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Pb and Sr isotope measurements by inductively coupled plasma–mass spectrometer: efficient time management for precision improvement

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Abstract

One of the factors limiting the precision of inductively coupled plasma mass spectrometry is the counting statistics, which depend upon acquisition time and ion fluxes. In the present study, the precision of the isotopic measurements of Pb and Sr is examined. The time of measurement is optimally shared for each isotope, using a mathematical simulation, to provide the lowest theoretical analytical error. Different algorithms of mass bias correction are also taken into account and evaluated in term of improvement of overall precision. Several experiments allow a comparison of real conditions with theory. The present method significantly improves the precision, regardless of the instrument used. However, this benefit is more important for equipment which originally yields a precision close to that predicted by counting statistics. Additionally, the procedure is flexible enough to be easily adapted to other problems, such as isotopic dilution.

Keywords: Inductively coupled plasma mass spectrometry; Lead isotope ratios; Strontium isotope ratios; Time optimisation; Precision improvement

Nomenclature

I_i	abundance of isotope *i*
n_i	number of ions of isotope *i* reaching the multiplier, in ions
t_{tot}	total acquisition time (s)
P_i	percentage of integration time spent for isotope *i* (%)
f_i	ion flow rate of the isotope *i* (ions s^{-1})
(I_i/I_j)	unknown isotopic ratio
$(I_i/I_j)^{\mathrm{Std}}$	known isotopic ratio (constant or certified)
a	mass discrimination coefficient per atom mass unit (a.m.u.)
Δm	mass unit discrepancy
σ_u	standard deviation of the variable *u*
r.s.d.$_u$	relative standard deviation of *u*
RSD$_u$%	relative standard deviation of *u* (%)
r.s.e.$_u$	relative standard error
τ	dead time (ns)

1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) was the subject of considerable improvement during the last decade thanks to the progress of electronics and use of well designed materials. A deep knowledge of the equipment has allowed researchers to better understand, identify and characterize most of the sources of noise and, as a consequence, some solutions were proposed to efficiently reduce them [1–4]. Such reductions of non-random noise made it possible for several workers to report a high precision of isotopic measurements with within-run relative standard deviations (RSD%) of about 0.1%, at least for ratios close to unity. When optimal instrumentation conditions are applied, counting statistics can be considered as one of the essential parameters limiting overall precision. As an example, experiments undertaken

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with $^{132}Xe/^{129}Xe$, $^{107}Ag/^{109}Ag$ and $^{206}Pb/^{207}Pb$ ratios showed that the best precision attainable was between 1 and 3 times higher than that predicted by counting statistics [5,6].

Counting statistics can be improved by the use of more concentrated analyte, extending the time spent on each isotope and increasing the number of repetitive measurements (these options are not mutually exclusive). However, these options may not be appropriate for the following reasons: (1) a highly concentrated solution is not suitable because, firstly, the ability of the multiplier to record ion flows is generally limited to about 2×10^6 ions s^{-1}. At this rate, the multiplier lifetime is considerably reduced and severe troubles due to memory effects are possible. Secondly, dead time correction cannot be precisely performed due to the occurrence of pulse pile-up phenomena [7–9]. (2) Increasing total acquisition time, by changing the number of repeats or the time spent on each isotope, is invariably expensive and time-consuming and reduces the major advantages of ICP-MS over the laborious but more precise TIMS method. Additionally, it is debatable that increasing time, systematically, implies a real improvement of precision, because of a possible poor long-term stability of the ICP-MS response arising from nebulisation and vaporisation processes or from mass bias drift [9]. In the case of isotopic ratios, this problem is less important because of the rationing operation. As a matter of fact, each isotope should be approximately equally affected by long-term variations, and thus the ratios should remain constant. Unfortunately, such an ideal case is not quite met because of two main reasons: (i) all measurements constituting a sweep are not perfectly simultaneous, and (ii) mass bias drift can lead to a shift of the nominal centre of the isotope peak. Thus, the ratios may slowly evolve through time, resulting in a loss of within-run reproducibility, and making a precise mass bias correction difficult. Actually, this last point is not definitely clear and contradictory results are frequently reported. For example, Ting and Janghorbani [10] have observed that isotopic ratios remain constant over long-term measurements for any element despite large variations of ion-beam intensities, but Begley and Sharp [9] have suggested an instability of the mass scale calibration, leading to significant variations of Pb ratios through time.

Another, easier, method is available to improve the level of precision of isotopic measurements by choosing optimal division of available time, especially for elements composed of isotopes having very different abundances. Commonly, the simplest analytical procedure is to spend the same integration time on each isotope using peak jump mode. Equal integration times are obviously beneficial, in terms of precision, to the ratios, including the most abundant isotopes, whereas the others are at a disadvantage. Most software allows the division of the available time into unequal parts, in order to compensate for discrepancies of abundance. A previous study on factorial optimisation of data acquisition factors for Pb isotope determinations has clearly shown that the most relevant factor was the timing [11]. These workers simply fixed the problem by assigning 15 times more time to ^{204}Pb (which represents only 1.4% of total Pb) than for the other isotopes. Other approximate solutions have been previously proposed for Pb by choosing integration times inversely proportional to their abundance [12]. As will be seen, these proposals are suitable, but they probably do not perfectly correspond to the optimal choice. Additionally, when mass bias correction may be operated via an internal stable ratio, as for Sr, the problem is to find out the ideal proportion of time dedicated to each isotope in order to provide the best analytical precision. In this paper, these two examples are discussed. We also verify that the choices of timing, derived from mathematical considerations, are reasonable, from a practical point of view.

2. Instrumentation

The equipment used in this study is a quadrupole-based ICP-MS type, POEMS, supplied by Thermo Jarrell Ash Co, USA. The ICP-MS is installed in a clean room under a controlled temperature (20 ± 0.5°C). The primary vacuum pumps are located outside the ICP-MS room in order to reduce their vibrational influences. Ions present in the argon plasma enter in the MS spectrometer via a nickel sampler and skimmer cones. High purity grade (> 99.998%) Ar was used. A peristaltic pump, allowing a variable sample flow rate control by the main

Table 1
Operating conditions

ICP conditions	
Auxiliary gas	1.5 l min^{-1}
Nebuliser gas	0.64 to 0.69 l min^{-1}
RF power	1350 W
Nebuliser type	Concentric Meinhard
Spray chamber	Scott chamber
Pump rate	~0.8 ml min^{-1}
Mass spectrometer	
Resolution	87 for Pb and 86 for Sr
Measurement mode	Peak jumping
Points/peak	3 (0 and ± 0.005 amu)
Acquisition time	42 s of measurement for Pb and 90 s for Sr
Dwell time	variable (see text)
Replicate	10

The most common operating parameters are given between parentheses.

software, was used for sample introduction. The flow rate was maintained at about 0.8 ml min^{-1}. The main operating conditions are reported in Table 1 and more details about the rationale for their choice will be given elsewhere (Monna et al. in prep.). All preparations were made in a clean laboratory (class 1000, US Federal norm). Deionised water was produced by a Milli-Q system from Millipore Corp., USA, with resistivity better than 18 MΩ cm. Nitric acid was a suprapure grade, provided by MERCK, Germany. Lead and strontium certified solutions were obtained from the National Bureau of Standards, newly NIST (NBS 981: $^{206}\text{Pb}/^{204}\text{Pb} = 16.937 \pm 0.009$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.492 \pm 0.008$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.722 \pm 0.019$, and NBS 987 : $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.710248 \pm 0.000026$).

3. Theoretical basis

As for radiochemical analysis, the precision of ICP-MS measurements is drastically limited by the integrated number of detected events. Commonly, precision given by Poisson distribution is expressed in terms of standard deviation, σ, as:

$$\sigma_i = \sqrt{n_i} = \sqrt{f_i \cdot P_i \cdot t_{\text{tot}}} \tag{1}$$

or in terms of relative standard deviation:

$$\text{r.s.d.}_i = \frac{\sqrt{n_i}}{n_i} = \frac{1}{\sqrt{f_i \cdot P_i \cdot t_{\text{tot}}}} \tag{2}$$

On the other hand, if a variable, u, is calculated from several independent variables: $u = f(x,y,x,\ldots)$, then the error propagation law allows the calculation of the standard deviation of u by:

$$\sigma_u^2 = \left(\frac{\partial u}{\partial x}\right)^2 \cdot \sigma_x^2 + \left(\frac{\partial u}{\partial y}\right)^2 \cdot \sigma_y^2 + \left(\frac{\partial u}{\partial z}\right)^2 \cdot \sigma_z^2 \ldots \tag{3}$$

From Eq. (1) to Eq. (3), the relative standard deviation of the ratio I_i/I_j is obtained by:

$$\text{r.s.d.}_{(I_i/I_j)_{\text{mes}}} = \sqrt{\text{r.s.d.}_{I_i}^2 + \text{r.s.d.}_{I_j}^2} = \sqrt{\frac{1}{t_{\text{tot}}}} \cdot \sqrt{\frac{1}{f_i \cdot P_i} + \frac{1}{f_j \cdot P_j}} \tag{4}$$

If N repeats are operated and averaged, the r.s.d. of the resulting mean, so-called relative standard error (r.s.e.) is defined by:

$$\text{r.s.e.}_{(Ii/Ij)} = \text{r.s.d.}_{(Ii/Ij)}/\sqrt{N} \tag{5}$$

So far, the precision of the mean may be given at the 95% confidence interval. This confidence range is defined by $\pm\, t_{0.025;N-1} \times \text{r.s.e.}_{(Ii/Ij)}$, with $t_{0.025;N-1}$ given by t-distribution statistics tables.

4. Results and discussion

4.1. Dead time determination

Dead time has a well-known effect on the pulse height measurements, especially at a high ion rate. It systematically leads to the loss of signal with increasing concentration [13]. Physically, it corresponds to a short time, after the arrival of an ion to the multiplier, where the system is blind to any other ion. A correction is possible using a probabilistic law, which is true if the ion rate is much less than $1/\tau$[14]:

$$f_{i\ \text{cor}} \approx f_{i\ \text{meas}}/(1 - f_{i\ \text{meas}} \cdot \tau) \tag{6}$$

where $f_{i\ \text{cor}}$ is the corrected value, $f_{i\ \text{meas}}$ is measured and τ is the dead time, expressed in nanoseconds. Usually, this parameter is determined using isotopic ratio measurements for which the difference of

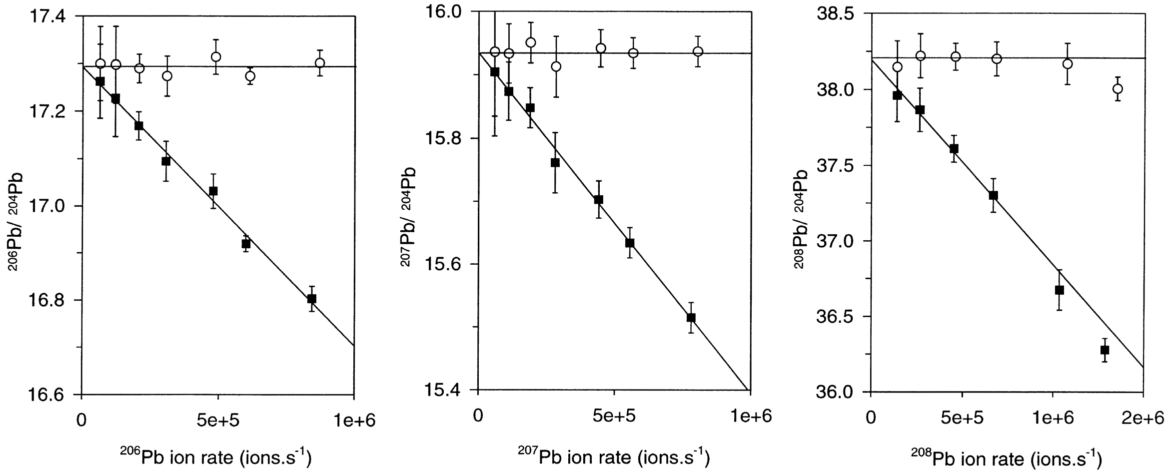

Fig. 1. Dead time. Evolution of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb versus concentration. (■) measured ratios, (○) corrected ratios using $\tau = 36.27$ ns.

abundance between each pair of isotopes is large enough.

As shown in Fig. 1, increasing concentration causes a linear decrease of the ^{206,207,208}Pb/^{204}Pb ratios. The trends are linear up to an ion rate of the numerator isotope of about 7×10^5 ions s^{-1}. After this value, the measured ratios are lower than expected by the linear trend. This phenomenon, the so-called pulse pile-up, is well known and was explained as a loss of gain at high count rate due to the inability of the multiplier's dynode string to supply enough current to maintain constant dynode voltage drops [9,14]. Considering only the linear range (0–7×10^5 ions s^{-1}), the dead time is calculated at 36.20 ns ($r^2 = 0.992$), using the ^{206}Pb/^{204}Pb ratios, at 36.21 ns ($r^2 = 0.993$), with ^{207}Pb/^{204}Pb, and at 36.41 ns ($r^2 = 0.996$), with ^{208}Pb/^{204}Pb, with a mean of 36.27 ± 0.29 ns (95% confidence level). This value is comparable to those previously reported: 32.5 ns [9], 44 ns [15] or 70 ns [14]. In this study, we have taken care to only analyse solutions producing ion flows always less than 7×10^5 ions s^{-1}, to obtain accurate and precise dead time correction.

4.2. Pb isotopes

4.2.1. Interest and background

Pb has by four stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. In the upper Earth's crust they have approximately the following abundances: ^{204}Pb = 1.4%, ^{206}Pb = 24.1%, ^{207}Pb = 22.1%, ^{208}Pb = 52.4%, which characterizes a 'common' lead. Among them, only the ^{204}Pb is not radiogenic, the others being produced by the radioactive decay of U or Th. Pb isotopic compositions have a great interest for the geosciences. They allow the characterization and identification of various sources of Pb in natural systems, and hence make possible a reliable description of complex mixing. For simplicity of calculation, ratios are usually expressed with ^{204}Pb as the denominator. In environmental sciences, ratios can also be expressed using ^{204}Pb isotope, but due to the analytical constraint of ^{204}Pb measurement, most environmental scientists use the couple ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios, although some important information can be hidden by their sole utilisation [16]. Therefore, the determination of ^{208,207,206}Pb/^{204}Pb ratios, even approximately, is often very informative.

4.2.2. Simulation

With our equipment, it has been previously observed that a precise dead time correction of 36.2 ns is generally efficient up to an ion flow of 7×10^5 ion s^{-1}; beyond this value systematic, but hardly predictable, losses occur, due to pulse pile-up. This can be considered as the first constraint. The second constraint is given by the total integration time for each repeat. In order to limit the total acquisition time to about 10 min, one analysis is composed of

10 repeats of 42 s each, variably divided by four, for each Pb isotope. Actually, after each jump a short settling time (generally a few milliseconds) is required for a complete stabilisation of the MS. Extra time for one repeat is about 20 s, and total time spent for a repeat is about 60 s. At that point, a few other assumptions must be made: errors related to background, blank, mass bias and dead time corrections are considered as negligible, and there is neither isobaric interference nor oxide formation at *m*/*z*, corresponding to Pb.

Considering the Poisson statistic only (RSD_p%), the expected precision of each ratio has been computed from the above parameters using Eq. (4), using a home-made QBasic program. It was decided to devote the same acquisition time for both ^{206}Pb and ^{207}Pb isotopes because their abundances are similar ($^{206}Pb/^{207}Pb$ ratios generally vary from 1.04 to 1.20 for a ‘common Pb’). The simulated precision of each ratio is reported by a colour code on ternary diagrams for easier visual representation [Fig. 2(a)–(f)]. The poles of these diagrams represent the proportion of time spent on ^{204}Pb, ^{208}Pb and the sum $^{206}Pb+^{207}Pb$.

In Fig. 2(a) and (b), the gradient representing the evolution of precision mainly follows the ^{204}Pb axis. That testifies that precision of $^{206,207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios essentially depend on the time spent on the less abundant ^{204}Pb isotope. The average precision of these three ratios is reported in Fig. 1(c). An optimal position (closed circle) corresponds approximately to the following timings: 73% for ^{204}Pb, 10% for each of ^{206}Pb and ^{207}Pb and 7% for ^{208}Pb. The Fig. 2(d)–(f) illustrate the precision of ratios used in environmental applications: $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, and their averages, respectively. Obviously, the precision of the $^{206}Pb/^{207}Pb$ ratios only evolve with the ‘$^{206}Pb+^{207}Pb$’ axis, due to the construction of the diagram itself. The error is lowest when the whole time is dedicated to them. Similarly, the precision of $^{208}Pb/^{206}Pb$ ratios is better when no time is dedicated to the ^{204}Pb measurement. Fig. 2(f) allows the definition of another optimal position where about 40% of time is used for each of ^{206}Pb and ^{207}Pb, while 20% is devoted to the ^{208}Pb isotope. At that point, it is crucial to note that changing initial conditions (concentration and total time of measurement), will modify the colours which reflect the degree of precision, but will change neither the shape of the gradients, nor the optimal timing positions. Basically, these positions should indicate the ideal timings for environmental applications (best $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios), and for studies having a more geological approach (best $^{206,207,208}Pb/^{204}Pb$ ratios). Nevertheless, as it has already been indicated, it is interesting to check the ratios, including the ^{204}Pb isotope, even for environmental applications. Hence, the point is to find a timing that allows the achievement of a good precision for the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios, whereas $^{206,207,208}Pb/^{204}Pb$ are also well enough constrained, and to ascertain that such optimizations have a practical significance.

4.2.3. Experiments

A set of experiments was conducted with a Pb solution giving 5.3×10^5 ions s^{-1} of ^{208}Pb and taking 10 repeats of 42 s each. The time was distributed from strictly equal times [Fig. 3(a)], to times inversely proportional to abundance [Fig. 3(d)], with two intermediate positions [Fig. 3(b)–(c)]. Four consecutive analyses were done for each timing. When using inversely proportional timing [Fig. 3(d)], the recorded number of ions is the same for each isotope and, as a result, the within-run RDS_p% is the same for each ratio (about 0.20%). Such values are systematically higher than those predicted by the distribution, ‘c’. Indeed, a close examination of the Fig. 2(c) and (f) indicates an overall degradation of precision when moving from the ‘c’ to the ‘d’ position. Even if the discrepancies are not flagrant, the experimental within-run relative standard deviation (RSD_{exp}%) seems to follow the same tendency. If time is divided into equal parts [Fig. 3(a)], the RSD_p% of both $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios are about 0.07%–0.09%, while those including the ^{204}Pb are typically at 0.26%. However, moving from ‘a’ to ‘b’ is beneficial to the ratios, including the ^{204}Pb isotope, since their RSD_p% decreases to about 0.2%, while the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios are not significantly changed. These findings about timing are all the more important, in that within-run RSD_{exp}% closely follows the expected RSD_p%. This suggests that analytical precision is mainly controlled by counting statistics, at least on our system.

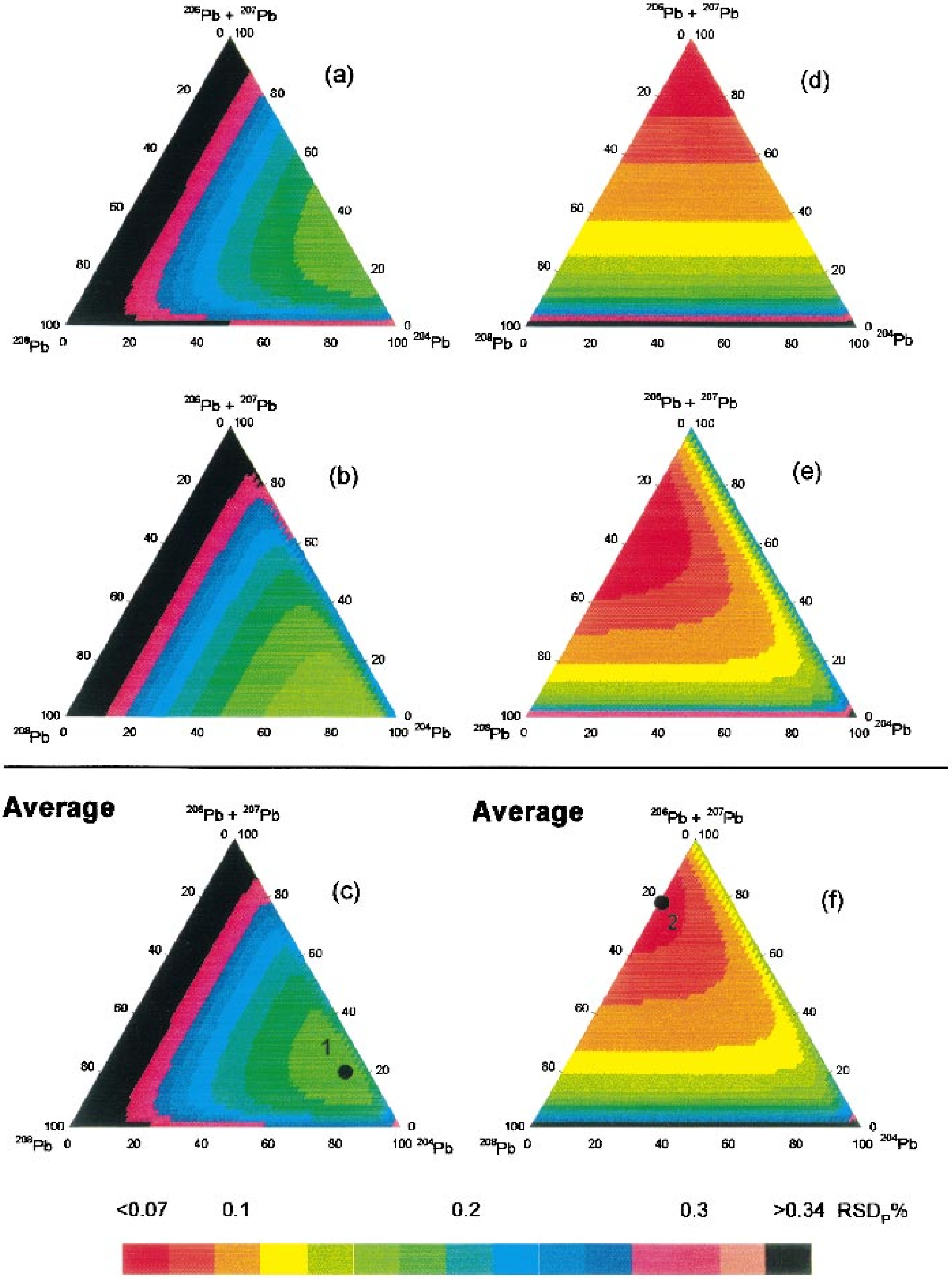

Fig. 2. Theoretical RSD$_p$% of Pb isotopic ratios considering $f_{208Pb} = 6 \times 10^5$ ions s^{-1} and $t_{tot} = 60$ s: (a) ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb, (b) ^{208}Pb/^{204}Pb, (c) average RSD$_p$% of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb, (d) ^{206}Pb/^{207}Pb, (e) ^{208}Pb/^{206}Pb, and (f) average RSD$_p$% of ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb. (●): optimal positions.

Hence, timings ‘a’ and ‘d’ can be definitely abandoned. In the environmental studies, the distribution ‘b’ seems the best. It suitably optimizes the precision of the $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ and $^{208}\mathrm{Pb}/^{206}\mathrm{Pb}$ ratios, which are the most widely used as indicators of Pb pollution, and it keeps a good control on the other ratios. For more geological applications, one would retain the distribution ‘c’, because it should theoretically provide the best precision on the ratios including the $^{204}\mathrm{Pb}$.

In addition to precision, analyses also need accuracy. Corrections for interference and mass bias can consume additional acquisition time and may modify the ideal timings mentioned above. Analytically, Pb isotopic measurements by ICP-MS in nitric 1% v/v solution are not adversely affected by the occurrence of undesirable oxides, but isobaric interference of $^{204}\mathrm{Hg}$ (6.85% of total Hg) can occur at $m/z = 204$. This interference may be corrected using $^{202}\mathrm{Hg}$. In our opinion, it is highly recommended for routine procedures to operate a pre-concentration and purification of Pb on ionic resins [17] to get rid of Hg interference, and hence saving analysis time. This also enables the adjustment of the analyte concentration as close as possible to the maximum acceptable value, without any problem of matrix effect through time. Mass bias correction has also to be performed. As Pb does not present naturally constant ratio, mass bias is generally assessed either by using repetitive measurements of standard solutions or by adding Tl. The latter method makes possible correction via a stable internal $^{203}\mathrm{Tl}/^{205}\mathrm{Tl}$ ratio [9,18,19]. Several algorithms of mass bias correction are generally used, based upon linear (Eq. (7)), power (Eq. (8)) or exponential (Eq. (9)) relationships:

$$(I_i/I_j)_{\mathrm{corr}} = (I_i/I_j)_{\mathrm{meas}} \cdot (1 + \Delta m \cdot a) \tag{7}$$

$$(I_i/I_j)_{\mathrm{corr}} = (I_i/I_j)_{\mathrm{meas}} \cdot (1 + a)^{\Delta m} \tag{8}$$

$$(I_i/I_j)_{\mathrm{corr}} = (I_i/I_j)_{\mathrm{meas}} \cdot \exp(\Delta m \cdot a) \tag{9}$$

The application of one of these laws means that a same mass discrimination per mass unit (factor a) must be calculated whatever the couple of isotopes considered.

The factor a, representing the mass discrimination per mass unit, may vary following the operational settings. However for a given setting, this factor should be the same on the whole Pb mass range, and should allow correction of all Pb ratios, whatever the pair of isotopes considered (only the Δm factor will change). This, mathematically, means that the analysis reported in an isotopic diagram (i.e. $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$ versus $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$) should fall on a straight line. So, in an ideal case, analysis reported in a classical mass bias diagram should lie on a line defined from these equations [20]. 62 repetitive measurements of an NBS 981 solution are plotted on $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$ versus $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$, $^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$ versus $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$ and $^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$ versus $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$ diagrams [Fig. 4(a)–(c)]. They never fall on the predicted discrimination lines, which suggests the inability of our ICP-MS to conform to the above theory. Actually, different mass bias factors — a — are calculated for each isotopic pair. For this reason, a mass bias correction by internal addition of Tl was suspected of being inappropriate, at least on our equipment, because the mass discrimination factor calculated from the measured $^{203}\mathrm{Tl}/^{205}\mathrm{Tl}$ ratio will not be applicable to every Pb/Pb ratio. As a result, a correction that does not strictly imply a relationship between each isotopic couple was preferred. To the best of our knowledge, no ‘definitive’ method exists, but one of the most common is to measure a solution of NBS 981, every 4 or 5 unknown samples and to correct these from the deviation observed on standards [11,12,21,22]. If a slight variation occurs between two consecutive standards, a linear interpolation can be readily applied. Corrections are individually operated for each ratio via a multiplier factor $\alpha_{I1/I2}$ defined by Eqs. (10) and (11):

$$\left(\frac{I_i}{I_j}\right)_{\mathrm{corr}} = \left(\frac{I_i}{I_j}\right)_{\mathrm{meas}} . \alpha_{I_i/I_j} \tag{10}$$

$$\text{with } \alpha_{I_i/I_j} = \left(\frac{I_i}{I_j}\right)^{\mathrm{Std}} \Big/ \left(\frac{I_i}{I_j}\right)^{\mathrm{Std}}_{\mathrm{meas}} \tag{11}$$

Repetitive analysis of NBS 981 over nearly 16 h clearly indicates a good stability of our instrument for isotopic measurements (Fig. 5, circles), despite a concomitant large ion beam fluctuations of almost 15%. Starting from this set of data, every fifth measurement is used to compute the correction (by Eqs. (10) and (11)), which is then applied to

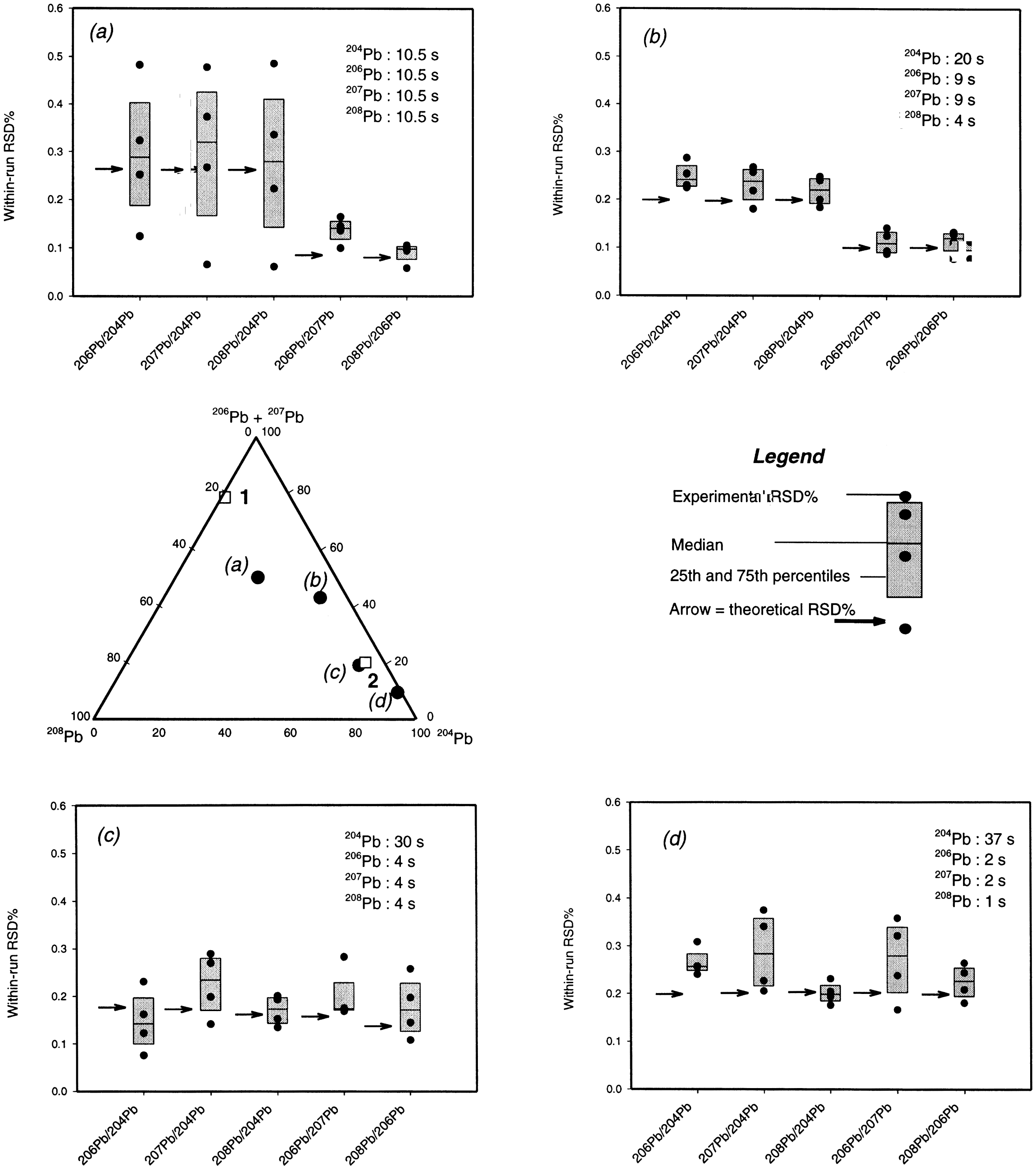

Fig. 3. Experimental within-run $\mathrm{RSD}_{\mathrm{exp}}$% using different timings. Operating conditions: $f_{208\mathrm{Pb}}$ (5.3×10^5 ions s^{-1} and $t_{\mathrm{tot}} = 42$ s: (a) strictly equal time, 25%, 25%, 25%, 25%, (b) 47.6%, 21.4%, 21.4%, 9.6%, (c) 71.5%, 9.5%, 9.5%, 9.5%, and (d) 88%, 4.8%, 4.8%, 2.4% for $P_{204\mathrm{Pb}}$, $P_{206\mathrm{Pb}}$, $P_{207\mathrm{Pb}}$ and $P_{208\mathrm{Pb}}$, respectively. Median of $\mathrm{RSD}_{\mathrm{exp}}$%, 25th and 75th percentiles as vertical boxes. Black arrows represent the predicted $\mathrm{RSD}_{\mathrm{p}}$%. (□) theoretical optimal timings.

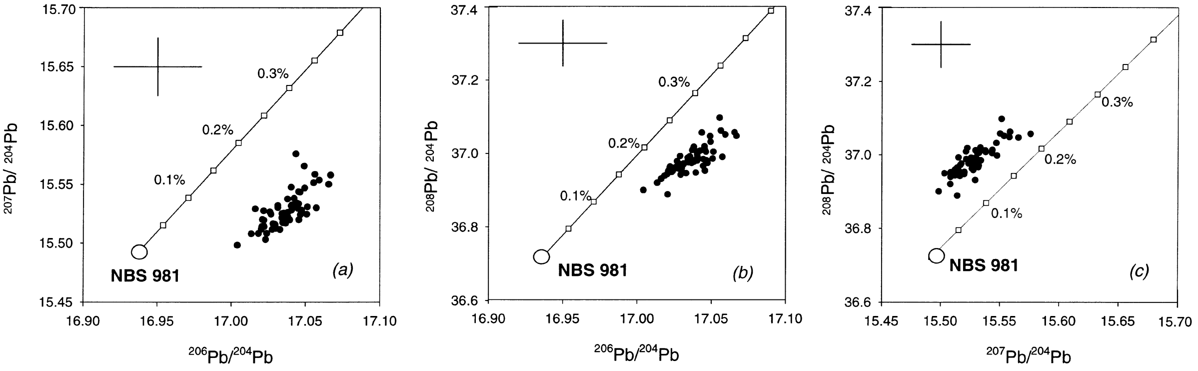

Fig. 4. NBS 981 analysis reported in mass bias diagrams: (a) ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb, (b) ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb, and (c) ^{208}Pb/^{204}Pb versus ^{207}Pb/^{204}Pb. Theoretical mass bias, calculated by linear model (see text), is represented by the line, and graduations correspond to mass discrimination per mass unit (in %). Error bars are given at 95% confidence level.

the four intermediate measurements. After such external correction, the results are very close to the certified values (Fig. 5, filled boxes, Table 2). This strongly suggests that using an external standard every fifth samples is sufficient to adequately correct for short term mass bias variability. Nonetheless, this correction induces a fall of precision, coming from the analytical error, related to external standards determination. The standard deviation of corrected samples is approximately:

$$\text{r.s.d.}_{(I_i/I_j)_{\text{corr}}} \approx \sqrt{\text{r.s.d.}^2_{(I_i/I_j)_{\text{meas}}} + \text{r.s.d.}^2_{(I_i/I_j)^{\text{Std}}_{\text{meas}}}} \qquad (12)$$

If both the unknown samples and standards have the

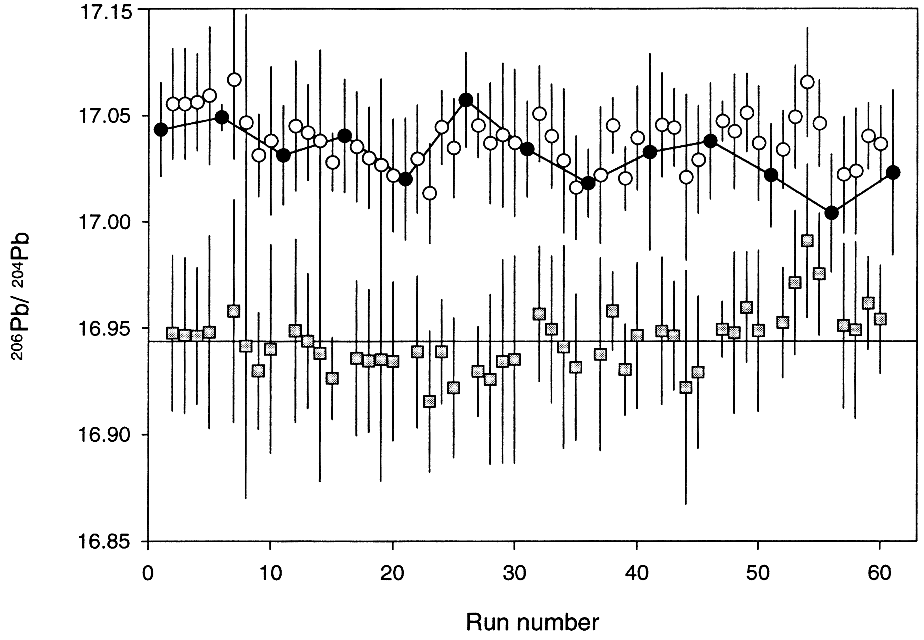

Fig. 5. Repetitive ^{206}Pb/^{204}Pb measurements of NBS 981 over 16 hours (circles); in black, data used for external correction. Filled boxes, after operating external mass bias correction. Certified value, ^{206}Pb/^{204}Pb = 16.937 ± 0.009. Errors bars are given at 95% confidence level.

same concentration and are measured using the same timing, then their errors are comparable and one obtains:

$$\text{r.s.d.}_{(I_i/I_j)_{\text{corr}}} \approx \sqrt{2}\cdot\text{r.s.d.}_{(I_i/I_j)_{\text{meas}}} \tag{13}$$

Thus, the external mass bias correction results in a precision decrease on each ratio of about $\sqrt{2}$, independently of timing.

On natural samples, a procedure including Pb separation on ionic resin and external mass bias correction, via repetitive measurements of NBS 981, was found very reliable in all cases and allows the saving of precious analytical time that would have been devoted to Hg and/or Tl. Ideal timings determined above can be extensively used for precise and accurate routine analysis of Pb isotopes with any ICP-MS instrument.

4.3. Sr isotopic chemistry

4.3.1. Interest and background

Sr has four stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr with mean abundances of 0.56%, 9.86%, 7.00% and 82.58%, respectively. Among these isotopes, only the ^{87}Sr is radiogenic and is produced by the radioactive decay of ^{87}Rb : $^{87}\text{Rb} = {}^{87}\text{Sr} + \beta^-$ (half-life = 4.88 × 10^{10} years). Commonly, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is used by geochemists to monitor the variations of abundance of the ^{87}Sr isotope. Generally, Sr isotopic composition is measured with a thermal-ionisation mass spectrometer (TIMS), because of its high precision ($\text{RSD}_{\text{exp}}\% = 0.002\%$). However, in certain conditions, ICP-MS can constitute an alternative [23,24]. For example, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were used to investigate the origin of sediments from the Atlantic ocean. In that case, the utilisation of ICP-MS was possible because of the large spread of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.703 to 0.743 [23].

4.3.2. Simulation

Sr has a constant isotopic ratio: $^{88}\text{Sr}/^{86}\text{Sr} = 8.3752$, which usually serves to precisely correct (from mass bias) the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Although we did not use Eqs. (7)–(9) for Pb, they may be investigated for Sr isotopes. From Eq. (3), and considering the power, exponential and linear algorithms the resulting r.s.d. is deduced. Both power and exponential models give:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{corr}} = \frac{f_{^{87}\text{Sr}}}{f_{^{86}\text{Sr}}}\cdot\sqrt{\frac{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{\text{Std}}}{\frac{f_{^{88}\text{Sr}}}{f_{^{86}\text{Sr}}}}} \tag{14}$$

and

$$\text{r.s.d.}_{(^{87}\text{Sr}/^{86}\text{Sr})_{\text{corr}}}$$

$$= \sqrt{\frac{1}{t_{\text{tot}}}}\cdot\sqrt{\frac{1}{f_{^{87}\text{Sr}}\cdot P_{^{87}\text{Sr}}} + \frac{1}{4\cdot f_{^{88}\text{Sr}}\cdot P_{^{88}\text{Sr}}} + \frac{1}{4\cdot f_{^{88}\text{Sr}}\cdot P_{^{88}\text{Sr}}}}$$

$$= \sqrt{\text{r.s.d.}^2_{^{87}\text{Sr}} + \tfrac{1}{4}\cdot\text{r.s.d.}^2_{^{88}\text{Sr}} + \tfrac{1}{4}\cdot\text{r.s.d.}^2_{^{86}\text{Sr}}} \tag{15}$$

The linear model is expressed as:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{corr}} = \frac{f_{^{87}\text{Sr}}}{f_{^{86}\text{Sr}}}\cdot\frac{1}{2}\cdot\left(1 + \frac{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{\text{Std}}}{\frac{f_{^{88}\text{Sr}}}{f_{^{86}\text{Sr}}}}\right) \tag{16}$$

This gives the following r.s.d.:

$$\text{r.s.d.}_{(^{87}\text{Sr}/^{86}\text{Sr})_{\text{corr}}} = \sqrt{\frac{1}{f_{^{87}\text{Sr}}\cdot P_{^{87}\text{Sr}}\cdot t_{\text{tot}}} + \frac{1}{f_{^{86}\text{Sr}}\cdot P_{^{86}\text{Sr}}\cdot t_{\text{tot}}}\cdot\frac{f^2_{^{88}\text{Sr}}}{\left(f_{^{88}\text{Sr}} + \left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{\text{Std}}\cdot f_{^{86}\text{Sr}}\right)^2} + \frac{1}{f_{^{88}\text{Sr}}\cdot P_{^{88}\text{Sr}}\cdot t_{\text{tot}}}\cdot\frac{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{\text{Std}^2}\cdot f^2_{^{86}\text{Sr}}}{\left(f_{^{88}\text{Sr}} + \left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{\text{Std}}\cdot f_{^{86}\text{Sr}}\right)^2}} \tag{17}$$

Table 2
Corrected NBS 981 measurements

NBS 981	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
N	48	48	48	48	48
Mean	**16.944**	**15.495**	**36.738**	**1.0935**	**2.1682**
Max	16.991	15.464	36.858	1.0955	2.1709
Min	16.916	15.535	36.666	1.0917	2.1651
Individual precision*	± 0.036	± 0.029	± 0.075	± 0.0019	± 0.0036
Mean α	0.9944	0.9978	0.9931	0.9966	0.9987
Certified value	16.937	15.492	36.722	1.0937	2.1682

* 95% confidence level.

This later equation can be also approximated by Eq. (15). As a consequence, the three algorithms produce the same precision. As for Pb, the expected $^{87}Sr/^{86}Sr$ within-run RSD$_p$% is readily computed using Eq. (15), by varying the P_{86Sr}, P_{87Sr} and P_{88Sr} parameters. These results are reported in the ternary diagram (Fig. 6), where an ideal timing is calculated at $^{86}Sr \approx 27\%$, $^{87}Sr \approx 64\%$ and $^{88}Sr \approx 9\%$. The theoretical precision produced by such a timing can now be compared with the procedure which would consist of only the measurement of the $^{87}Sr/^{86}Sr$ ratios (without any time devoted to the ^{88}Sr isotope).

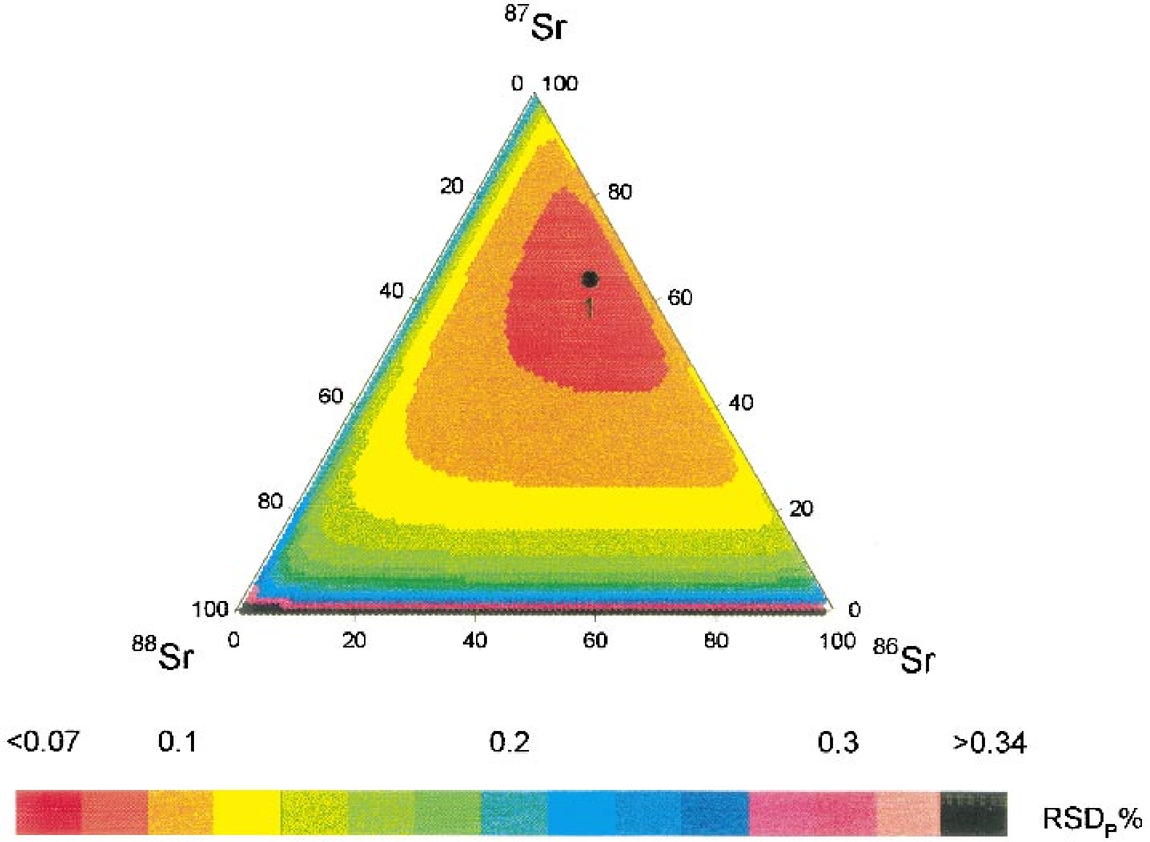

Fig. 6. Theoretical RSD$_p$% of $^{87}Sr/^{86}Sr$ ratio after internal stable ratio correction, considering $f_{88Sr} = 6 \times 10^5$ ions s^{-1}, $t_{tot} = 90$ s. (●) optimal position.

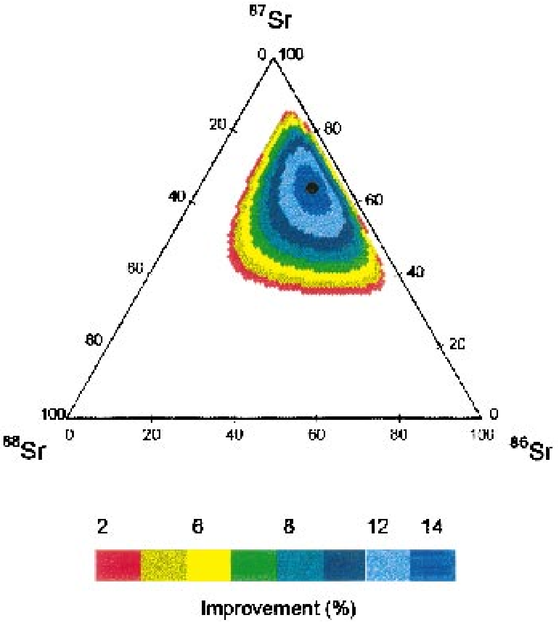

Fig. 7. Theoretical discrepency of ^{87}Sr/^{86}Sr ratio precision, using internal correction or not (with the same total analytical time). Coloured areas are at the advantage of internal correction via ^{88}Sr/^{86}Sr ratio; the improvement (expressed in percent) is represented by a colour code.

A simulation has been computed for both methods, taking 90 s of total integration time and 6×10^5 ions s^{-1} of ^{88}Sr. Using Eq. (4), the best time sharing, considering only the two isotopes, is 46% and 54% for ^{87}Sr and ^{86}Sr, respectively, and the expected RSD_P% of ^{87}Sr/^{86}Sr ratio is 0.086%. This value can be compared to the internal correction method using various timings. It appears (Fig. 7) that the utilisation of the ^{88}Sr/^{86}Sr internal correction can provide better (coloured area) or worst (white zone) precision, depending on the timing. However, the maximum precision is obtained using internal correction with the ideal timing determined above. The improvement is almost 15% in comparison with the other method. Actually, internal correction does act, not only as a possible way of mass bias correction, but also as a way to reduce the uncertainty related to the ^{86}Sr isotope determination. Indeed, if a variation of the ^{86}Sr signal affects the ^{87}Sr/^{86}Sr ratio, this drift is more or less compensated for by the concurrent correction of the ^{88}Sr/^{86}Sr ratio, where the ^{86}Sr isotope also appears in the denominator. This is advantageous, in spite of the consumption of analytical time, for the ^{88}Sr isotope.

4.3.3. Experiments

Five different time distributions were used to examine the significance of these calculations with respect to real conditions (Fig. 8). Rapid examination shows that RSD_exp% is always better after simultaneous internal correction than without, as theory predicts it. Although the three timings, ‘a’, ‘d’ and ‘e’ produce comparable precision, because they fall in a rather stable domain (see Fig. 6), the position, ‘e’ seems to be the best. This is not surprising, because this distribution is the closest to the ideal timing. The timing, ‘c’, devotes the shortest time of analysis to the ^{87}Sr isotope, and consequently it is the least precise. Eq. (15) shows that the error related to the ^{87}Sr isotope has the largest influence on the overall precision. Finally, timing ‘b’ gives intermediate results. Our analysis of pure Sr solution closely follows the theory since within-run RSD_exp% differs typically by less than a factor of 1.5 from that predicted by counting statistics.

Nonetheless, analysis of natural samples may be complicated by the appearance of isobaric interferences and doubly-charged species formations on masses belonging to Sr isotopes. The most important are encountered at $m/z = 86$: Kr and Yb^{2+} and at $m/z = 87$: Yb^{2+}, Lu^{2+} and Rb. Separation on chromatographic columns totally eliminates the problems related to rare earth elements, but sometimes the resin does not completely eliminate Rb (Rb = ^{85}Rb and ^{87}Rb). A method including the measurement at $m/z = 85$, 86 and 87 in both Rb and Sr aliquots was alternatively proposed; more details can be found in [23]. However, such a technique necessitates two different determinations for each sample, which consumes analytical time and effort. It is probably more efficient to increase the step of Rb purification [25] to be totally free of Rb interference and to use the timing as defined above. The interference related to the presence of Kr in Ar is easily solved by taking high purity grade gas and by operating blank correction. In the present study, it was observed that the blank signal at $m/z = 86$ (^{86}Kr represents 17.3% of total Kr) was always less than 100 ions s^{-1} with a background taken at $m/z = 89$ at about 20 ions s^{-1}.

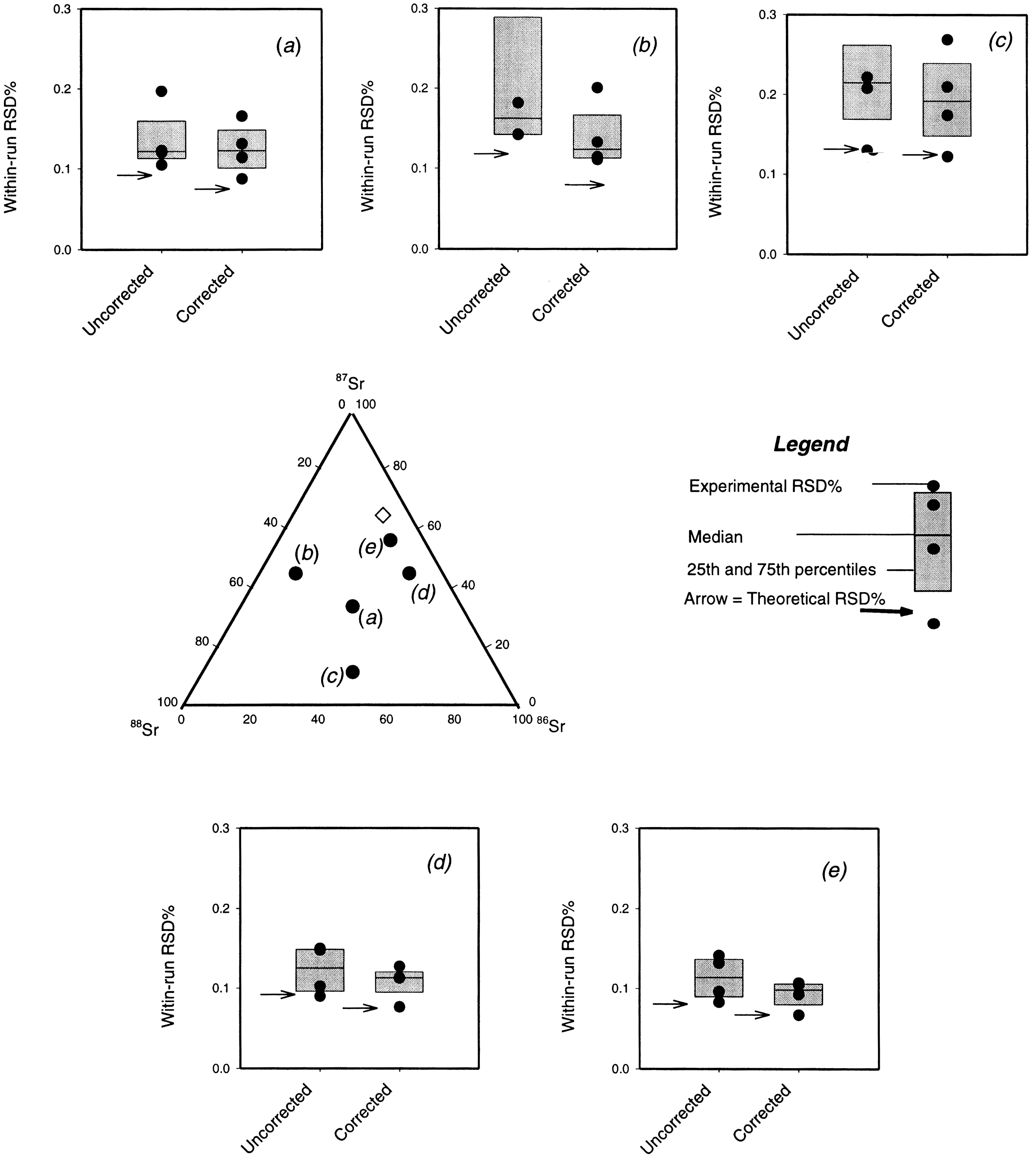

Fig. 8. Experimental within-run RSD% using different timings. Operating conditions $f_{88Sr} \approx 6 \times 10^5$ ions s^{-1} and $t_{tot} = 90$ s: (a) strictly equal time, 33.3%, 33.3%, 33.3%, (b) 11.1%, 44.4%, 44.4%, (c) 44.4%, 11.1%, 44.4%, (d) 44.4%, 44.4%, 11.1%, and (e) 33%, 56%, 11% for P_{86Sr}, P_{87Sr} and P_{88Sr}, respectively. Median of RSD$_{exp}$%, 25th and 75th percentile as vertical boxes. Black arrows represent the predicted RSD$_p$%. (♦): ideal timing.

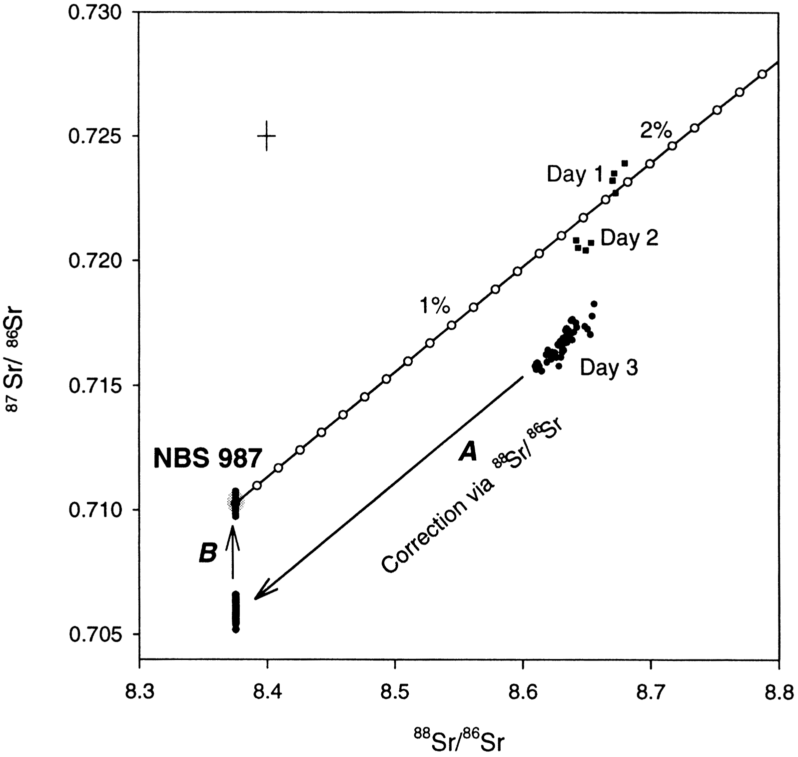

Fig. 9. Three sets of NBS 987 measurements (black points) reported in mass bias diagram. Theoretical mass bias calculated by linear model (see text) is the line, and the graduations correspond to mass discrimination per mass unit (in %). Arrow A: internal correction via $^{88}Sr/^{86}Sr$ ratio, arrow B: complementary external correction. Error bars are given at 95% confidence level.

The efficiency of the internal correction to solve the systematic mass drift was checked from three sets of NBS 987 measurements on three separate days (Fig. 9). The results of analysis made on days 1 and 2 are close to the mass discrimination line, and further correction via external standard (as it was done for Pb) may appear redundant. However, fifty repetitive NBS 987 measurements carried out on day 3 do not fall on the line, suggesting different degrees of mass bias for both $^{88}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios. Indeed, at least with our ICP-MS, the agreement with the theoretical laws describing the mass bias (Eq. (7)-9) appears erratic. In that case, correction by internal $^{88}Sr/^{86}Sr$ ratio alone (noted A on Fig. 9) may not be sufficient, and external correction seems to be necessary (noted B on Fig. 9). As before, every fifth solution is taken as a standard, the others being considered unknowns. Fig. 10(a) shows that there was a slight drift of the $^{88}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios through time. However, internal correction by $^{88}Sr/^{86}Sr$ ratio straightens this trend [box symbols on Fig. 10(b)], and external correction, as defined by Eqs. (10) and (11), provides an acceptable accuracy, despite a fall of precision of $\sqrt{2}$ (Table 3).

Table 3
Corrected NBS 987 measurements

NBS 987	$^{87}Sr/^{86}Sr$
N	49
Mean	**0.71025**
Max	0.71075
Min	0.70972
Individual precision*	± 0.00070
Certified value	0.710248

* 95% confidence level.

To conclude on Sr isotopic measurements, when the optimal timing is applied, a preliminary correction of $^{87}Sr/^{86}Sr$ ratios by $^{88}Sr/^{86}Sr$ is always beneficial to the precision. In a general manner, several NBS 987 standards must be regularly inserted in the set of

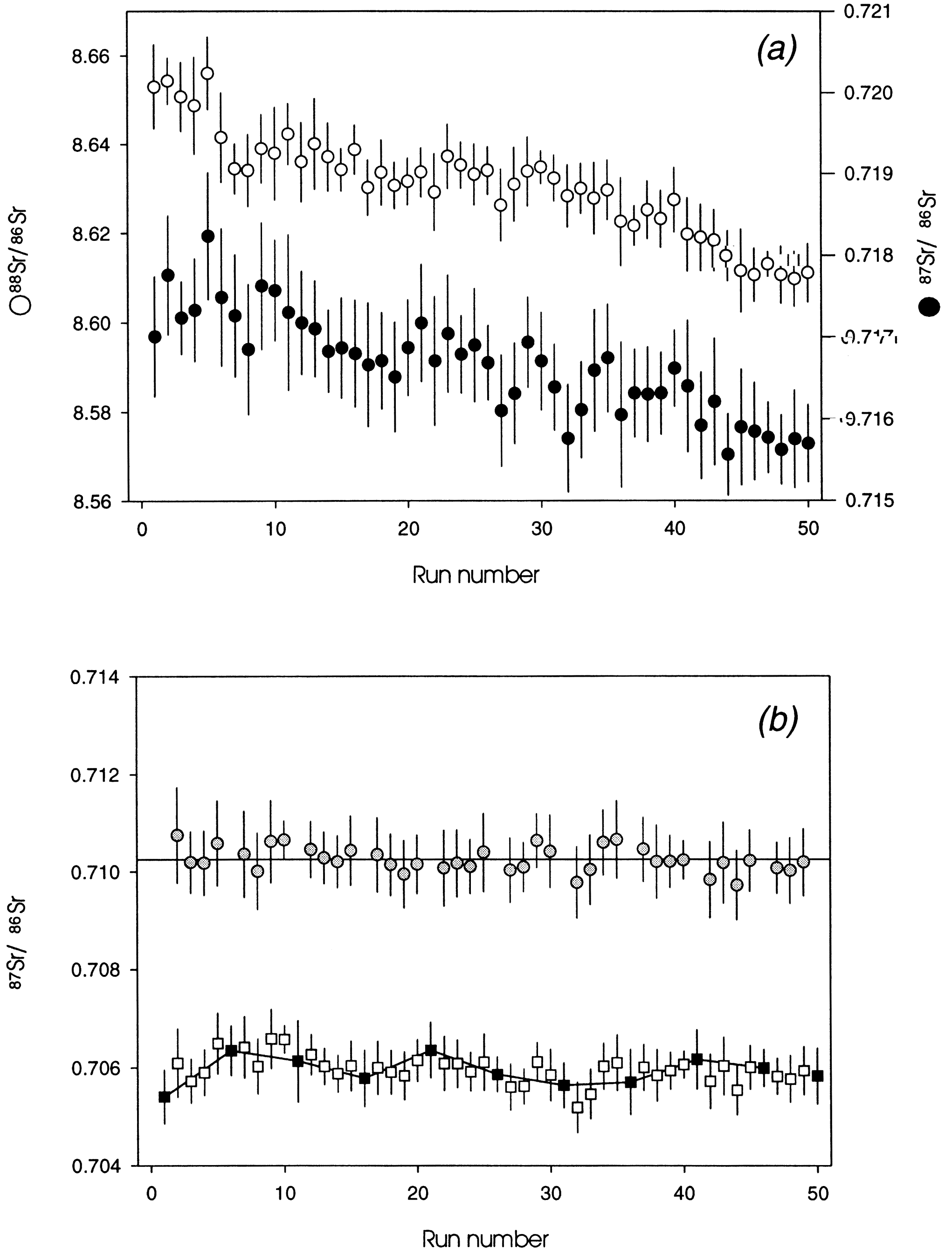

Fig. 10. (a) Repetitive $^{88}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ measurements of NBS 987 (circles) and (b) $^{87}Sr/^{86}Sr$ ratios after a two-step correction procedure. The first step corresponds to the boxes where the $^{87}Sr/^{86}Sr$ ratios are corrected by $^{88}Sr/^{86}Sr$ ratios. The black boxes are the data used for further external correction. The gray circles correspond to the final results after external correction. Certified value: $^{87}Sr/^{86}Sr = 0.710248$. Errors bars are given at 95% confidence level.

unknown samples. If, after internal correction, they give the true value, then only internal correction has to be used on unknown samples. If the internal correction is not fully efficient, then a further correction factor ($\alpha_{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}}$) is calculated from each standard and directly applied to unknown samples. In the latter case, the error must be re-evaluated by multiplying by $\sqrt{2}$. We can reasonably expect an analytical precision of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio at about $\pm 7 \times 10^{-4}$ at 95% confidence level, for 10 repeats of 90 s and an ion flow on $^{88}\mathrm{Sr}$ of about 7×10^{5} ions s^{-1}. Such a precision allows the advantageous use of the ICP-MS as a rapid means of isotopic Sr measurement when the range of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios is greater than 10^{-2}. It should also be noticed that mass bias per atom mass unit is much more important for Sr than for Pb (1.4%–1.7% for Sr and 0.1%–0.4% for Pb). Such an observation is in agreement with the findings of other workers [13], and was explained as space-charge effects and repulsion between positively charged ions after the skimmer, which mostly affects the light ions.

5. Summary and conclusion

This study confirms that the timing factor is a very relevant parameter on the precision of the determination of isotopic ratios by ICP-MS. In a general manner, experimental precision closely follows what is predicted by the counting statistics alone, and as a consequence, efforts must be made to improve this factor. For Pb, timing has been optimized in order to produce the best precision in two different cases: (i) when the ratios which include the $^{204}\mathrm{Pb}$ isotope are preferred, and (ii) when the Pb isotopic ratios are used for environmental purposes. Theory and practical applications show that the solutions which were proposed in the past to reduce the influence of the abundance discrepaencies, such as using timings inversely proportional to the abundance, do not correspond to an optimal choice. For Sr, it was noticed that with optimal timing, a preliminary correction of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios by stable $^{88}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios significantly improved the precision, as compared with the sole measurement of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio. The best way of operating the mass bias correction is much more debatable. Indeed, it probably depends on the equipment used and seems to differ from day to day. A solution has to be chosen empirically. In all cases, although it requires additional effort, a preliminary purification by ionic resins is desirable, to get rid of most interferences. This consequently saves precious acquisition time that would have to have been used to correct them. We believe that the timings proposed here can be advantageously applied on any system. In the worst case, it would not produce a degradation of precision. It is unlikely that quadrupole-based ICP-MS will soon replace the use of TIMS in geological applications. However it could constitute a convenient alternative in situations where a wide range of Pb or Sr ratios are observed, or possibly be used to quickly select interesting samples for more precise TIMS measurements.

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