio. Thus, Eq. (4) can be written as:

$$x_m = \left(\frac{D_i}{D_j}\right) x_0 f^{D_i - D_j} \tag{5}$$

We do not know the exact relationship between distribution coefficient and mass number during run in the mass spectrometer. Nevertheless, for different nuclides of the same element, which also fall in a narrow range of mass number, the distribution coefficient values are probably very similar, and the relationship can probably be approximated to very gentle-slope linear. For mass number i, we can write:

$$D_i = D_l + \xi(m_i - m_l) \tag{6}$$

where l is the mass number of a convenient nuclide, and ξ, negative and very small in absolute value, is the slope of the correlation. Thus, difference $D_i - D_j$ can be written as:

$$D_i - D_j = \xi(m_i - m_j) \tag{7}$$

For samples which are pure or nearly pure elements, the distribution coefficient values are certainly close to one. Thus, mass l can be ideally chosen such that $D_l = 1$, and Eq. (6) gives:

$$\frac{D_i}{D_j} = \frac{1 + \xi(m_i - m_l)}{1 + \xi(m_j - m_l)} \tag{8}$$

Since $|\xi|$ is very small, the following approximation of (8) may be written by binomial series truncating:

$$\frac{D_i}{D_j} = (1+\xi)^{m_i-m_j} \tag{9}$$

Then, substituting (7) and (9) in (5), we obtain:

$$x_m = x_0(1+\xi)^{m_i-m_j} f^{\xi(m_i-m_j)} \tag{10}$$

and

$$x_0 = x_m\left(\frac{a}{f^{\xi}}\right)^{m_i-m_j}, \tag{11}$$

where $a = 1/(1+\xi)$.

2.1. ‘Linear’ model of isotope fractionation

Adding x_m to both members we have:

$$x_m - x_0 = x_m\left\{1 - \left[1 + \left(\frac{a}{f^{\xi}} - 1\right)\right]^{m_i-m_j}\right\}. \tag{12}$$

Since $|\xi|$ is very small, a/f^{ξ} is positive and very close to 1, so that $|a/f^{\xi} - 1|$ is very small. Thus, we can again approximate to:

$$x_0 = x_m\left[1 + (m_i - m_j)\left(\frac{a}{f^{\xi}} - 1\right)\right] \tag{13}$$

Eq. (13) is identical to Dodson’s Eq. (1) [15,16], and, as emphasized in [15,17], since $|a/f^{\xi} - 1|$ is very small, it may be interpreted as an approximation of the “power” law:

$$x_0 = x_m\left[1 + \left(\frac{a}{f^{\xi}} - 1\right)\right]^{m_i-m_j}. \tag{14}$$

From (13), we obtain:

$$\frac{x_m - x_0}{x_m(m_j - m_i)} = \frac{a}{f^{\xi}} - 1 \tag{15}$$

i.e., at any instant, the difference between the measured and initial ratios per unit of measured ratio and per unit of mass difference between the isotopes at the denominator and the numerator is the same for any isotope ratio.

The term of the first member of Eq. (15) is the fractionation factor F_x per amu, and Eq. (15) shows how this parameter can be interpreted from a physical point of view in terms of RDL.

Since at any instant f and $\xi(a)$ are the same for any isotope pair, it also shows that the linear hypothesis is fulfilled, i.e., that the assumption of the independence of the fractionation factor per amu from the isotope ratio is justified in a first approximation.

2.2. Linear *s.s.* model of isotope fractionation

In the previous section, we illustrated one of the linear approximations, which can be obtained by series expanding and truncating the power-law equation of isotope fractionation [3–5,9] to the first order term.

Following the terminology in [9], we can use the term ‘linear’ to indicate this model of isotope fractionation and distinguish it from the ‘true’, effectively linear or linear *s.s.* model of isotope fractionation. This linear *s.s.* model is also an approximate model which can be derived by series expanding and truncating the power-law equation of isotope fractionation to the first-order term. The ‘linear’ and the linear *s.s.* models, although almost equivalent, are however not completely equivalent.

In the case of the linear *s.s.* hypothesis of isotope fractionation, the fractionation factor per amu is defined as the instantaneous difference between the measured and the true values of the isotope ratio per unit of true value and per unit of mass difference between the two isotopes which define the ratio, and straight-line distributions are expected between the measured values of any of two isotope ratios during run in the mass spectrometer.

Starting from Eq. (11), and following a series expanding and truncating procedure as illustrated in Section 2.1 we obtain:

$$\frac{x_m - x_0}{x_0(m_j - m_i)} = 1 - \frac{f^{\xi}}{a}. \tag{16}$$

As in the case of Eq. (15), also Eq. (16) shows that, if the isotopic fractionation process due to evaporation of the sample in the source of the mass spectrometer follows RDL, and if the relationship between the vapor/residue distribution coefficient and mass is linear in the range of mass of the isotopes of the element, and the slope of this linear function is sufficiently small in absolute value, the linear *s.s.* model is reasonably fulfilled in a first close approximation.

2.3. Linear approximation of the exponential model of isotope fractionation

A linear approximation can also be derived from the exponential model of isotope fractionation. In the case of an isotope ratio $x = i/j$, the exponential hypothesis of isotope fractionation is [3,4]:

$$\frac{x_0}{x_m} = \left(\frac{m_j}{m_i}\right)^{p}, \tag{17}$$

where p, which is usually called the *fractionation exponent*, changes its value during run but has the same value at any instant for any isotope ratio.

This equation can be changed into the following:

$$\ln\left(\frac{x_0}{x_m}\right) = \ln\left(1 + \frac{x_0 - x_m}{x_m}\right) = p\,\ln\left(\frac{m_j}{m_i}\right),$$

function $\ln(1+k)$ can be series-expanded and, if k is sufficiently small, the following approximation does hold:

$$\frac{x_0 - x_m}{x_m} \approx p\,\ln\left(\frac{m_j}{m_i}\right) \tag{18}$$

i.e.,

$$\frac{x_m - x_0}{x_m\,\ln(m_i/m_j)} \approx p. \tag{19}$$

Since p has the same value at any instant for all the isotope ratios of the element, Eq. (19) represents a linearization of the exponential formula if we define the fractionation factor as:

$$F_x = \frac{x_m - x_0}{x_m\,\ln(m_i/m_j)} \tag{20}$$

Linear model (19) can also be obtained from RDL Eq. (5) as illustrated in the two previous sections, by assuming a relationship between mass and vapor/residue partition coefficient which is exponential, as follows:

$$D_i = D_l + b\,\ln\left(\frac{m_l}{m_i}\right), \tag{21}$$

where b is a positive constant.

Since Eq. (19) can be changed to:

$$\frac{x_m - x_0}{x_m(m_j - m_i)} \approx -\frac{p}{m_j} \tag{22}$$

and Eq. (21) can be linearized to:

$$D_i = D_l - \frac{b}{m_i}(m_i - m_l), \tag{23}$$

it can be concluded that the fractionation exponent $p_0 = p$ for $f \sim 1$ is close to slope $-b$ of the linear function which is obtained when vapor/residue partition coefficient D is plotted vs. $\ln m$.

Table 1
^{86}Sr/^{88}Sr, ^{87}Sr/^{86}Sr and ^{87}Sr/^{88}Sr ratios in sample NBS 987 (11) calculated using the linear model of instrumental isotope fractionation which is derived from the exponential hypothesis, and the straight-line best fit parameters of the x_m vs. x_m/y_m and x_m vs. y_m distributions. All the errors are calculated by combining unfavourably the errors on slope and y-intercept of each distribution, and the errors on masses of the isotopes which define the ratios which are involved in the distribution, and are expressed at 95% c.l. The weighted average values are calculated from [26].

NBS 987 (11) Distribution	^{86}Sr/^{88}Sr	Err	^{87}Sr/^{86}Sr	Err	^{87}Sr/^{88}Sr	Err
$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m/(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$	0.119464	0.000379	0.710093	0.005617	0.084833	0.000940
$(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m/(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$	0.119539	0.000956	0.709899	0.001401	0.084862	0.000846
$(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m/(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m$	0.119500	0.001240	0.710020	0.009222	0.084836	0.000222
$(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m$ vs. $(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m/(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$	0.119424	0.000664	0.710422	0.013820	0.084832	0.001178
$(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m/(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$	0.119488	0.000369	0.710017	0.005592	0.084841	0.000930
$(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m/(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m$	0.119542	0.001238	0.709884	0.009198	0.084850	0.000221
$(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m/(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m$	0.119490	0.000937	0.710015	0.001379	0.084841	0.000830
$(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m$ vs. $(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m/(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$	0.119564	0.000665	0.709901	0.013612	0.084870	0.001156
$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m/(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$	0.119505	0.000681	0.709963	0.006027	0.084849	0.001204
$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m/(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m$	0.119377	0.001404	0.710393	0.006285	0.084796	0.000247
$(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m/(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m$	0.119613	0.001205	0.709677	0.003559	0.084891	0.001281
$(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m/(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m$	0.119373	0.000676	0.710368	0.006025	0.084795	0.000239
$(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m$ vs. $(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m/(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$	0.119509	0.000677	0.710030	0.010083	0.084848	0.000724
$(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m$ vs. $(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m/(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m$	0.119409	0.002364	0.710291	0.003513	0.084807	0.001260
$(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m/(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m$	0.119593	0.001398	0.709736	0.006225	0.084871	0.000248
$(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m/(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$	0.119472	0.000682	0.710093	0.006055	0.084840	0.001208
$(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m/(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_m$	0.119575	0.000703	0.709791	0.006216	0.084869	0.000244
$(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m/(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$	0.119440	0.001199	0.710284	0.003635	0.084841	0.001285
$(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m$ vs. $(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m/(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$	0.119634	0.002423	0.709663	0.003631	0.084891	0.001285
$(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m$ vs. $(^{88}\mathrm{Sr}/^{87}\mathrm{Sr})_m/(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$	0.119470	0.000682	0.710098	0.010130	0.084829	0.000726
$(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$	0.119515	0.000232	0.709926	0.003458	0.084848	0.000578
$(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$ vs. $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$	0.119439	0.000235	0.710121	0.003501	0.084817	0.000585
$(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_m$ vs. $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_m$	0.119518	0.000461	0.709919	0.000669	0.084849	0.000407
$(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_m$ vs. $(^{86}\mathrm{Sr}/^{87}\mathrm{Sr})_m$	0.119441	0.000472	0.710147	0.000708	0.084821	0.000420
Weighted averages	**0.11948**	**0.00011**	**0.71001**	**0.00040**	**0.084837**	**0.000083**

We have therefore shown that linear approximations (15), (16) and (19) can be interpreted in terms of a process of Rayleigh's distillation, where a linear or an exponential relationship exists between mass and distribution coefficient.

These linear models imply the occurrence of linear distributions in the x_m vs. y_m (Eq. (16)) and/or in x_m vs. x_m/y_m (Eqs. (15) and (19)) diagrams. Thus, if during a mass spectrometer run distributions are observed in these diagrams, which are linear within the limit of experimental error, we can interpret the result as if, in the adopted experimental conditions, the isotopic instrumental fractionation of the element were generated from a Rayleigh's distillation process.

If this occurs, and a sample is available, the isotopic composition of which is known, we can use the above equations to obtain interesting new information. We chose for this purpose the fractionation results obtained for the evaporation of strontium of the worldwide used Sr isotopic NIST standard reference material 987, loaded as a nitrate on a single tungsten filament.

The ^{86}Sr/^{88}Sr ratio of Sr in SRM 987 (which is a Sr carbonate; alkalimetric assay, weight percent 99.98 ± 0.02) was determined by calibration for instrumental bias by means of samples of known ^{86}Sr/^{88}Sr ratios, gravimetrically prepared from chemically pure and nearly isotopically pure ^{86}Sr and ^{88}Sr solutions. The ^{87}Sr/^{86}Sr and ^{84}Sr/^{86}Sr isotopic ratios were then determined by normalizing the measured values to the value of the ^{86}Sr/^{88}Sr ratio [22].

At present, in the usual laboratory routine, the value of the ^{87}Sr/^{86}Sr ratio of this standard material is normalized to an assumed conventional 'true' ^{86}Sr/^{88}Sr value of 0.1194 [23]. In this case, a value close to 0.71025 is usually recognized as an index of correct instrumental behavior.

However, if the linear hypothesis of instrumental isotopic fractionation is fulfilled within the limits of experimental error, it is also possible, as proposed in [14], to determine the values of isotopic ratios of this reference material avoiding the procedure of normalization.

3. Materials and methods

For extensive details about sample preparation and mass spectrometry conditions see [14]. In some runs ^{88}Sr/^{86}Sr and ^{87}Sr/^{86}Sr ratios were measured by sampling the three peaks ^{86}Sr, ^{87}Sr and ^{88}Sr; in the others, ^{88}Sr/^{86}Sr and ^{84}Sr/^{86}Sr ratios were measured by sampling ^{84}Sr, ^{86}Sr and ^{88}Sr. The intensity of the ^{86}Sr reference peak was generally in the range 300–500 mV. Small changes in filament current were sometimes required to maintain the ^{86}Sr signal approximately within this range of intensity.

The data acquisition program was [24]. Blocks of 30 ratios each were sampled. Depending on sample, approximately 160–700 data blocks were acquired to fractionate the ^{86}Sr/^{88}Sr ratio of approximately 1% u^{-1}, where u is the unit of mass difference between the isotopes which define the ratio (~ from 0.1205 to 0.1181). Typical percent errors on the mean in a block were <0.04 and <0.03 for ^{88}Sr/^{86}Sr and ^{87}Sr/^{86}Sr, respectively. Correction for resistor decay constants was 750 ppm ratio and 300 ppm ratio for ^{88}Sr/^{86}Sr and ^{87}Sr/^{86}Sr, respectively.

4. Results and discussion

Fourteen mass spectrometric analyses were run. In eleven of them ^{88}Sr, ^{86}Sr and ^{87}Sr peaks were sampled, and in the others ^{88}Sr, ^{86}Sr and ^{84}Sr peaks were sampled. All the run data give linear distributions in the x_m vs. y_m and x_m vs. x_m/y_m diagrams within the limit of experimental error, so that the isotopic fractionation process can be interpreted in terms of the linear models of fractionation and, consequently, in terms of a Rayleigh's distillation process in which a linear or exponential relationship exists between mass and distribution coefficient.

Since the linear hypothesis is fulfilled by the data, it is possible to determine the value of the isotopic ratios in the standard material by means of the method in [14]. The values of the masses of the isotopes used in the calculations are from Atomic Mass Data Center (AMDC) files [25].

Table 2
Certified values (CV) of ^{86}Sr/^{88}Sr, ^{87}Sr/^{86}Sr and ^{87}Sr/^{88}Sr isotopic ratios in NIST standard reference material 987 [23], and the values of these ratios calculated using the linear model of instrumental isotope fractionation which is derived from the exponential hypothesis. Each determination is the weighted average of the 24 results which are calculated from the respective x_m vs. x_m/y_m and x_m vs. y_m distributions. The global weighted average values of the determinations (WA), and the respective MSWD and probability values, are calculated from [26]. Errors at 95% c.l.

	^{86}Sr/^{88}Sr	Err	^{87}Sr/^{86}Sr	Err	^{87}Sr/^{88}Sr	Err
	0.11937	0.00033	0.71050	0.00120	0.08480	0.00026
	0.11945	0.00033	0.71050	0.00100	0.08488	0.00023
	0.11952	0.00022	0.70992	0.00082	0.08485	0.00017
	0.11949	0.00023	0.71001	0.00085	0.08484	0.00018
	0.11949	0.00015	0.71001	0.00057	0.08484	0.00012
	0.11946	0.00015	0.71009	0.00058	0.08483	0.00012
	0.11934	0.00012	0.71048	0.00044	0.084785	0.000092
	0.11942	0.00028	0.71016	0.00061	0.08482	0.00013
	0.11938	0.00031	0.71040	0.00120	0.08482	0.00025
	0.11951	0.00026	0.71002	0.00099	0.08485	0.00021
	0.11948	0.00011	0.71001	0.00040	0.084837	0.000083
WA	**0.119445**	**0.000053**	**0.71016**	**0.00019**	**0.084826**	**0.000040**
	MSWD = 0.52 Prob = 0.88		MSWD = 0.45 Prob = 0.92		MSWD = 0.14 Prob = 0.999	
CV	**0.119352**	**0.000046**	**0.71034**	**0.00026**	**0.084780**	**0.000064**

The linear model which best fits the measured values is unambiguously the linear approximation of the exponential formula: since we know the values of the isotopic ratios from the NBS certificate and the masses of the isotopes from AMDC, we can calculate the slope and the y-intercept for any different x_m vs. y_m or x_m vs. x_m/y_m distribution, and observe that the values calculated with the linear model (19) are definitely closer to those of the slope and y-intercept obtained by straight-line best fit of the distributions than the values calculated using linear models (15) or (16).

As an example, let us consider distribution x_m vs. x_m/y_m, where $x = {}^{86}\mathrm{Sr}/{}^{87}\mathrm{Sr}$ and $y = {}^{88}\mathrm{Sr}/{}^{87}\mathrm{Sr}$, and calculate the slope and y-intercept of this distribution starting from mass data and from the isotopic values reported in the certificate according to linear models (15) and (19). In the case of model (15), the predicted slope is $m_1 = 0.16933$, and in that of model (19) the predicted value is $m_2 = 0.16837$.

The values of the slope of this distribution in the eleven spectrometric runs calculated by straight-line best fit of the data points are between 0.16760 and 0.16887, the arithmetic mean value is 0.16833, and the weighted average 0.16834 ± 0.00023 (2σ), which are much closer to 0.16837 than to 0.16933.

Calculating the isotopic ratio values with the linear model (19) determines higher consistence and reproducibility of the respective isotopic ratio values from the various distributions. For each run, 24 distributions are usable to calculate the isotopic ratios values (an example is given in Table 1), and, for sample NBS987 (11), Fig. 1a and b respectively show the values of ^{86}Sr/^{88}Sr calculated using the linear model (19) from the exponential hypothesis and the values of the same ratio calculated using the linear model (15) from the power hypothesis. The respective weighted average values, calculated from [26], are also shown.

Comparisons between these two figures clearly show the difference in reproducibility between the two linear models. Although the mean value is substantially the same, in the case of the linear model from the power hypothesis the calculated values are much less easily reproducible, or not at all reproducible, within the calculated error. This indicates that the distributions of measured values cannot be explained by the linear model from the power hypothesis.

Table 2 shows, for each of the eleven runs in which ^{86}Sr, ^{87}Sr and ^{88}Sr were sampled, the weighted average of the 24 results. The global weighted averages are also given, with MSWD and probability values: $^{86}\mathrm{Sr}/^{88}\mathrm{Sr} = 0.119445 \pm 0.000053$, $^{87}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.71016 \pm 0.00019$, $^{87}\mathrm{Sr}/^{88}\mathrm{Sr} = 0.084826 \pm 0.000040$.

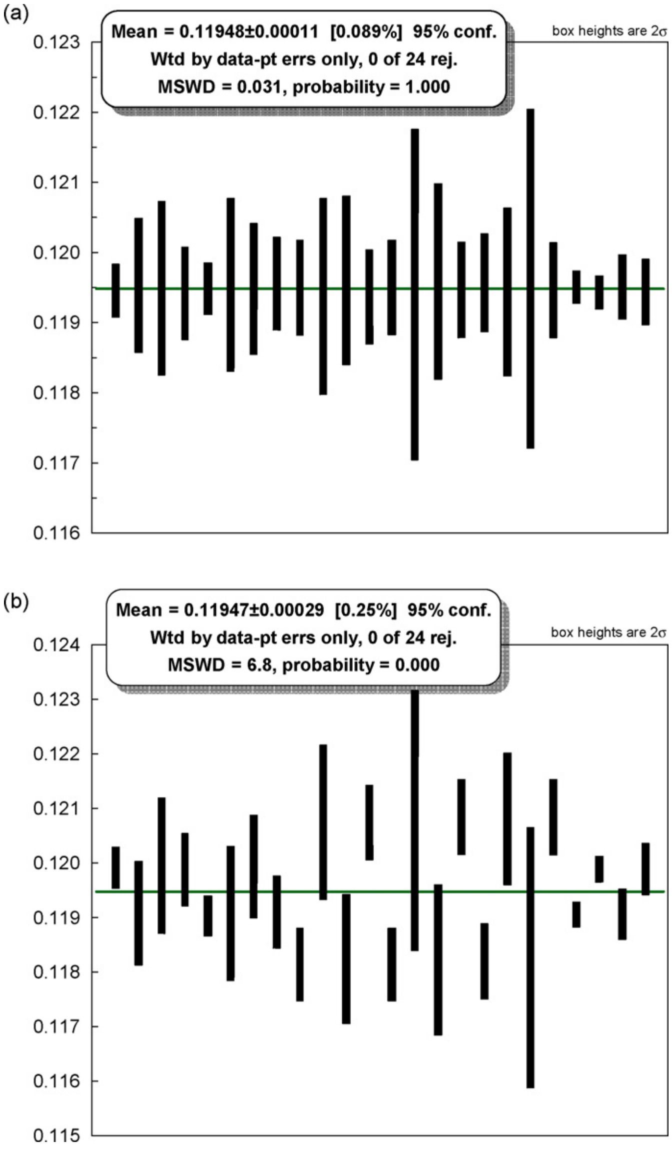

Fig. 1. (a and b) ^{86}Sr/^{88}Sr ratio in sample NBS987 (11) of NIST SRM 987 calculated (a) using the linear model of instrumental isotope fractionation which is derived from the exponential hypothesis and (b) using the linear model derived from the power hypothesis.

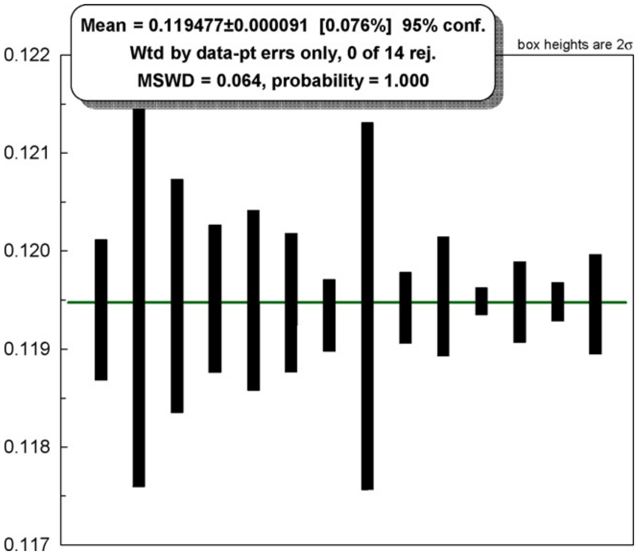

Fig. 2. Fourteen determinations of the ^{86}Sr/^{88}Sr ratio in NIST SRM 987 calculated using the linear model of instrumental isotopic fractionation derived from exponential hypothesis (see text for further explanations).

If the hypothesis on which the calculation model is based is fulfilled during the mass spectrometer run, the isotopic ratio values calculated from the various distributions are reproduced within the calculated error, and therefore it is sufficient only one distribution to determine the values of the isotopic ratios in the sample. Nevertheless, although the isotopic ratio values calculated from the various distributions are identical within the limit of the calculated error, the average values differ. Therefore, a dispersion index of the average values of the isotopic ratios calculated from the 24 distributions (e.g., standard deviation) seems to be useful in indicating how the hypothesis on which the calculation model is based was fulfilled during the mass spectrometer run.

The lower the dispersion value, the more the hypothesis on which calculation is based is fulfilled. Therefore it seem also reasonable to calculate the weighted average of the values of arithmetic mean calculated for the runs affected by the respective dispersion values, yielding the following values: ^{86}Sr/^{88}Sr = 0.11947 ± 0.00011, ^{87}Sr/^{86}Sr = 0.71016 ± 0.00035, ^{87}Sr/^{88}Sr = 0.084839 ± 0.000041 (errors at 95% confidence level). The global mean value of the ^{86}Sr/^{88}Sr ratio calculated for all the fourteen runs, 0.119477 ± 0.000093, is shown in Fig. 2.

4.1. *Estimation of change of vapor/residue distribution coefficient with mass*

We consider, as an example, 'linear' model of isotope fractionation (15). Similar calculations according to the other linear models of fractionation give results which are not substantially different.

With Eq. (15) for initial conditions ($f \approx 1$), we can estimate a maximum value of ξ ($\xi < 0$) from the value of the fractionation factor which results from the measured values of the isotopic ratios in the first block/s of data:

$$F \approx -\xi. \tag{24}$$

In the adopted experimental conditions, the values of ξ estimated accordingly, by comparing the 'true' value of the ^{86}Sr/^{88}Sr ratio (the certified or determined value) with the measured value are in the approximate range −0.006 to −0.004 amu^{-1}. Assuming that the value of the distribution coefficient is approximately 1, the change in D with mass is approximately −0.6 to −0.4% amu^{-1}.

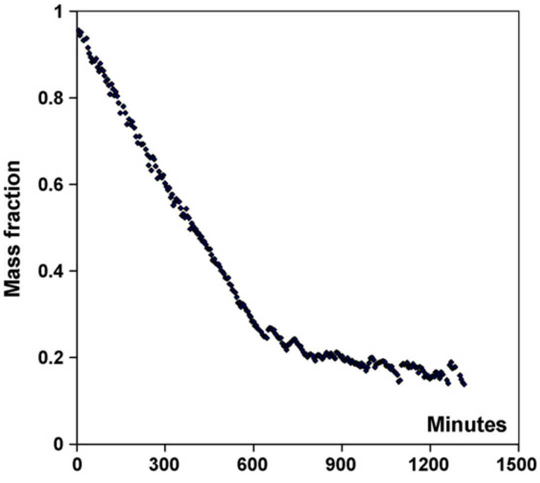

Fig. 3. Relationship between residual mass fraction and time for sample NBS 987 (9). Residual mass fraction is calculated with ξ value, which can be estimated from first data blocks (−0.0055 amu^{-1}).

If the measured values of the ratios are observed to change slowly with time during the initial part of the run, the calculated ξ value, although generally lower in absolute value than the true one, reasonably approximates the latter.

Linearization of the exponential relationship (21)–(23) gives $\xi \approx -b/m$, where m is any mass in the mass range of the element, and we have approximately b between 0.35 and 0.55.

4.2. *Calculation of residual mass fraction of the sample on the filament and rate of sample consumption*

As ξ is estimated, Eq. (15) can be used to calculate the value of the residual mass fraction of sample f at any instant during the run. We have:

$$f = [(1 + F)(1 + \xi)]^{-1/\xi}. \tag{25}$$

This allows us to study the relationship between residual mass fraction and time t.

An example of the observed sample consumption in the adopted experimental conditions is illustrated in Fig. 3, which refers to sample NBS 987 (9). This sample took about 1320 min to fractionate the ^{86}Sr/^{88}Sr ratio from the shown initial value of 0.1207–0.1181.

Although not as in the case of NBS 987 (9), in the spectrometric runs sample consumption was approximately constant with time in the range $f \approx 1$ to f = 0.3–0.25. Least-squares linear regression calculations gave the slope values of function $f(t)$ in the range −0.0013 to −0.0005 min^{-1} (i.e., rates of consumption between 0.05 and 0.13% min^{-1}), depending on time of total consumption T, with R^2 values generally higher than 0.98.

However, this part of the evolution trend does not correspond to 70–80% of the time needed for total consumption, but only, approximately, 40–50%. Thus, it is not possible to estimate time T required for total sample consumption from ξ values and from the observed 'initial' rate of change of the fractionation factor:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}t}\right)_{f=1} \approx \frac{\xi}{(1 + \xi)T}. \tag{26}$$

Since it is reasonable, at least within part of the run, to expect an approximately constant rate of sample consumption if the operative conditions do not change, the constant rate of sample consumption which is observed when the residual mass fraction values are calculated by the ξ values estimated according to Eq. (24) suggests that the evaporation process of strontium is adequately described by Rayleigh's distillation model.

If we choose values of ξ which are definitely lower than the limit value suggested by the first blocks of data (for example, in the range -0.01 to $-0.02\,\text{amu}^{-1}$, instead of -0.006 to $-0.004\,\text{amu}^{-1}$), the calculated f values are not linear with time. Nevertheless, such values are not reasonable.

In the second part of all runs, for values of residual mass fraction lower than 0.3–0.25, df/dt invariably becomes lower. Behavior is from roughly linear (as in the case of sample NBS 987 (9), Fig. 3) to very scattered, particularly if some adjustments of the filament current are needed to maintain the signal within an acceptable range of intensity. Since it does not seem reasonable to interpret this change of slope in terms of an abrupt change in ξ at $f = 0.30$–0.25, nor can a change in ξ explain a small part of the observed data, the change in df/dt seems due to the change in the contribution $d[(1+F)^{-1/\xi}]/dt$ in Eq. (25), i.e., to a change in dF/dt, which reflects the observed change in the rate of change of the value of the isotopic ratio.

4.3. *Value of residual mass fraction when the measured values of isotopic ratios coincide with true values*

From Eq. (15) or (25), we can calculate the residual mass fraction f_0 of the sample, at the instant when the measured values of the isotopic ratios 'pass through' the true values. If $F = 0$,

$$f_0 = (1+\xi)^{-1/\xi} \tag{27}$$

Since in our experimental conditions the values of ξ estimated from the first-block data are in the range -0.006 to $-0.004\,\text{amu}^{-1}$, f_0 calculated according to Eq. (27) falls in the range 0.3668–0.3671. This narrow range, which only differs by 0.1%, is because function (27) changes very smoothly with ξ within a large range of possible ξ values. If ξ is in the range -0.1 to $-0.00001\,\text{amu}^{-1}$ – a difference of four orders of magnitude – f_0 changes from 0.3487 to 0.3678, with a difference of only 5.5%. This means that the effect of discrepancy between the estimated and actual values of ξ in calculating f_0 is substantially reduced.

Therefore, according to the proposed model, 63.3–63.4% of the sample is approximately consumed when the measured values of the isotopic ratios coincide with the true ones.

Value f_0 can be also calculated by Eq. (5), if we let $x_m = x_0$, and the difference between the values obtained by Eqs. (27) and (5) for the same value of ξ shows the overall effects of the approximations used in the calculation model after Eq. (5). For ξ in the range -0.006 to $-0.004\,\text{amu}^{-1}$, the difference in the f_0 value is between 0.2 and 0.3%.

Calculation of the value of the residual mass fraction of the sample at the instant at which the measured value of the isotopic ratio passes through the actual value was previously proposed by [13], who examined the different empirical laws of isotopic instrumental fractionation and concluded that, in any case, for all empiric and approximate models, $f_0 = 1/e = 0.3678$.

The values calculated in this work on the basis of the estimated values of $\xi = dD/dm$ are very close to the value proposed by [13]. However, an immutable $f_0 = 1/e$ value for each run, as suggested in [13], cannot be reasonable. Instead, the value of f_0 must depend on the value of the parameter which, in the run, discriminates the isotopes of the element from the viewpoint of mass, i.e., it must depend on ξ, as shown in Eq. (27). This parameter depends on the adopted experimental conditions, and, within the experimental conditions, due to the empirical character of the TIMS technique, it is often different from run to run.

Clearly, if ξ tends to 0, f_0 must tend to 1, because condition $\xi = 0$ means no discrimination at all of the various isotopes of the element from the viewpoint of mass during the evaporation process. Instead, as ξ becomes higher and higher in absolute value, f_0 must progressively tend to 0.

5. Conclusions

The description of the process of evaporation of the isotopes of an element in thermal ionization-source mass spectrometry in terms of Rayleigh's distillation law [21] leads to interpreting the linear models of instrumental isotopic fractionation, derived as approximations of the power-law model of fractionation [3–5], as resulting from a linear dependence between mass and the vapor/residue distribution coefficient, with sufficiently small absolute values of slope ξ.

The fractionation factor per amu – defined as the instantaneous difference between the measured value of one isotope ratio and the respective true (initial) value per unit of measured/true value per unit of difference of atomic mass between the two isotopes which define that ratio [3–5] – is a function of slope ξ and of the residual mass fraction of the sample on the filament and, at a first approximation, is independent of the isotopic ratio.

The model shows that it is possible to estimate the value of slope ξ and the value, at any instant, of the residual mass fraction of the sample, thus revealing the percent rate of sample consumption.

A linear model of fractionation can be derived as an approximation of the exponential hypothesis [3,4]. This model can also be explained in terms of Rayleigh's distillation law, resulting from a relationship between mass and vapor/residue partition coefficient which is exponential.

Experimental data on instrumental isotopic fractionation of Sr in NIST SRM 987, loaded as a nitrate on single tungsten filament, show that the process may be interpreted in terms of the linear hypothesis of fractionation, and, therefore, the process of evaporation of the isotopes from the filament modeled in terms of Rayleigh's distillation law, with an approximately exponential relationship between mass and partition coefficient in the mass range ^{86}Sr–^{88}Sr. Accordingly, the values of the ^{86}Sr/^{88}Sr, ^{87}Sr/^{86}Sr and ^{87}Sr/^{88}Sr ratios can be determined by the method in [14], yielding the following values for the global weighted averages of the weighted averages of the results calculated from the various distributions: $^{86}\text{Sr}/^{88}\text{Sr} = 0.119445 \pm 0.000053$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.71016 \pm 0.00019$ and $^{87}\text{Sr}/^{88}\text{Sr} = 0.084826 \pm 0.000040$ (errors at 95% confidence level).

In the adopted experimental conditions, the change in D with mass is calculated in the range -0.006 to $-0.004\,\text{amu}^{-1}$ (reasonably, -0.6 to $-0.4\%\,\text{amu}^{-1}$), and the dependence of the residual mass fraction on time is calculated to be approximately linear within a large range of residual mass fraction of the sample from $f \sim 1$ to $f \sim 0.3$–0.25, with rates of sample consumption between 0.05 and $0.13\%\,\text{min}^{-1}$. Since it is reasonable, if operative conditions are not changed, to expect for approximately constant rates of sample consumption, at least during part of the mass spectrometer run, this suggests that evaporation (and isotopic fractionation) processes are adequately described in terms of Rayleigh's distillation model.

The residual mass fraction of the sample at the instant at which the measured value of the isotopic ratios coincide with the true value, f_0, is a function of slope ξ, and changes from run to run according to changes in ξ. The value of f_0 changes very smoothly with ξ, showing very little variability over a large range of possible ξ values (a change of 5.6% for ξ from -0.1 to $-0.00001\,\text{amu}^{-1}$). f_0 can be calculated by estimating ξ from the fractionation factor data, and is in the range 0.366–0.367 in the operative conditions used in this study.

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