

Fractionation correction and multiple collectors in thermal ionization isotope ratio mass spectrometry

K. Habfast

Kiesselbachstr. 26, D-28329 Bremen, Germany

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Abstract

A comprehensive theory for the correction of time- and mass-dependent evaporation-related mass fractionation effects is developed. The Rayleigh distillation equation and the Langmuir equation describing evaporation are combined and are formulated here as the “Rayleigh-Langmuir” fractionation model, which provides the only currently available fundamental or “causal” description of evaporation of isotopes in a vacuum. This “Rayleigh law” relates the depletion of isotopes in a sample (fractionation) to the amount of sample left in a reservoir. Other, commonly used fractionation laws (exponential law, power law, linear law, etc.) are more or less *ad hoc*, being based on empirical evidence. The relevant observational facts on which such laws are based are reviewed, and the laws are compared concerning their ability to fit the experimental data. Important time-independent (static) discrimination effects are also discussed. Fractionation correction algorithms for static and dynamic multiple Faraday collector data acquisition schemes are given, applying causal and empirical laws. It is shown that the fundamental limit to the ability to measure the true isotope ratio in a solid sample by thermal ionization mass spectrometry is currently determined by incomplete knowledge of the evaporation process, insufficient reproducibility of the evaporation process, and an inability to measure with sufficient accuracy the parameters that define static discriminations. (Int J Mass Spectrom 176 (1998) 133–148) © 1998 Elsevier Science B.V.

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1. Introduction

In a single or multiple filament thermal ionization ion source, a solid sample is evaporated in a vacuum and the volatilized species are then ionized at a hot surface. The evaporation process causes increasing depletion of the lighter isotope in the sample with the increasing amount of material removed by the evaporation, referred to as *mass fractionation*. During analysis, the measured isotope ratio changes with time, precluding the accurate determination of the true isotope ratio of the sample by direct measurement. If a sample contains at least two pairs of isotopes (i.e. at

least three isotopic species), and if the true ratio of one of these pairs is known, then this can be used as an internal standard ratio. The true ratio of the other pair of isotopes can, in principle, be calculated by using a “fractionation law” that relates the degree of depletion of the isotopic species with a suitably time-dependent parameter, such as the amount of sample evaporated. The elimination of this parameter from a pair of independent ratios is called *normalization*.

Lord Rayleigh’s diffusion equation [1], combined with Langmuir’s evaporation equation [2], provides a fundamental description of evaporation of isotopes in

a vacuum. Other fractionation laws based on empirical evidence rather than first principles have been proposed (empirical laws). Both the fundamental and the empirical approaches assume complete mixing of the sample at all times during evaporation and knowledge of the mass or the kind of the evaporating particles. In an effort to better describe real evaporation behavior, additional “free parameters” have been added to the laws. However, if values for these parameters are not known or cannot be determined accurately, such approaches are of limited help in improving the normalization process.

Measurement of isotope ratios are not only biased by dynamic evaporation-related fractionation effects but also by static, time-independent discriminations. The most important static discriminations arise from mass-dependent transmission of the ion optical system of the mass spectrometer and from variations in the ion collection efficiencies of the Faraday cups. Like dynamic discriminations, static discriminations can be eliminated if an appropriate “discrimination law” is known. Static discrimination effects in thermal ionization mass spectrometry (TIMS) are normally much smaller than those from dynamic discrimination.

For single collector “one-beam-at-a-time” data acquisition schemes, most static effects cancel out when computing the ratio of two ion currents measured in the same cup. Those that do not cancel are insignificant because of the limited measuring precision. The advent of multiple collector arrays that offer much higher precision dramatically changed this. However, static mass discrimination can be eliminated by normalization only if the discrimination law has a mass dependence similar to that of the fractionation law. Effects like a <100% collector efficiency cannot be corrected for at all in this way unless they have been calibrated in a separate experiment.

The various dual collector dynamic schemes, in which all ratios are measured sequentially in the same pair of collectors, offer a good compromise between single beam (dynamic) and multiple beam (static) data acquisition schemes. An accurate fractionation correction is fully guaranteed, given a detailed knowledge of the evaporation process, and most static mass

discriminations and, in particular, cup efficiency defects are significantly reduced.

However, incomplete knowledge of the details of the evaporation process, inadequate reproducibility of the evaporation process, and our current inability to accurately measure some parameters of static discrimination set limits on the accuracy of the determination of an unknown ratio by normalization. For elements such as Sr or Nd, these limits are of the same order of magnitude as the routinely achieved external precision, and cannot be lowered by striving to achieve higher (internal or external) precision of the acquired data. More detailed knowledge of evaporation behavior and new sample loading processes that offer more reproducible and more predictable evaporation behavior are required for accurate normalisation, as well as instrumental improvements, for a better control of static discriminations.

2. The Rayleigh-Langmuir fractionation model

Langmuir’s evaporation equation [2] for the evaporation of a sample into vacuum relates the number dn of moles, evaporating into vacuum per unit time with the mole fraction (or isotope abundance) f of a species in the sample

$$\frac{dn}{dt} = \frac{p_s \cdot f}{\sqrt{2 \cdot \pi \cdot m \cdot R \cdot T}} \quad (1)$$

where p_s is the saturation vapour pressure and m is the molecular (or atomic) weight of the evaporating particles. For two species (i, j), the ratio of the evaporation rates will then be

$$\frac{dn_i}{dn_j} = \frac{p_i}{p_j} \cdot \sqrt{\frac{m_j \cdot f_i}{m_i \cdot f_j}} = \frac{p_i}{p_j} \cdot \beta \cdot \frac{n_i}{n_j} \quad (2)$$

with $\beta = \sqrt{m_j/m_i}$ as the so-called fractionation coefficient ($m_i < m_j$) and n_i, n_j as the number of particles (moles) of species i resp. j . We assume $p_i = p_j$, which is appropriate for two isotopic species evaporating in a vacuum. Hence

$$\frac{dn_i}{n_i} = \beta \cdot \frac{dn_j}{n_j} \quad (3)$$

This equation is easily integrated. With $n_i = n_{io}$ resp. $n_j = n_{jo}$ being the amount of sample at the beginning of the evaporation, we get

$$\frac{n_i}{n_{io}} = \left(\frac{n_j}{n_{jo}}\right)^\beta = \frac{n_j}{n_{jo}} \cdot \left(\frac{n_j}{n_{jo}}\right)^{\beta-1} \quad (4)$$

Defining n_i/n_j as the isotope ratio R_{ij} in the sample at a time, when n_j particles are left in the sample, and $(n_{io}/n_{jo}) = S_{ij}$ the “true” isotope ratio (at the beginning of the evaporation), we get:

$$\frac{R_{ij}}{S_{ij}} = \left(\frac{n_j}{n_{jo}}\right)^{\beta-1} \quad (5)$$

This equation is very similar to Lord Rayleigh’s diffusion formula [1], in which β is interpreted as the ratio of the diffusion rates of two gases. The above equation is, therefore, referred to as the *Rayleigh fractionation law*. It relates the isotope ratio in the sample at time t to the amount ratio n_j/n_{jo} of one of the constituents at time t . The inability to measure R_{ij} is easily circumvented by applying Langmuir’s equation a second time to the vapour phase. Mass balance requires that $(dv_i/dv_j) = (dn_i/dn_j)$, dv_i resp. dv_j being the number of particles, appearing in the vapour per unit time.

Hence, from Eq. (2):

$$\frac{dv_i}{dv_j} = \beta \cdot R_{ij} \quad (6)$$

By measuring an ion current, one measures rates of flow of material (dv/dt [mol/s]). The ion current i (with ion source sensitivity E given in [Coulomb/mol]) is, therefore,

$$i = E \cdot \frac{dv}{dt} \quad (7)$$

The ion current ratio r_{ij} of two species i resp. j (sensitivity E_i resp. E_j) is given by

$$r_{ij} = \frac{E_i}{E_j} \cdot \frac{dv_i}{dv_j} \quad (8)$$

Assuming $E_i = E_j$, which is appropriate for thermal ionisation of two isotopes, we get, by using Eq. (5) and Eq. (6), a useful formula [3] for a Rayleigh fractionation law:

$$\frac{r_{ij}}{S_{ij}} = \beta \cdot \left(\frac{n_j}{n_{jo}}\right)^{\beta-1} \quad (9a)$$

Similarly, if the ratio is related to the amount n_j of constituent i , one obtains:

$$\frac{r_{ij}}{S_{ij}} = \beta \cdot \left(\frac{n_i}{n_{io}}\right)^{(\beta-1)/\beta} \quad (9b)$$

Finally, if the ratio r_{ij} is related to the sum n of the amounts of constituents i and j , a more complicated form is obtained:

$$\frac{r_{ij}}{S_{ij}} = \beta^\beta \cdot \left(\frac{S_{ij} + 1}{r_{ij} + \beta} \cdot \frac{n}{n_o}\right)^{\beta-1} \quad (9c)$$

This last equation, in which r_{ij} and S_{ij} are only implicitly available, has also been described by Kanno [4] as a special case of a more general problem, namely the evaporation of more than one chemical form of each isotopic species.

3. Empirical fractionation models

A variety of interpolation algorithms or “laws,” based on empirical evidence, have been used to describe mass fractionation (Fig. 1). There are only two observable facts that serve to constrain empirical fractionation laws for thermal ionization. (1) The ratio r_{ij} ($m_i < m_j$) of two ion currents is higher than the true ratio ($r_{ij} > S_{ij}$) at the beginning of the evaporation process and it changes with time, passing through the true ratio ($r_{ij} = S_{ij}$) at some point, after which the ratio becomes lower than the true ratio. Except for these two characteristic points, the detailed course of fractionation with time is more or less arbitrary and is (mainly) determined by the time dependence of the evaporation rate, which is a function of, among other things, the temperature of the filament. (2) The degree and speed of fractionation depends on the absolute masses of *both* isotopic species.

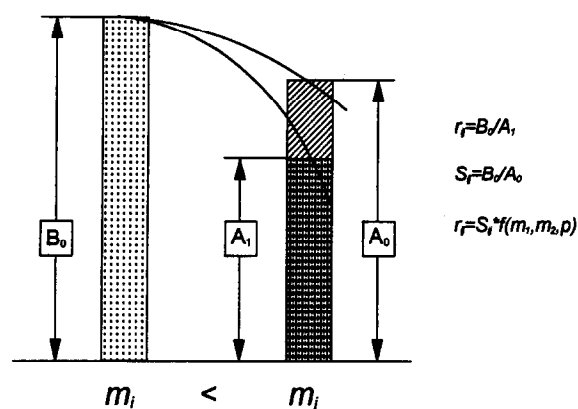


Fig. 1. Nomenclature for ad-hoc fractionation laws (p = “fractionation coefficient”).

The only aim of all empirical “laws” is to remove the time dependence of the measured ratios by the introduction (and subsequent elimination) of an empirical “fractionation factor” that, therefore, must be a function of time alone.

A simple formula that reflects both observable facts and that results in sufficiently time independent ratios, is the *exponential law* proposed by Russell et al. [5]:

$$\frac{r_{ij}}{S_{ij}} = \left(\frac{m_j}{m_i}\right)^p \quad (10)$$

where p , the *fractionation factor*, is a suitably defined function of time, but is independent of mass. The time dependence of p is assumed to be the same for all ratios, so that, for example, for $p = 1/2$ (at $t = 0$ and assumption of Langmuir-type evaporation), $r_{ij} = \beta \cdot S_{ij}$ and for $p = 0$ (at some later time), $r_{ij} = S_{ij}$, which is consistent with the observations. Replacing p with an arbitrary function $q(t)$, which fulfils the condition that it runs from 1 to 0 during the course of the evaporation, such as $q_j = n_j/n_{j0}$ in the Rayleigh law, and which intersects the two characteristic points, we can write:

$$p(t) = \frac{1}{2} \cdot [1 + \ln q(t)] \quad (11)$$

and, hence,

$$\frac{r_{ij}}{S_{ij}} = \left(\frac{m_j}{m_i}\right)^{1/2(1+\ln q)} = \beta \cdot \beta^{\ln q} = \beta \cdot q^{\ln \beta} \quad (12)$$

As $\beta \approx 1$, we have $\ln \beta \approx \beta - 1$.

This explicitly time-dependent exponential law is closely related to the Rayleigh law, if q is intuitively interpreted as an entity similar to n_i/n_{i0} , the (relative) amount of sample, left on the filament at the time when r_{ij} is measured.

Following this kind of intuition, a simpler “linear” law can be derived [6] that is in good accordance with the Rayleigh law and also with observations over a wide range of q :

$$\frac{r_{ij}}{S_{ij}} = \beta + (\beta - 1)\ln(q) \quad (1 \geq q > 0) \quad (13)$$

Because this equation can also be obtained from Eq. (9c) by applying the following approximations:

$$\frac{1 + \beta \cdot R_{ij}}{1 + S_{ij}} \approx \beta; \quad \ln\left(\frac{r_{ij}}{s_{ij}}\right) \approx \frac{r_{ij}}{S_{ij}} - 1$$

it is referred to here as the *linearized Rayleigh law*.

In the early years of thermal ionisation mass spectrometry, Dodson [7] proposed the “linear fractionation law”:

$$\frac{r_{ij}}{S_{ij}} = 1 + \alpha \cdot \Delta m_{ij} \quad (\Delta m_{ij} = m_j - m_i) \quad (14)$$

where α is a “fractionation constant” ($\alpha \ll 1$), considered by Dodson as being independent from time. If $\alpha = 1/(2 \cdot m_i)$, experimental data are reasonably fitted. This linear law has been expanded to the so-called power law:

$$\begin{aligned} \frac{r_{ij}}{S_{ij}} &= (1 + \alpha)^{\Delta m_{ij}} \\ &\approx 1 + \alpha \cdot \Delta m_{ij} + \frac{\alpha^2}{2}(\Delta m_{ij} - 1)\Delta m_{ij} + \dots \end{aligned} \quad (15)$$

Introducing an arbitrary function $q(t)$ into the linear (14) and power (15) laws, respectively, results in reasonable, time-dependent fractionation laws:

Linear law:

$$\frac{r_{ij}}{S_{ij}} = 1 + \frac{\Delta m_{ij}}{2 \cdot m_i} [1 + \ln(q)] \quad (16)$$

Power law:

$$\frac{r_{ij}}{S_{ij}} = \left(1 + \frac{1 + \ln(q)}{2 \cdot m_i}\right) \Delta m_{ij} \quad (17)$$

It is important to note the mass dependency of the fractionation constant, α , if these laws are to be used as the base for a normalization formula.

To demonstrate the freedom allowed in defining empirical fractionation models, we present a new “root law,” which fits the precise data obtained with modern instrumentation (but offers no advantages for normalisation over the other laws and is, hence, excluded from further detailed discussion):

$$\begin{aligned} \frac{r_{ij}}{S_{ij}} &= \sqrt{\frac{m_j}{m_i} + \left(\frac{m_j}{m_i} - 1\right) \ln(q)} \\ &= \sqrt{\beta^2 + (\beta^2 - 1) \ln(q)} \end{aligned} \quad (18)$$

4. Comparisons of fractionation laws

If the whole sample is evaporated and recollected in a condensate, the condensate must have the (true) isotope ratio S_{ij} of the original sample. The integration of the evaporation rates, i.e. of r_{ij} [Eqs. (9a,b,c), (12), (13), (16), and (17) for $0 \leq q \leq 1$] must therefore result in S_{ij} , if the particular fractionation law describes the evaporation correctly. This is, as expected, true for Eq. (9a,b,c), for Eq. (13) (because of $\lim_{q \rightarrow 0} [q \ln(q)] = 0$), and, interestingly, also for the linear law, Eq. (16), but only approximately true for the exponential law, Eq. (12):

$$\int_0^1 r_{ij} dq = S_{ij} \frac{\beta}{\ln(\beta) + 1} \approx S_{ij} \quad (12a)$$

The starting value $r_{ij,0} = \beta \cdot S_{ij}$ (for $t = 0$, $q = 1$), the first characteristic point, is identical for the Rayleigh, exponential, linearized Rayleigh, and root laws, but not for either the linear or power laws. For

$r_{ij} = S_{ij}$ (the second characteristic point), we obtain from Eq. (9a):

$$q_j = \beta^{1/(1-\beta)} \quad (14a)$$

from Eq. (9b):

$$q_i = \beta^{\beta/(1-\beta)} \quad (14b)$$

and from all empiric or approximated models (Eqs. (12), (13), (16), or (17):

$$q = \frac{1}{e} \quad (14c)$$

Note that the value of q in these models is independent from mass. This is not the case for q_i nor q_j in the Rayleigh law. However, we find

$$\lim_{\beta \rightarrow 1} (q_j) = \lim_{\beta \rightarrow 1} (q_i) = \frac{1}{e} \quad \text{and} \quad q_j < \frac{1}{e} < q_i$$

It is noted without proof that the Rayleigh law for the fraction q_t of the total sample, i.e. Eq. (9c), results in $q_t = \frac{1}{e}$ at $r_{ij} = S_{ij}$, if $S_{ij} = 1$.

For all fractionation models the observed ratio equals the true ratio at $\sim 63\%$ evaporation of the sample. The small fundamental difference between the empirical laws and the Rayleigh law has an important consequence for normalization. Because q_i and q_j depend on mass, the relative amount q of sample, for which r_{ij} equals S_{ij} , is different for two different isotope ratios in a multi-isotope system and, hence, causes a mass dependent offset of the fractionation lines, as shown later. This is intuitively difficult to understand and may be one of the reasons for the popularity of the empirical fractionation models. However, it can easily be explained. There exist three equivalent formulations of the same fundamental law with different interpretations for their q parameter. This points to the fact that the fractionation factor of all empirical laws not only depends on time but also (to a lesser degree) on the isotope ratio itself.

Therefore, it might be questionable to directly compare the dependence of the fractionation models on q , because q means something different in each particular law. However, if q is interpreted as the

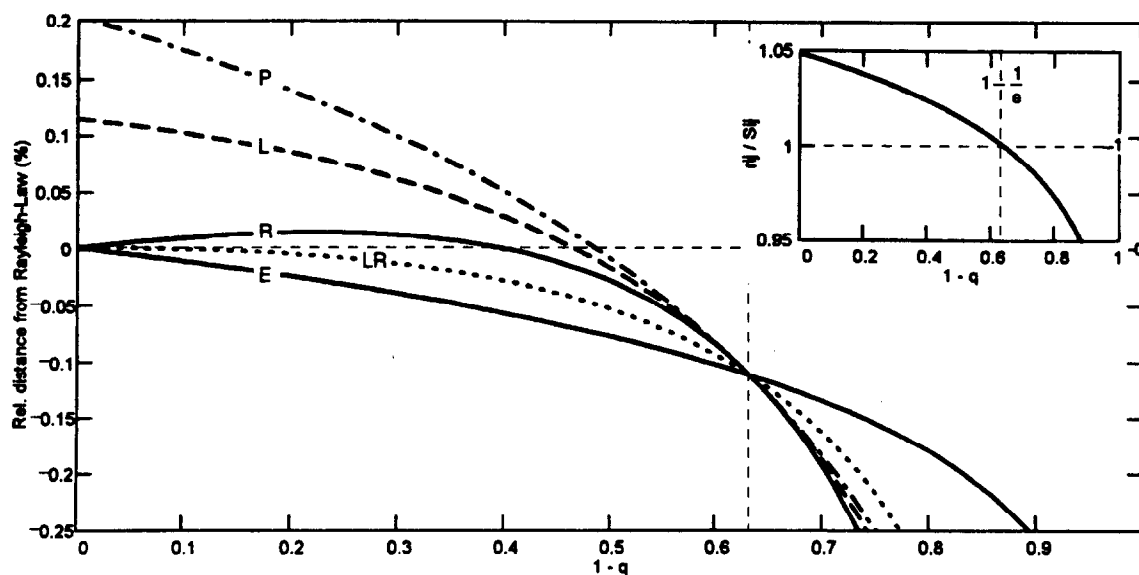


Fig. 2. Fractionation with time for causal and empirical fractionation models. The percent difference of the empirical models from the Rayleigh law is plotted vs. the relative amount q of sample left on the filament at time t . The Rayleigh law itself [i.e. $r_{ij}/S_{ij} = f(q)$] is shown in the insert. (E, exponential law; LR, linearized Rayleigh law; R, Root law; L, linear law; P, power law.)

quantity, which is eliminated in calculating the normalization formula, such a comparison is valid. As shown in Fig. 2 for a pair of isotopes with 10% mass difference (^{40}Ca and ^{44}Ca), the exponential, linearized Rayleigh, and root law approach the Rayleigh law over a wide range of q . The more sample is evaporated (i.e. versus the end of the sample's lifetime), the more pronounced are the deviations of the various models from each other. Hence, the region where only a small percentage of sample remains on the filament and when the sample is highly fractionated, is the most suitable region for comparison of the models. By contrast, if a choice of the "correct" model appears to be questionable, this region should be avoided.

5. Evaporation related free parameters

The various observed deviations of the isotope ratio from the true ratio are only roughly modeled by idealized fractionation laws. Hart et al. [8] and Fletcher et al. [9] have pointed to many remaining problems common to all idealized fractionation mod-

els. Kanno [4] and Habfast [6] have given generalized Rayleigh-type fractionation models, which include simultaneous evaporation (and ionization) of several chemical species. In order to more realistically describe the processes in the ion source, all models are to be modified by the addition of numerous parameters.

The most unrealistic assumption of all models is that of complete mixing of the sample. Instead, for the direction perpendicular to the surface, for example, a layer of a certain thickness at the surface (reservoir 1) will exhibit higher depletion of the light isotope than the bulk of the sample (reservoir 2), and there will be a concentration gradient between both reservoirs that will enhance diffusion. In the equilibrium state, the average thickness of reservoir 1 will be constant until it reaches the bottom of reservoir 2 during the course of the evaporation, and it will be determined by the relative rates of diffusion and evaporation. Consequently, the observed ratio will be depleted relative to what it would be if there were complete mixing, and the observed rate of fractionation will be slower,

because unfractionated material is constantly being delivered into the evaporating surface layer. Assuming no diffusion at all, the observed isotope ratio will, in this special case, be equal to the true ratio in the sample all the time during the evaporation. Mathematically, this situation is in full analogy to that encountered in the viscous gas inlet system [10] and can, in principle, be described by a differential equation of the form $\partial c/\partial t = \lambda \cdot \partial^2 c/\partial x^2$, $c(x, t)$ being the isotope ratio. Eberhardt et al. [3], as well as Fletcher et al. [9], have reported fast initial changes of the observed isotope ratio, which, indeed, can be expected from this mixing model, because a certain time is needed before the (un)mixing equilibrium is reached. Similar reasoning predicts nonreproducible evaporation behaviour toward the point of exhaustion of the sample, most probably because of laterally inhomogeneous unmixing.

The equilibrium state of the proposed mixing model can be approximated by introducing an “observed” fractionation coefficient

$$\beta^{\text{obs}} = K(\beta - 1) + 1$$

$$\text{(i.e. } 1 \leq \beta^{\text{obs}} \leq \beta \text{ for } 0 \leq K \leq 1),$$

which simulates the average depletion in the surface layer. K is a “dilution factor” with $K = 0$ for the case of no mixing and $K = 1$ for complete mixing. In particular, it may be interpreted as $K = D/D + V$, where D or V are, respectively, the rates of diffusion and evaporation. As an example, the Rayleigh law becomes:

$$\frac{r_{ij}}{S_{ij}} = [K(\beta - 1) + 1] \left(\frac{n_j}{n_{j0}} \right)^{K(\beta-1)} \quad (10\text{aa})$$

Plots of fractionation for selected values of K are shown in Fig. 3(a). According to this model, an incompletely mixed sample behaves (a) as if the evaporated particles (mass m) would be seemingly heavier ($m^{\text{mix}} = m + \mu^{\text{mix}}$) [Fig. 3(b)], and (b) as if the sample size q' would be larger: $q' = q^K$.

Samples are usually loaded as salts or oxides (CaF_2 , CaO) and they are mostly “conditioned” before the measurement in order to convert the sample into a

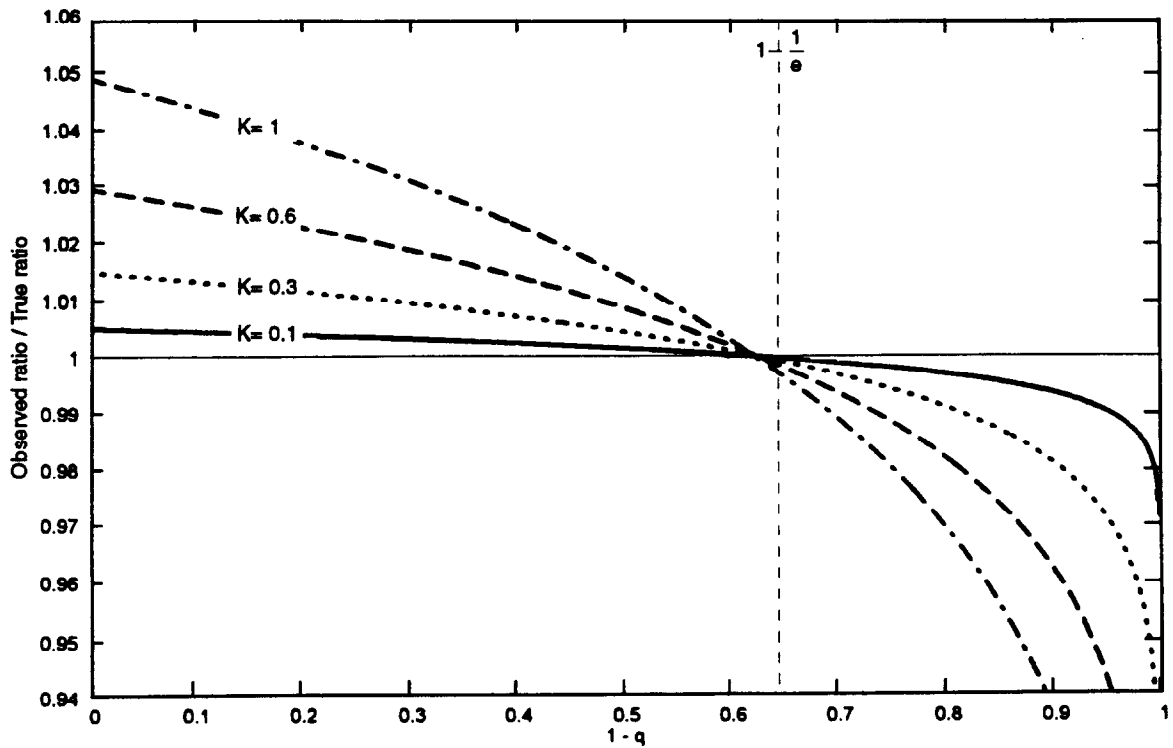
chemical form that exhibits suitable evaporation behavior. The final chemical form and, hence, the molecular weight m^{evap} of the evaporating species is often not known in detail, but it is, for molecular evaporation, higher than the mass m^+ of the ions ($m^{\text{evap}} = m^+ + \mu^{\text{neutr}}$). Consequently, the fractionation coefficient β needs to be modified correspondingly. Similar reasoning for the choice of the correct masses must be applied for a single filament ion source with no clear spatial separation of the evaporation and the ionization process, although very probably also with the succession (*molecular*) evaporation \rightarrow dissociation \rightarrow ionization.

A salt may even simultaneously evaporate in two or more chemical species, e.g. 80% CaF_2 and 20% CaF for a sample, loaded as CaF_2 . As has been shown by Habfast [6], the simultaneous evaporation of, for example, two chemical species (coefficients β_1 , β_2), both producing the same ion species (coefficient β^+), can be interpreted as if a single species (fractionation coefficient $\beta^{\text{obs}} \leq \beta^+$, apparent mass $m^{\text{app}} = m^+ + \mu^{\text{app}}$; Fig. 3(c)) had evaporated ($\beta_1 < \beta^{\text{obs}} < \beta_2$).

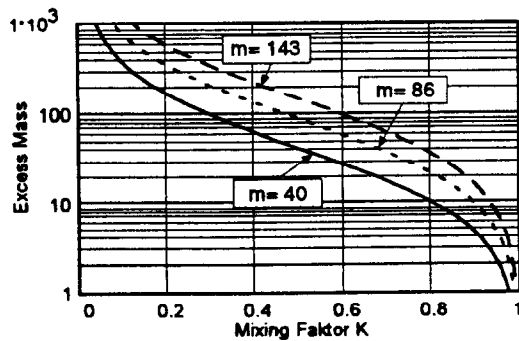
Taken together, the two most prominent uncertainties of the evaporation process in the ion source, namely incomplete mixing and the value of the “observed mass” of the particles can be assessed by a number of free parameters (K , μ^{mix} , μ^{neutr} , μ^{app}), which all suggest the use of a coefficient β^{obs} that is smaller than the coefficient of the observed ions.

6. Normalisation formulae and fractionation lines

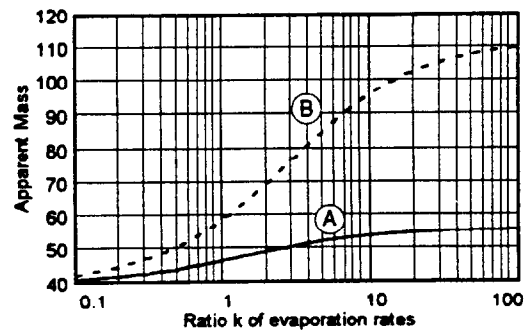
By the elimination of the time-dependent parameter q from two simultaneously valid fractionation equations for two isotope ratios of the same element, an unknown isotope ratio can be related to a known ratio. For convenience, it is assumed (Fig. 4) that the unknown ratio (r_1 , S_1) and the known ratio (r_2 , S_2) have the isotope with the lowest of their masses (m_1) in common. Such a convention is particularly important in the case of the Rayleigh, linear, and power laws. It can be achieved in any case, however, sometimes only by the use of a third “auxiliary” ratio. Furthermore, all relevant isotope ratios are always



a



b



c

Fig. 3. Incomplete mixing of the evaporating sample. (a) Fractionation of $^{40}\text{Ca}/^{44}\text{Ca}$ with time (according to Rayleigh law) for different mixing coefficients. (b) Excess mass μ^{mix} as a function of the mixing factor K . (c) Apparent mass μ^{app} as a function of the ratio k of the evaporation rates for the coevaporation of CaO/Ca (A), and CaCl_2/Ca (B).

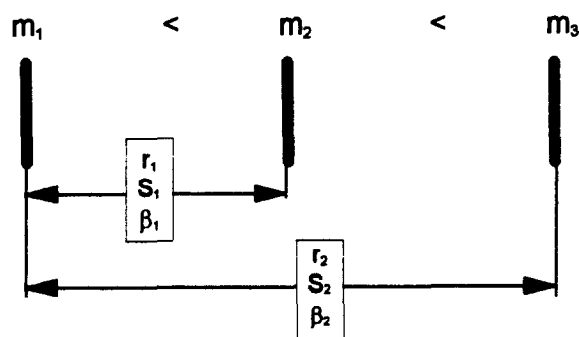


Fig. 4. Notation for normalisation formula.

defined with the ion current of the lighter isotope in the numerator. Fractionation coefficients (β) have the lighter isotope mass in the denominator. Elimination of q results in the following normalization formulas ($m_2, m_3 > m_1$) [8]:

Rayleigh law:

$$\frac{r_1}{S_1} = \frac{\beta_1}{(\beta_2)^x} \left(\frac{r_2}{S_2} \right)^x \quad x = \frac{\beta_2 (\beta_1 - 1)}{\beta_1 (\beta_2 - 1)} \quad (19)$$

Exponential law:

$$\frac{r_1}{S_1} = \left(\frac{r_2}{S_2} \right)^x \quad x = \frac{\ln(\beta_1)}{\ln(\beta_2)} \quad (20)$$

Power law:

$$\frac{r_1}{S_1} = \left(\frac{r_2}{S_2} \right)^x \quad x = \frac{m_2 - m_1}{m_3 - m_1} \quad (21)$$

Linearized Rayleigh law:

$$\frac{r_1}{S_1} = (1 - x) + x \cdot \frac{r_2}{S_2} \quad x = \frac{\beta_1 - 1}{\beta_2 - 1} \quad (22)$$

Linear law:

$$\frac{r_1}{S_1} = (1 - x) + x \cdot \frac{r_2}{S_2} \quad x = \frac{m_2 - m_1}{m_3 - m_1} \quad (23)$$

If free parameters are to be included, the values for β_1 and β_2 need to be replaced by the best assessment for β_1^{obs} and β_2^{obs} . With these formula, the unknown ratio S_1 can be computed by using the measured ratios r_1

and r_2 and the known ratio S_2 . The graph of the function $r_1/S_1 = f_n(r_2/S_2)$ is called the *fractionation line* (Fig. 5). All values of $S_1 = [r_1/f_n(r_2/S_2)]$, if plotted versus the time at which the values of r_1 and r_2 have been measured, are expected to be positioned on a line of zero slope (referred to here as the *correction line*), provided that the chosen fractionation model $f_n(\cdot)$ correctly describes the evaporation process.

The question arises whether it is possible to select the most appropriate fractionation law on the basis of precise ratio data alone? The slopes of the Rayleigh, linearized Rayleigh, and exponential fractionation lines depend on β , i.e. on the selection of appropriate free parameters, whereas the slopes of the fractionation lines of the linear and the power laws do not contain β , but only mass differences, which are not influenced by any one of the evaporation related free parameters. Hence, if observed data, normalized by application of the power or the linear law, are positioned on a nonzero slope correction line, these two laws can be excluded from further consideration because there is no means to modify the slope significantly by selecting “better” free parameters.

By contrast, correction lines, computed by application of the Rayleigh, exponential, or linearized Rayleigh law can, in many cases, be forced to exhibit zero slope by choosing suitable free parameters, such as assuming an “apparent” mass [6] higher than the mass of the ions (Fig. 6). However, the condition that the correction line should exhibit zero slope is necessary but not sufficient to unequivocally differentiate between the fractionation models. By arbitrarily modifying β , the fractionation line of the Rayleigh law is not only rotated (like the two others), but is also simultaneously shifted along the r_1/S_1 axis, because it does not pass through the characteristic point ($r_1/S_1 = 1, r_2/S_2 = 1$). Together with the fact that the second derivatives of the Rayleigh and exponential fractionation lines are practically equal and different from zero for all masses, this has the following consequences.

For a given pair of masses, $m_R = m_0 + \mu$ resp. $m_E = m_0$, chosen for normalizing according to, respectively, the Rayleigh (R) and exponential (E)

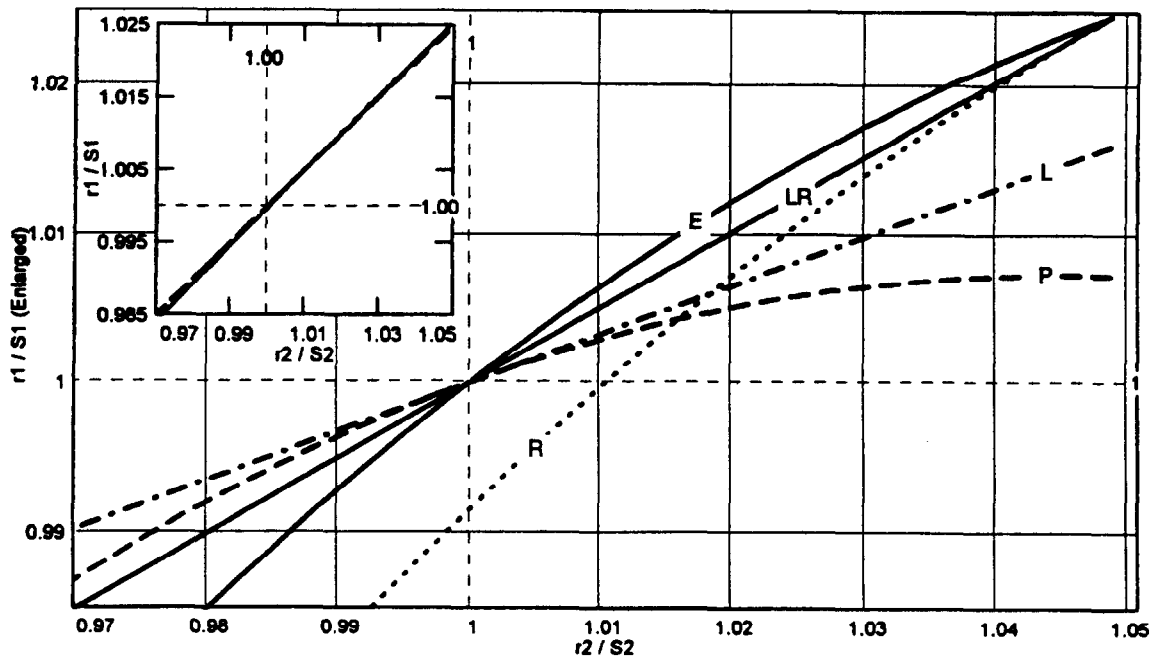


Fig. 5. Fractionation lines for $^{40}\text{Ca}/^{42}\text{Ca}$ normalized to $^{40}\text{Ca}/^{44}\text{Ca}$. Deviations to the truly linear linearized Rayleigh law are 30-fold enlarged. (E, exponential law; LR, linearized Rayleigh law; R, Rayleigh law; L, linear law; P, power law.)

laws, the corresponding fractionation lines become equidistant, showing the same slope for all values of $r_{\text{obs}2}/S_2$. Hence, data points, if normalized according to the Rayleigh law (S_{R1}), by assuming particles of mass m_R , or the exponential law (S_{E1}), by assuming particles of mass m_E , will both plot on zero slope correction lines [Fig. 6(D)]. Their relative distance will be

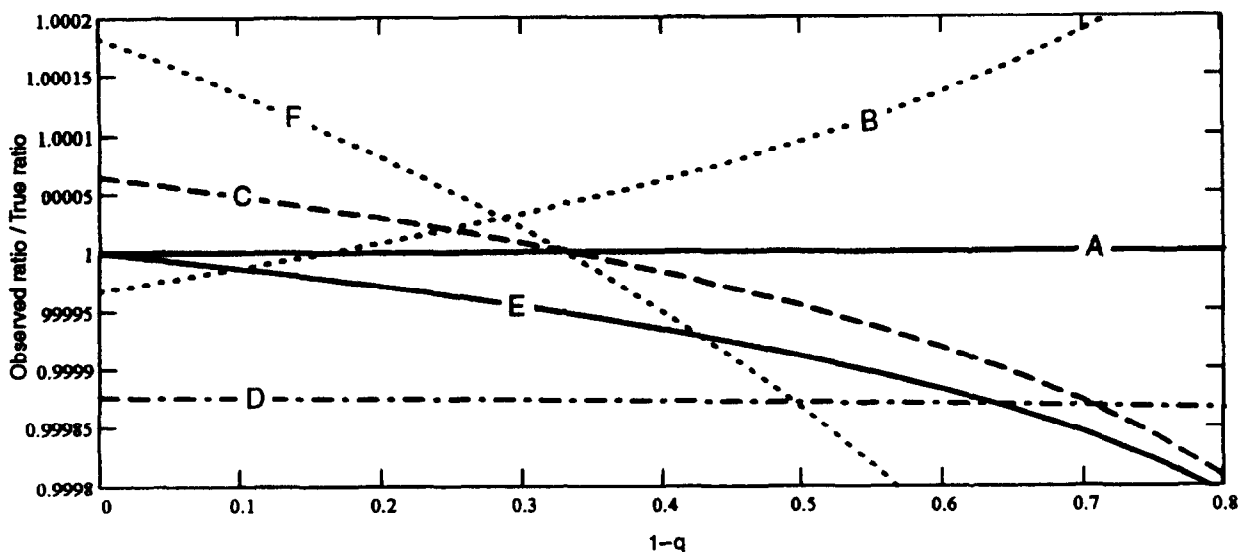
$$\Delta = \frac{S_{R1} - S_{E1}}{S_{E1}} = \left(\frac{\beta_{R1}}{\beta_{R2}^g} - 1 \right) \quad (24)$$

$$\left(g = f \frac{\beta_{R1}}{\beta_{R2}^f}, f = \frac{\beta_{R2}(\beta_{R1} - 1)}{\beta_{R1}(\beta_{R2} - 1)} \right)$$

Offsets calculated for some common isotopic systems, showing this principle Rayleigh/exponential "dilemma" [5], are given in Table 1. Without detailed proof, it is noted that the excess mass μ to enforce equidistance is related almost linearly to m_R , independent of the relative mass differences $\Delta m_R (\mu \approx 0.364 m_R + 6.8)$. This sets some limits for the choice of μ . Over a wide range of the evapo-

ration, a Rayleigh/linearized Rayleigh dilemma exists as well. Its offset is about half of the offset of the Rayleigh/exponential dilemma. Only at the very end of the evaporation process (>80% sample evaporated) can significantly higher differences be expected. Finally, a linearized Rayleigh/exponential dilemma does not exist, as both fractionation lines pass through (1, 1).

Only in rare cases does the nature of the evaporation process stay constant during the entire evaporation period [9]. For instance, the chemical form of the particles evaporating from the filament may change if the filament temperature is changed. The time to reach constant depletion of the evaporating surface layer may extend over a significant part of the whole measurement, or different parts of the sample may exhaust at different time because of the inhomogeneous thickness of the sample layer. Independent from the choice of a particular fractionation model or the selection of free parameters, many effects (referred to as artifacts), which have their origin in the



	Sample is <u>evaporating</u> according to RAYL with	Data are <u>normalized</u> , using the RAYL or the exponential law (EXPO)	Remarks
A	Excess mass = 20 (e.g. CaO; $K = 0.9$)	RAYL: Excess mass = 20 (like evaporation)	1)
B	Excess mass = 20	RAYL: Excess mass = 20 (ion mass)	4)
C	Excess mass = 0 (e.g. loaded as CaO, evaporating as Ca)	RAYL: Excess mass = 10 (e.g. assumption of CaO: Ca = 1:3; i.e. ratio of evaporation rates $k = 3$)	2)
D	Excess mass = 20	EXPO: Excess mass = 0 (ion mass)	3)
E	Excess mass = 20	EXPO: Excess mass = 20	4)
F	Excess mass = 0	EXPO: Excess mass = 20	2)

Remarks: 1) This is a reasonable assumption for two free parameters, but may be speculative. 2) The average of *all* normalized values (for $1 < q < 0.2$) is very near to the average of the Rayleigh normalization. 3) This set of (often used) parameters shows the Rayleigh/exponential dilemma. 4) The average of *all* normalized values (for $1 < q < 0.2$) is higher/lower than the average of Rayleigh normalization.

Fig. 6. Simulation of fractionation correction (Rayleigh law, RAYL).

specific sample handling or measuring technique used, can have significant influence on the slope of the correction line or on its reproducibility and, hence, on the value and the variance of the computed "true ratio."

7. Other discriminations

The adulteration of isotopic patterns by instrumental or methodical artifacts is a common phenomenon in isotope ratio mass spectrometry. For instance,

Table 1
Rayleigh/exponential dilemma

$m = 40, \Delta m_1 = 2, \Delta m_2 = 4$	$m = 86, \Delta m_1 = 1, \Delta m_2 = 2$	$m = 143, \Delta m_1 = 1, \Delta m_2 = 3$
146 ppm	7.7 ppm	6 ppm

inductively coupled plasma ion sources exhibit static mass discrimination effects. Because of the lack of a causal law such static discriminations have been corrected [11,12] by applying the same empirical laws as used for the correction of evaporation induced fractionation. However, there is a fundamental difference in the interpretation of the nature of the fractionation factor. Although the TIMS fractionation factor is a function of time alone with the aim of removing the time dependence of the measured ratios, the functional dependence of the fractionation factor for inductively coupled plasma mass spectrometry (ICP-MS) is unknown. But it has, nevertheless, been assumed to be constant and it is measured by using (a minimum of) two known isotope ratios. As for all such external calibrations, a classical system calibration needs to be performed before such measurements can be seriously compared with TIMS results. In a system calibration it is experimentally shown by carefully measuring a set of known isotope ratios (which cover a range of values of at least 100:1) that the empirical fractionation factor does not depend on the isotope ratio itself. It should be noted that no system calibration has hitherto been done with an accuracy of better than 100 ppm, mainly because of the lack of suitable isotope ratio standards.

Also in TIMS, the effect of dynamic mass discrimination (arising during evaporation) on the true ratio is overlain by many (albeit smaller) static discrimination effects that arise during the ionization process, in the ion optical system, or in the ion collector system. Static effects can be quantitatively described by applying multiplicative factors to the isotope ratio r_{ij} , resulting in a “measured isotope ratio”

$$r_{ij}^{\text{meas}} = \left(\prod_{k=1}^{k=n} \sigma_k \right) r_{ij}$$

Each $\sigma_k = 1 \pm \delta_k$ ($\delta_k \ll 1$) represents one of the static effects. The effects may depend on mass or may represent a constant bias for the isotope ratio. For instance, if the probabilities of ionization [see Eq. (8)] are different for two isotopes, this gives rise to such a

multiplicative factor. Mass-dependent discriminations can be assumed as being approximately proportional to mass differences: $\sigma_k^s = 1 + s_k \cdot \Delta m_k$. Three types of static discriminations deserve special consideration: (1) mass discriminations in both radial and axial directions arising during transit through beam stops or apertures (used to define the geometry of the beam and to prevent the ions from hitting the walls of the vacuum system). Although the sizes of such effects are virtually impossible to measure accurately, a semiquantitative assessment can be obtained by simply modifying the geometric beam parameters [13]. (2) Discriminations during dynamic multiple collector data acquisition caused by any slope on the peak flats, with the corresponding off-cup-center offset being proportional to the (nonzero) slope of the peak top. Because it is not possible to measure peak top flatness to better than ± 30 ppm, a quantitative assessment of this effect is possible only within these limits. (3) Recording channel related biases in multiple collector experiments. Accurate ion collection in a Faraday cup is by no means a trivial task. The impact of the accelerated (usually 10 kV) ions on the cup surfaces inevitably leads to the release of charged particles. If some of these particles escape from the cup, the efficiency ϵ of the cup will not be exactly 100%, as required. If this happens in one cup, it is very improbable that a second cup (for the simultaneous recording of a second ion beam) will show exactly the same offset. Also, the measuring resistors R of the dc current amplifiers have a different value for each cup. The *measured* ratios r_{ij}^{meas} of two ion beams, simultaneously recorded in a multiple Faraday cup ion collector system, are, hence, biased by so-called channel gain ratios $\gamma_{ij}^{\text{gain}}$.

$$r_{ij}^{\text{meas}} = \frac{\epsilon_i \cdot R_i}{\epsilon_j \cdot R_j} \cdot \frac{i_i}{i_j} = \gamma_{ij}^{\text{gain}} \cdot \frac{i_i}{i_j} = \gamma_{ij}^{\text{gain}} \cdot r_{ij} \quad (25)$$

In practice, a method to measure the (combined) gain ratio $\gamma_{ij}^{\text{gain}}$ to better than about 30 ppm is not known [14,15], although the resistor ratio alone may be measured more accurately [16]. Last but not least,

baseline offsets for single and multiple collector measurements are not negligible sources of error.

8. Multiple ion collection

The exponential law normalisation formula for the evaluation of a triple collector static measurement, including discriminations, is [see Eq. (20) and Fig. 4]

$$S_1 = \frac{\sigma_2^x \gamma_2^x}{\sigma_1 \gamma_1} \cdot r_1^{\text{meas}} \left(\frac{S_2}{r_2^{\text{meas}}} \right)^x \quad x = \frac{\ln(\beta_1^{\text{obs}})}{\ln(\beta_2^{\text{obs}})} \quad (26)$$

S_1, S_2 being the unknown or the known (or agreed on) isotope ratios, respectively.

Static mass-dependent discriminations (σ_i) not related to evaporation and recording channel related offsets (γ_i) are separately noted. Mass-dependent discriminations can be assumed to be approximately proportional to the mass differences Δm of the ion beams: $\sigma_i = 1 + s \cdot \Delta m_i (s \ll 1)$. For example, for $m_1 = 86$ (^{86}Sr), $\Delta m_1 = 1$ (^{87}Sr), $\Delta m_2 = 2$ (^{88}Sr), $s = 0.01$, and $x \approx 0.5$, we get $\sigma_2^x/\sigma_1 \approx 0.999951$. Such discriminations are practically canceled out for small values of s . This is not the case for the channel related factors γ_i , because they are not related by any “law.” Hence, the accuracy of a static multiple collector experiment cannot be better than the accuracy of knowing the channel gain ratios.

To overcome such limitations, dynamic multiple collector data acquisition schemes have been introduced. If all interested ratios can be measured as a combination of ion current ratios with equal mass difference, these pairs of ion beams are then sequentially measured in one and the same pair of collectors (which may show a gain ratio factor of γ). Fig. 7a shows the simplest case of such a scheme, which can be applied for measuring $^{86/87/88}\text{Sr}$. The corresponding normalisation equations get the following form by replacing $r_2 = r_1 \cdot r_3$:

$$S_1 = \frac{\sigma_3^x}{\sigma_1} \cdot \gamma^{2x-1} \cdot B \cdot (r_1^{\text{meas}})^{1-x} \cdot \left(\frac{S_2}{r_3^{\text{meas}}} \right)^x \quad (27)$$

with

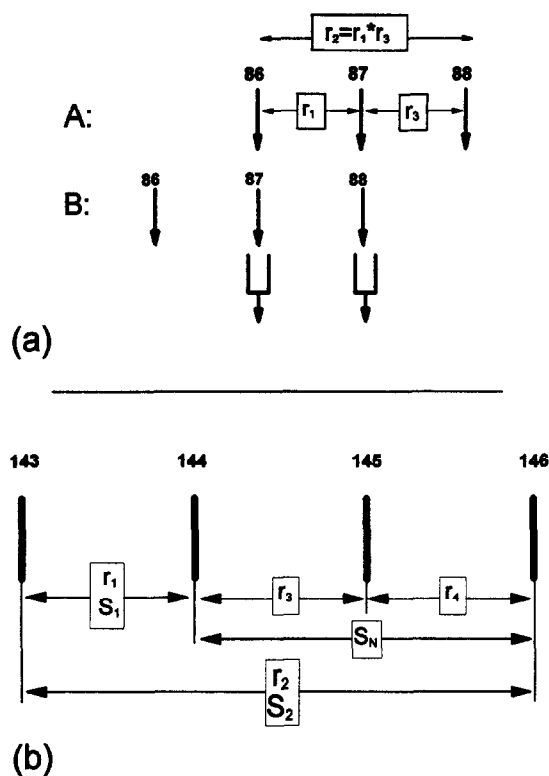


Fig. 7. Data acquisition scheme for (a) “dual collector dual jump” experiments for Sr and (b) “dual collector triple jump” experiments for Nd.

$$B = 1 \text{ and } x = \frac{\ln(\beta_1^{\text{obs}})}{\ln(\beta_2^{\text{obs}})}$$

for the exponential law, and

$$B = \frac{(\beta_2^{\text{obs}})^x}{\beta_1^{\text{obs}}} \quad \text{and} \quad x = \frac{\beta_2^{\text{obs}}}{\beta_1^{\text{obs}}} \cdot \frac{(\beta_1^{\text{obs}} - 1)}{(\beta_2^{\text{obs}} - 1)}$$

for the Rayleigh law.

The deviation λ of the channel gain ratio ($\gamma = 1 \pm \lambda$) from unity is reduced by a factor of ≈ 175 resp. ≈ 125 for the exponential or Rayleigh law. Other static mass discrimination effects are practically cancelled as well (for equal mass differences they are practically identical anyway). With the linearized Rayleigh law formula, channel gain ratio offsets are reduced by a factor of ≈ 500 .

Note that during the dynamic measurement of the ratios (Fig. 7), a sufficiently accurate assessment for

the gain ratio γ can be obtained, using, for instance, the ion current of ^{87}Sr , which is measured in both channels. Therefore, a separate measurement of the resistor ratio is not necessary.

Setting $x = 0.5$ in the above exponential correction formula results in the formula for the power law normalization, which is the well known classic correction equation for this class of data acquisition methods, in which the gain ratio discrimination is completely canceled:

$$S_1 = \frac{\sqrt{\sigma_3}}{\sigma_1} \cdot \sqrt{\frac{S_2 \cdot r_1^{\text{meas}}}{r_3^{\text{meas}}}} \quad (28)$$

Although the power law does not sufficiently compensate for fractionation effects [8], it is still widely used in commercial software packages for dynamic dual collector measurements.

Similar formulae can easily be developed for other jumping schemes, e.g. for the triple jumping scheme for Nd. With the nomenclature in Fig. 7(b) and replacing $r_2 = r_1 \cdot r_3 \cdot r_4$ resp. $S_2 = S_1 \cdot S_N$ (to secure common lower masses), the exponential law normalization formula for Nd is

$$S_1 = \frac{(\sigma_3 \cdot \sigma_4)^{x(1-x)}}{\sigma_1} f^{(3x-1)/(1-x)} \cdot \left(\frac{S_N}{r_3^{\text{meas}} \cdot r_4^{\text{meas}}} \right)^{x(1-x)}$$

$$x = \frac{\ln(\beta_1^{\text{obs}})}{\ln(\beta_2^{\text{obs}})} \quad (29)$$

Because of the formal identity of the basic mathematical equations, the above equation may replace a more complicated formula, recently published [12] for the correction of ICP-MS results. We do, however, not claim that mass discriminations in ICP-MS are correctly described by an exponential law.

9. Conclusions

Fractionated (i.e. time-dependent) isotope ratio data can be accurately normalized by the fractionation laws only if these laws include free parameters, to describe the details of the real evaporation process and to reflect some instrumental artifacts that adulter-

ate the measured isotope ratios. Unfortunately, most, if not all, of these free parameters cannot in practice be individually identified and they are neither directly accessible by simple ion current ratio measurement nor available in the literature. This gives ample room for speculation, e.g. for the assessment of a sufficiently precise value for β^{obs} and K , if ultra high reproducibility is required. Their mere existence and the question, how precisely their relative size can be assessed for any particular experiment, sets a limit (that is completely independent from the achieved precision of the actually measured ion current ratio data) for all attempts to identify the most appropriate fractionation model and for the computation of the true isotope ratio.

For light elements like Ca (evaporating as CaO or CaF/CaF₂), the current analytical precision easily allows detection of nonideal evaporation behaviour [5,8,9], but the current state of the art of sample loading cannot prevent nonideal or unstable evaporation behavior. The use of one set of parameters to characterize the entire run is in most cases unrealistic. In such cases, the preference for any one of the β -containing fractionation models is arbitrary or even speculative and, because of the existence of offsets between the laws, the error bars on the true isotope ratio will be (much) worse than would be expected from the precision of the measured data.

For heavy elements (e.g. Sr, Nd), or for light elements loaded as a much heavier compound (e.g. as Ca₂ [9]), the currently routinely achievable analytical precision (15–20 ppm) is in the same order of magnitude as the errors arising from the inability to parameterize the “correct” details of the evaporation process (Fig. 8 [17]). This statement is also true for static discrimination effects, which start to be important at an analytical precision level of <20 ppm. Therefore, the question of whether the causal Rayleigh law or one of the β -containing empirical fractionation models is more appropriate seems to be moot. Nevertheless, a few experiments for Nd have been described [13,18] that exhibit a sufficiently stable evaporation process, allowing an external precision of 4–6 ppm.

Generally, to routinely achieve high accuracy data

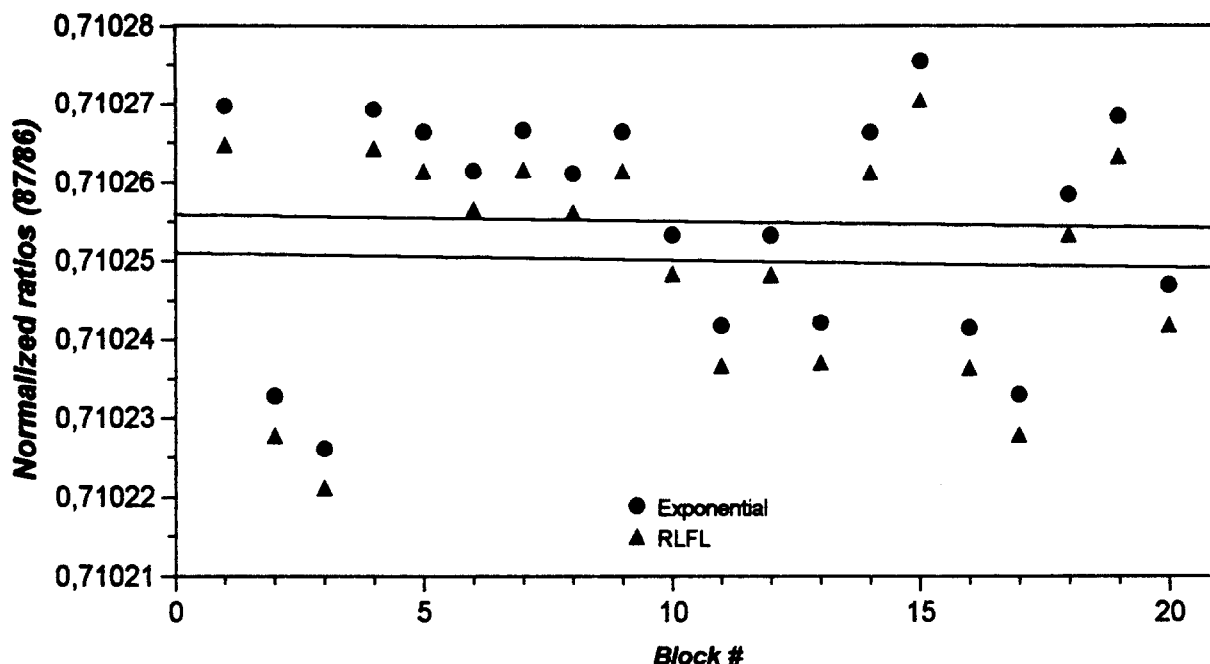


Fig. 8. High precision data ($\sigma_{n-1} < 15$ ppm), obtained from a “dual collector dual jump” experiment (Strontium), using a single filament ion source. Block means of 20 blocks, 10 ratios each, are plotted vs. time (block #), normalized using (a) the Rayleigh law (excess mass $\mu = 40$, caused, e.g. by a mixing coefficient of $K \approx 0.7$ or by the coevaporation of a heavier Sr compound) and (b) the exponential law (excess mass $\mu = 0$) to demonstrate the Rayleigh/exponential dilemma. The distance of the correction lines is 7 ppm, as expected, and their average slope is < 0.1 ppm/block.

(<15 ppm) on heavier elements, it will be necessary to improve the stability and reproducibility of the evaporation process and to stabilize or eliminate all static discriminations, especially those from recording channel bias (for static multiple collector measurements). Otherwise, the appropriate fractionation law cannot be identified and higher analytical precision will not result in higher accuracy.

By comparing all measured “true” ratios of samples with the “true” ratio of an agreed on standard sample, treated and measured identically to the samples, this situation is reduced to the challenge of keeping (at least all identified) free parameters as constant as possible during one run *and* between the regular standard measurements. Moreover, detailed reporting of all relevant procedures is a prerequisite for interlaboratory comparisons of published sets of data.

All β -containing fractionation models extended by

free parameters can be used to assess the basic error limits for fractionation correction and, very importantly, they are of great help for designing optimized measuring procedures and improved instrumentation. The identification of fundamental differences between the empirical laws and the causal, strictly evaporation related Rayleigh fractionation law for TIMS should serve as a cautionary note on the current use of empirical correction methods for high precision data obtained on multiple collector ICP-MS.

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