

Noise identification and sampling frequency determination for precise Pb isotopic measurements by quadrupole-based Inductively Coupled Plasma Mass Spectrometry

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Abstract. Analytical precision of the isotope ratios measured by quadrupole-based ICP-MS is drastically controlled by the low-frequency noises which originate from nebulisation and vaporisation processes, and from sample introduction systems. The undesirable influence of these latter can be however reduced by choosing efficiently the operating parameters. In the present study, the choice of the stabilisation time necessary in peak jump mode, and the one of the number of sweeps are discussed in the light of noise power spectra obtained with various speeds of the peristaltic pump used as sample introduction system. Obviously, the settings proposed are probably efficient only on our own ICP-MS, but they can be determined without any difficulty on any other equipment, only by following the methodology detailed here. With such guidelines, experimental within-run RSD % were observed following closely those predicted by the counting statistics (~ 110 %). The isotopic measurements of natural samples (overbank sediments, airborne particulate matter, lichens and rainwater) exhibited fair accuracy and good reproducibility, making highly convenient the use of the ICP-MS, at least in an environmental purpose.

Keywords. Inductively coupled plasma mass spectrometry – lead isotope ratios – instrumental parameters – optimisation – noise – quality control.

Introduction

The precision of isotopic ratios measurements by quadrupole-based ICP-MS is known as ultimately limited by the counting statistics. Starting from the observations done by Quételet *et al.* [1] about the importance of the time management, we have previously investigated how, for a given acquisition time, the within-run relative standard deviation (RSD %) of the isotopic ratios could be reduced [2]. We proposed to divide optimally the available time in order to compensate the differences of abundance of the isotopes used in ratioing. This work gave clues for reducing the theoretical random error on the basis of the best time sharing, but did not investigate the operating parameters which must be taken into account to approach this theoretical precision limit. Many sources of noises, identified by power analysis of noise, have also an ominous influence on the precision, the detection limits, and the dynamic range. They may originate from the sample introduction system, the main power or from other parts of the instrument [3-11]. However, their amplitude can be directly reduced. For instance, the audiofrequency peaks associated with instability at the boundary of the plasma with surrounding atmosphere, may

be removed by using an adapted torch arrangement, while the white noise is efficiently reduced when the spray chamber is cooled [10]. Another complementary alternative consists to optimise the acquisition parameters for minimising their influence on the precision. It was found out that rapid sweeps act as a substitute of simultaneous measurements, as that can be done with multi-collector system [9]. As a matter of fact, it can be mathematically demonstrated that all the noises occurring at period more than twice that of the sampling frequency (that means the time elapsed between the start of the measurement of the first isotope and the end the last one) are reduced by ratioing the isotopes.

In the present study, we attempt to give some guidelines to obtain a precision on isotopic ratios close to that predicted by counting statistics. Investigations were undertaken to determine the most efficient sampling frequency, (i) by reducing the stabilisation time necessary to ensure the stability of the quadrupole after each jump, and (ii) by increasing the sweeps. Noise power spectra, established with various peristaltic pump speeds, were also examined to minimise as much as possible the amplitude of low-frequency, discrete, and white noises.

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Experimental part

Reagents

Deionised water was produced by a Milli-Q-system presenting conductivity always better than $18 \text{ M}\Omega\cdot\text{cm}^{-1}$. Suprapure nitric acid was supplied by Merck, Germany. NBS 981 isotopic standard Pb solution was obtained from the National Bureau of Standards (newly NIST, USA). Chemical preparation and dilutions were all achieved in a clean lab (class 100-1000).

Apparatus

The ICP-MS used was a POEMS1 (Thermo Jarrell Ash Co, USA), installed in a clean and thermostatised room. The vacuum pumps were placed outside the ICP-MS room in order to reduce the vibrations in the immediate vicinity of the instrument. The solutions were introduced in a cross-flow nebulizer *via* a 8 rollers peristaltic pump (Ismatec, especially designed for the POEMS1 instrument) with a software controlling the flow rate. The pressure of the rollers on the tube was fixed following the conventional technique, which consisted to apply just enough strength to disable the free aspiration. The plasma and the MS were lighted-up 1-2 hours before measurements to enable a good stability of the system. The torch was positioned as close as the torch box allowed (only a few millimeters). The instrument was tuned to give enough sensitivity in combination with a low background, a maximum of stability and well-shaped peaks: symmetric, and as flat as the ICPMS allows (Fig. 1, Tab. I). A dead time correction of 36.2 ns was experienced efficient on our instrument up to an ion flow of about $7 \times 10^5 \text{ ions}\cdot\text{s}^{-1}$ [2].

It was previously observed that low resolution may induce a significant overlap from one peak on the next left [12]. As a result, an over-estimation of the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, and a slight under-estimation of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios may occur. Preliminary investigations with a resolution varying from 80 to 90 showed that 86 produces fair sensitivity and acceptable overlap of 0.037 %.

Isotope measurements

The measurements of Pb/Pb ratios were done in peak jump mode (also named “peak hopping” by some constructors). This mode is more precise than plain scanning, in particular because the integration time can be adapted for compensating the isotopic abundance. 42 seconds of total acquisition time were consumed as follows: 20 s, 9 s, 9 s, and 4 s for ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb isotopes respectively. When the control of the less abundant ^{204}Pb isotope was not necessary, or impossible because of the low Pb content, the same timing than above was kept for the three remaining isotopes. Such a time distribution was found as providing the best theoretical precision [2]. Three channels per peak were measured at $0 \pm 0.008 \text{ a.m.u.}$ Various dwell times were investigated by changing the number of sweeps.

Table I. Operating parameters. The most usual settings are given between parenthesis.

<i>ICP conditions</i>	Auxiliary gas	1.5 L.min ⁻¹	
	Nebuliser gas	0.64 L.min ⁻¹	
	RF power	1350 W	
	Nebuliser type	Concentric Meinhard	
	Spray chamber	Scott chamber	
	Pump rate	Variable*: 0.54 to 1.50 mL.min ⁻¹	
<i>Mass spectrometer</i>	Lens settings	L1: -242 to -105 (~ -110 V)	
		L2: -25 to 26 (~ 20 V)	
		L3: -21 to 43 (~ 20 V)	
		L4: -140 to -250 (~ -210 V)	
		L5: -30 to 50 (~ 30 V)	
		L6: -10 to 5 (~ -8 V)	
		L7: -43 to -20 (~ -30 V)	
		L8: -180 to -30 (~ -45 V)	
		Def.: 0 to 10 (~ 0 V)	
		Off.: 4 to 6 (6 V)	
		Coll.: 750 to 1150 (~800 V)	
		Resolution	86
		Measurement mode	Peak jumping
Dwell time/ number of sweeps	Variable*		
Replicate	10		
Points/peak	3		
Total replicate time	22 s or 42 s*		

* see text for details

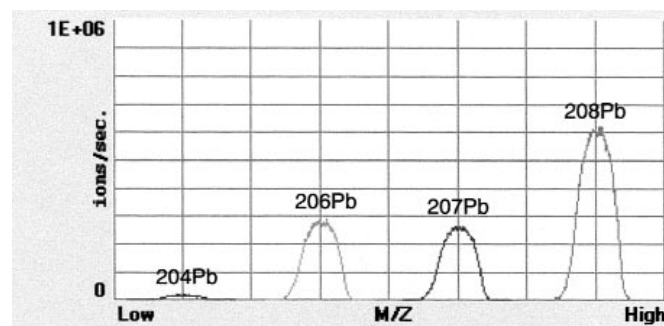


Figure 1. Shape peak requirement for ICP-MS isotopic measurements.

The expected precision (counting statistics alone) was also calculated for a comparative purpose. It was reported in term of within-run RSD % (relative standard deviation) and was determined as follows:

$$\text{r.s.d.}_{(I_i/I_j)_{\text{mes}}} = \sqrt{\text{r.s.d.}_{I_i}^2 + \text{r.s.d.}_{I_j}^2} = \sqrt{\frac{1}{f_i \cdot t_i} + \frac{1}{f_j \cdot t_j}} \quad (1)$$

where $\text{r.s.d.}_{(t_i/I_i)_{\text{mes}}}$ is the relative standard deviation of the ratio I_i/I_j , f_i and t_i are the ion flow and the total integration time of the isotope i respectively.

Noise identification

Noise power spectra (NPS) were computed following approximately the procedure described in Begley and Sharp [9]. They were obtained from the analysis of transient signals of a Pb solution producing about $\sim 2 \times 10^6$ cps at $m/z = 208$. Such a high ion flow cannot be used for isotopic measurements, because at that rate a reliable correction of dead time is no longer possible, but it is quite convenient for noise identification. Data collections were operated at: (i) 20 Hz (512 samples), allowing a resolution of 0.019 Hz, and (ii) at 1000 Hz (4096 samples) giving a resolution of 0.12 Hz. The resulting Nyquist frequency were of 10 Hz and 500 Hz respectively. The signals so obtained were filtered using a low pass filter of 10 Hz and 400 Hz respectively. Fast Fourier Transform (FFT) analysis were computed with the STATISTICA software package using a Hanning window. Noise amplitudes were obtained by calculating the sum of the squares of the real and imaginary components of the transformed data and of the signal average. Amplitude spectra were converted to power spectra using:

$$\text{dB} = 20 * \log (\text{noise amplitude/signal amplitude}) \quad (2)$$

The whole procedure was repeated 12 times at 20 Hz, and 24 times at 1000 Hz. These individual runs were averaged to get a more reliable NPS.

Results and discussion

Stabilisation time

With the peak jump mode, a short time of latency after each jump (T_{stab}) is necessary to ensure a good stability of the quadrupole before acquisition. If four masses are monitored (as for Pb), and N_{sw} sweeps are set, the total time spent for stabilisation TT_{stab} is:

$$TT_{\text{stab}} = 4 \cdot T_{\text{stab}} \cdot N_{\text{sw}} \quad (3)$$

By default, T_{stab} is fixed at 20 ms on the POEMS1 ICP-MS, but can also be diminished up to 10 ms without any problem. This means that 40 ms are systematically spent at each sweep. The use of a high number of sweeps increases the sampling frequency and, in all likelihood, should improve the precision. However, the overall time consumed only for stabilisation grows up proportionally, whereas the one purely dedicated to acquisition remains unchanged. It results that a considerable percentage of analytical time may be wasted only for stabilisation, therefore reducing drastically the speed of analyses. For example, 40 s are lost for stabilisation when the four Pb isotopes are measured during 42 s with 1000 sweeps; that means that about 50 % of the total

analytical time are definitely wasted (Fig. 2). In this case, the elapsed time between the start of the measurement of the first isotope and the end of the last one is 72 ms (42 ms + 3×10 ms), making a sampling frequency of ~ 13.9 Hz. Our purpose is thus to find a good compromise between high precision (generally produced by high sampling frequency) and fair time management, both being somehow mutually exclusive. In addition, it must be insured that a too high sweep frequency does not affect the accuracy of the Pb/Pb ratios.

Choice of a sweep frequency

An experiment has been conducted with an isotopically-known Pb solution in order to examine how the accuracy and the precision of the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios vary with the number of sweeps (*cf.* Tab. II for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, and the legend for the analytical conditions).

The accuracy appears to be affected by the choice of the number of sweeps. Up to 500 sweeps, the measured ratios are close to the expected value, but they progressively shift with the increase of the sampling frequency. High sampling frequencies do not seem to be suitable as they probably result in a loss in the recording of the different isotopes more or less perceptible following the duration of their individual integration.

At 100 sweeps, the within-run RSD % is rather high: ~ 0.8 % (Tab. II), probably because the sampling frequency (2.22 Hz) is almost the same to this issuing from the rollers of the pump (2.13 Hz). As a matter of fact, the fundamental noise (F_n) due to the pump corresponds to the frequency

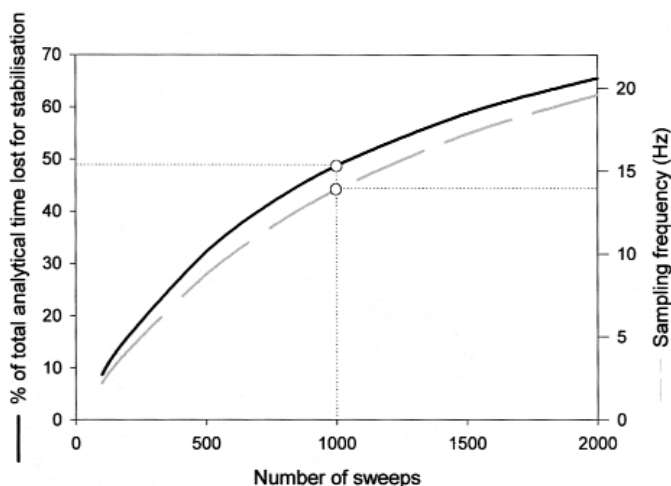


Figure 2. Percentage of total analytical time lost for stabilisation and sampling frequency vs. number of sweeps. The calculation was operated on a basis of 10 ms of stabilisation time, and 42 s of acquisition on the four Pb isotopes per replicate. Pump rotation speed of 16 rpm.

Table II. Accuracy expressed as deviation from the expected value (in %), and within-run precision of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios varying with the number of sweeps.

Number of sweeps	Deviation from the expected value (in %)	Within-run RSD %
100	0.34	0.83
250	-0.16	0.42
500	-0.16	0.30
750	-1.07	0.29
1000	-1.70	0.30

at which each individual roller squeezes the sample introduction tube [7]. It is obtained by:

$$F_n = N \cdot \omega / 60 \quad (4)$$

where N is the number of rollers of the pump (in our case: 8), ω is the rotation speed expressed in revolutions per minute. The experiment has been done at 16 rpm; that means a fundamental noise of 2.13 Hz. From 500 sweeps (making a sampling frequency of 8.77 Hz), the within-run RSD % decreases at about 0.3 %, and is not further improved by setting more sweeps.

To summarise, the use of 10 ms as stabilisation time and 500 sweeps for 42 s of acquisition time appeared to be a good compromise. These settings give an acceptable proportion of analytical time really dedicated to ion counting (67 %) and good accuracy.

Noise identification

Fast Fourier Transforms (FFT) of the transient signal were carried out with various rotation speed of the peristaltic pump: 11.2, 16, 24 and 32 rotations per minute; corresponding to solution uptakes of 0.54, 0.75, 1.15 and 1.50 mL.min⁻¹ respectively (Fig. 3a, left). An additional experiment was also performed using free aspiration (~ 0.8 mL.min⁻¹). Noise power spectra in the 0-10 Hz range (Fig. 3a) are similar to those already reported [5,9]. They can be decomposed into three different distinct components: (i) the white noise, actually the asymptote at the higher end of the frequency axis, (ii) the discrete noises, and (iii) the flicker noise, due to little fluctuation present in low frequency domain, so-called $1/f$. This latter frequency-dependent noise is known as mainly originating from the instabilities during nebulisation, desolvation and vaporisation processes which cause a drift [13]. Discrete noises are observed when the sample uptake was operated by the peristaltic pump. These shift through high frequency at high pump speed: 1.48, 2.11, 3.16 and 4.22 Hz for pump speed of 11.2, 16, 24 and 32 rpm respectively. Such frequencies fit almost perfectly to those expected by eq. 4. Additional discrete noises, corresponding to the harmonics, are also detected at 24 and 32 rpm, but not at 11.2 and 16 rpm. The amplitude of the noises coming from the pump increases

when the pulses become more frequent in opposition to that was previously reported [4]. As expected, no discrete noise is detected when the sample is freely aspirated, but white noise (~ -65 dB) and $1/f$ noise are greater than when sample introduction is mechanically constrained, similarly to that was already reported [7]. At that time the Ar flow alone controls the sample uptake.

In the range 0-400 Hz, discrete noises are pointed out at 50 Hz and sometimes at 100 Hz (only one spectrum is presented on Fig. 3b). These issues from the power supply ripple, and are supposed to originate from the r.f. generator and from the electronic devices. The presence of higher harmonics have been already reported [6,8,9], but they are not perceived here. Another discrete and audible “singing” noise, so-called audiofrequency peak, is often recognised between 200 and 600 Hz, depending on the plasma conditions, and is explained as the interaction of the surrounding air with the hot plasma going out of the torch [5,8,11]. Here its absence may be due to the fact that the torch is placed as close as possible to the aperture, because of a efficient torch design, or simply because it occurs at more than 400 Hz, and is not recorded.

Precision of the Pb/Pb ratios

The highest sensitivities are observed with sample introduction rate of 0.75 mL.min⁻¹ (16 rpm), 0.80 mL.min⁻¹ (free aspiration) and 1.15 mL.min⁻¹ (24 rpm). The use of 0.54 mL.min⁻¹ (11.2 rpm) produces a response about 30 % lower, whereas a decline of more than 10 % is recorded at 1.50 mL.min⁻¹ (32 rpm), likely as a consequence of the cooling down of the plasma. The worst within-run RSD % of the Pb/Pb ratios is observed in this later case (Fig. 3a, right), where the signal is the most unstable as suggested by high white noise (~ -62 dB), large amplitude of discrete noises, and the presence of strong harmonics. The sweep frequency of 8.77 Hz is also probably too close to the first harmonic (8.53 Hz). So, the use of high sample uptake is, in this case, neither beneficial to the signal stability, nor to the counting statistics because of the fall of sensitivity. Relatively high within-run RSD % are also generated by the take of sample at 11.2 rpm, in part because the counting statistics is penalised by a loss of sensitivity. Sample uptakes of 0.75 mL.min⁻¹ (16 rpm) and 1.15 mL.min⁻¹ (24 rpm) produce approximately the same precision: within-run RSD % at about 0.2 % for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, and 0.1 % for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. At 0.75 mL.min⁻¹, less sample is necessary to complete an analysis, the white noise is low (~ -68 dB), and the pump noise comes down at a frequency of 2.11 Hz, making efficient the reduction of its influence by ratioing. All these clues strongly support its use. As mentioned above, high white and $1/f$ noises are observed with free aspiration. In consequence the Pb/Pb ratios suffer of a lack of precision comparatively to the use of the pump in optimal conditions.

All the above tests were carried out with Pb solutions presenting concentrations close to the acceptable upper limit for allowing accurate isotopic measurements. That permitted a

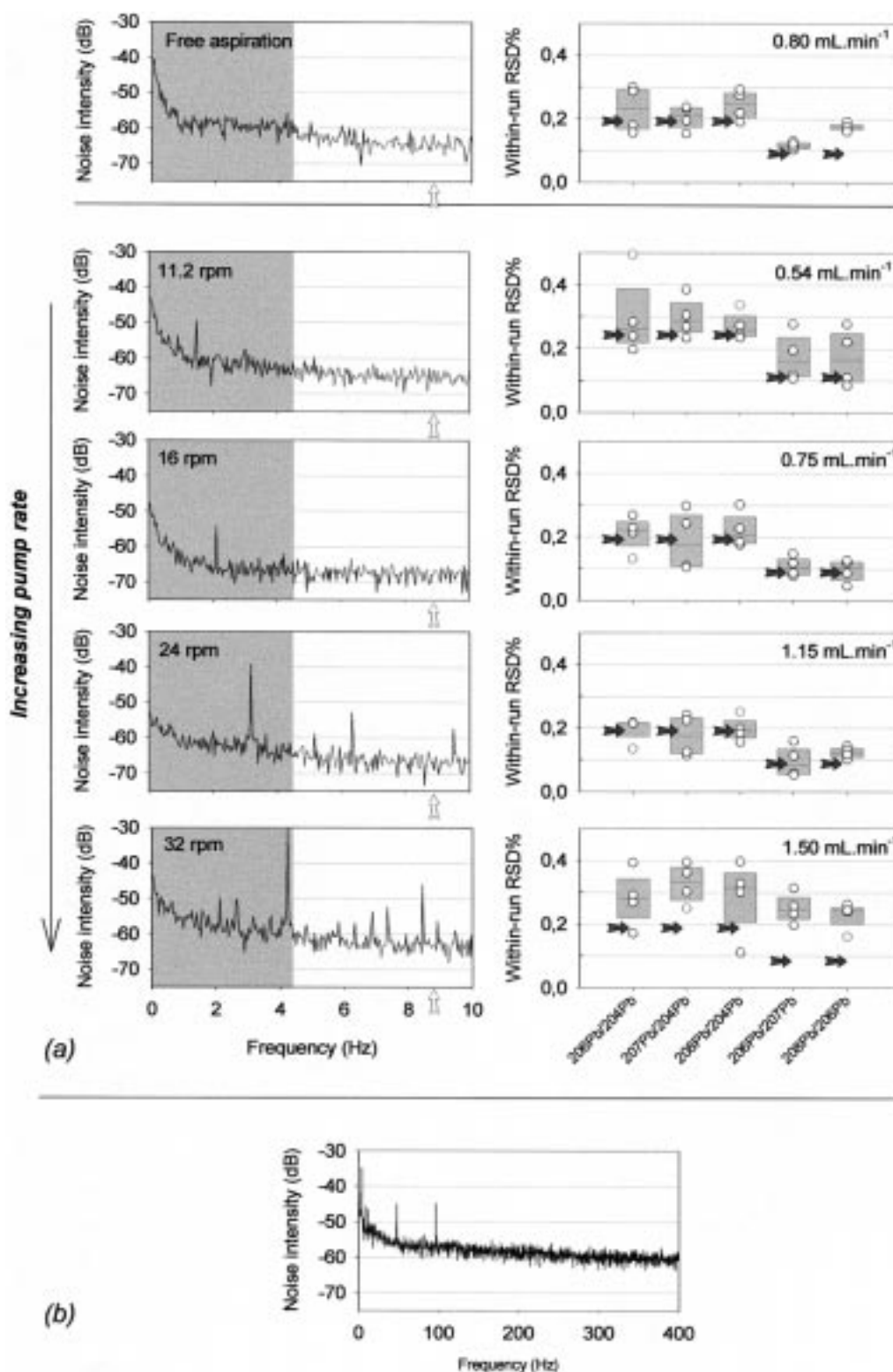


Figure 3. (a): Noise-power spectra from 0 to 10 Hz, and experimental within-run RSD % using free pumping and different pump rotation speeds (11.2, 16, 24 and 32 rpm). Left: the white arrows indicate the sampling frequency. The grey area represents the range of frequency in which the influence of noises is reduced by ratiating. Right: the open circles represent the experimental within-run RSD% of four consecutive analyses made of 10 replicates each, all done with the same settings. Median of RSD %, 25th and 75th percentiles as vertical boxes. Black arrows are the predicted RSD % by the Poisson's law. (b): Noise-power spectra from 0 to 400 Hz.

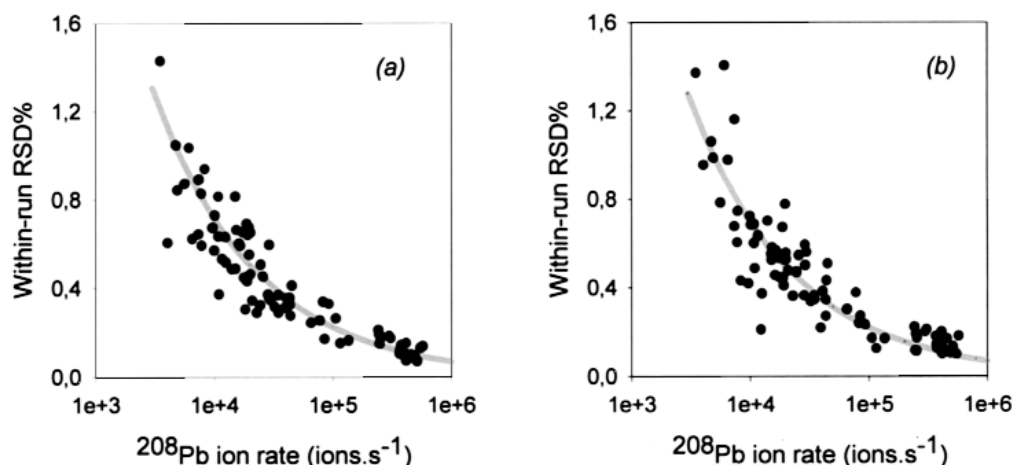


Figure 4. Experimental within-run RSD % of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (a), and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (b) of 74 rainwater solutions, and 16 Pb standards exhibiting ^{208}Pb ions flow ranging from 3 500 to 580 000 $\text{ions}\cdot\text{s}^{-1}$. Operating conditions: 22 s of total analytical time divided as follows 9 s, 9 s and 4 s for ^{206}Pb , ^{207}Pb , and ^{208}Pb respectively; stabilisation time: 10 ms; 500 sweeps. The grey curves represent the predicted RSD % considering the Poisson's law, and are given for a comparative purpose.

fair counting statistics and a precise measurement of the ^{204}Pb isotope. However, in some natural objects weakly concentrated, such natural waters, it is not always possible to reach an ion rate of $\sim 7 \times 10^5 \text{ ions}\cdot\text{s}^{-1}$ without a time consuming and potentially contaminant pre-concentration. In order to evaluate what degree of precision is reachable, 74 natural rainwater and 16 NBS 981 Pb solutions were directly analysed for their $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios without any pre-concentration. They exhibited ^{208}Pb ions flow ranging from 3500 to 580000 $\text{ions}\cdot\text{s}^{-1}$. The operating conditions were the following: 22 s of total analytical time divided in 9 s, 9 s and 4 s for the ^{206}Pb , ^{207}Pb , and ^{208}Pb isotopes respectively. Stabilisation time, number of sweeps and pump speed were kept as optimally determined in the first part of this study: 10 ms, 500 sweeps, and 16 rpm supplying $0.75 \text{ mL}\cdot\text{min}^{-1}$ of sample. The figure 4a-b reports the within-run RSD % of the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios resulting from the experiment. They clearly show that the precision closely follows the RSD % predicted by the counting statistics whatever the Pb content (grey curve on the figures). Dropping the ^{204}Pb isotope increases the sweep frequency up to 15.63 Hz, and reduces the influence of all the noises occurring on a wide frequency window (0-7.81 Hz). The long-term instabilities of the signal have practically no more significant influence on the overall precision, which is almost totally governed by the counting statistics (average of measured RSD % are 102 % and 109 % of that predicted by Poisson's law for the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, respectively).

Application to natural samples

After mass bias correction obtained by frequent measurement of NBS981 Pb standard solutions inserted in the set of unknown samples (see [2] for operational details), measurements show precision, accuracy and reproducibility as suggests the comparison with the results provided by precise thermo-ionisation mass spectrometry (TIMS) method, and numerous replicates performed on lichens, sediments and rainwater samples (Tab. III). The precision so reached is

about two orders of magnitude lower than the maximum range of variations observed in the nature. Indeed, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios can vary from ~ 1.08 in gasoline to ~ 1.21 for geogenic Pb of Western Europe [14,15], whereas the analytical precision of the same ratio is typically $1\text{-}3\cdot 10^{-3}$, at least when the Pb concentrations are sufficiently high. That makes the use of the ICP-MS quite suitable and convenient for quick environmental monitoring.

Conclusion

Whatever the type of spectrometer, it should be beneficial for the precision to reduce as much as possible the time needed for stabilisation of the quadrupole after a jump from one mass to another, in view to increase the sampling frequency. For the same reason, the number of sweeps set during an isotopic analysis should be kept as great as possible, but attention must be paid (i) to overall accuracy when the number of sweeps becomes high, and (ii) to not consume a considerable analytical time only for stabilisation. The close examination of noise power spectra established with various sample uptake rates does not only reveal the frequencies at which the noises occur, but also their amplitude, making so easier the choice of a pump speed in regard to the acquisition parameters. Some sample introduction flows appear practically more suitable than others, because they produce low white and frequency-dependent noises, and because the fundamental noise issuing from the pump itself can be more efficiently reduced by ratioing operations. Such a preliminary investigation is easy and fast to perform. It can provide information beneficial to the quality of measurements as demonstrated by the experimental within-run RSD % which closely follows that predicted by counting statistics.

Acknowledgement

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Tab. III. Accuracy and reproducibility of Pb isotopic measurements on natural environmental samples (sediments, lichens, airborne particulate matters, and natural rainwater).

	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
<i>Accuracy</i>					
<i>Aerosols</i>					
Toulouse	17.87 ± 0.04	15.57 ± 0.04	37.77 ± 0.08	1.147 ± 0.002	2.113 ± 0.004
Toulouse (TIMS) ¹	17.892 ± 0.004	15.622 ± 0.004	37.90 ± 0.01	1.1453 ± 0.0001	2.1184 ± 0.0004
Le Havre	17.23 ± 0.05	15.54 ± 0.06	37.03 ± 0.16	1.109 ± 0.002	2.149 ± 0.005
Le Havre (TIMS) ¹	17.236 ± 0.004	15.536 ± 0.005	37.09 ± 0.01	1.1094 ± 0.0001	2.1517 ± 0.0003
<i>Reproducibility</i>					
<i>Lichens</i> ²					
81EP	18.17 ± 0.05	15.56 ± 0.05	38.06 ± 0.13	1.168 ± 0.002	2.095 ± 0.006
81EP#	18.21 ± 0.05	15.60 ± 0.06	38.12 ± 0.12	1.168 ± 0.002	2.094 ± 0.004
25VUP	18.47 ± 0.03	15.71 ± 0.03	38.43 ± 0.08	1.176 ± 0.001	2.081 ± 0.004
25VUP#	18.51 ± 0.05	15.74 ± 0.04	38.60 ± 0.09	1.177 ± 0.001	2.085 ± 0.002
40VUP	18.74 ± 0.06	15.76 ± 0.05	38.73 ± 0.12	1.190 ± 0.001	2.067 ± 0.003
40VUP#	18.74 ± 0.04	15.75 ± 0.04	38.81 ± 0.09	1.191 ± 0.001	2.071 ± 0.001
<i>Overbank sediments</i> ³					
SB 42/1.3	18.80 ± 0.06	15.75 ± 0.06	38.91 ± 0.14	1.194 ± 0.001	2.070 ± 0.002
SB 42/1.3#	18.66 ± 0.04	15.63 ± 0.05	38.52 ± 0.10	1.194 ± 0.002	2.065 ± 0.003
SB 43/1.1	18.44 ± 0.03	15.58 ± 0.03	38.36 ± 0.06	1.183 ± 0.002	2.079 ± 0.004
SB 43/1.1#	18.49 ± 0.06	15.62 ± 0.05	38.39 ± 0.11	1.184 ± 0.002	2.076 ± 0.002
SB 43/1.3	18.46 ± 0.05	15.53 ± 0.05	38.28 ± 0.21	1.189 ± 0.003	2.075 ± 0.006
SB 43/1.3#	18.56 ± 0.04	15.61 ± 0.05	38.49 ± 0.11	1.189 ± 0.002	2.073 ± 0.006
SB 44/1.1	18.62 ± 0.04	15.73 ± 0.04	38.75 ± 0.08	1.184 ± 0.001	2.081 ± 0.002
SB 44/1.1#	18.65 ± 0.05	15.74 ± 0.05	38.79 ± 0.08	1.185 ± 0.001	2.080 ± 0.002
<i>Rainwaters</i>					
RW2	-	-	-	1.146 ± 0.002	2.122 ± 0.006
RW2#	-	-	-	1.142 ± 0.005	2.133 ± 0.008
RW10	-	-	-	1.156 ± 0.002	2.109 ± 0.006
RW10#	-	-	-	1.153 ± 0.003	2.119 ± 0.003
RW17	-	-	-	1.156 ± 0.003	2.114 ± 0.005
RW17#	-	-	-	1.153 ± 0.005	2.114 ± 0.005
RW25	-	-	-	1.157 ± 0.003	2.107 ± 0.005
RW25#	-	-	-	1.160 ± 0.004	2.107 ± 0.005
RW27	-	-	-	1.154 ± 0.004	2.113 ± 0.007
RW27#	-	-	-	1.157 ± 0.004	2.117 ± 0.010
RW28	-	-	-	1.155 ± 0.005	2.110 ± 0.007
RW28#	-	-	-	1.160 ± 0.004	2.105 ± 0.007
RW28#	-	-	-	1.158 ± 0.005	2.113 ± 0.007
RW40	-	-	-	1.154 ± 0.006	2.129 ± 0.009
RW40#	-	-	-	1.151 ± 0.002	2.125 ± 0.005
RW51	-	-	-	1.155 ± 0.003	2.099 ± 0.006
RW51#	-	-	-	1.156 ± 0.007	2.110 ± 0.015
RW56	-	-	-	1.158 ± 0.004	2.107 ± 0.008
RW56#	-	-	-	1.157 ± 0.003	2.103 ± 0.009

¹: TIMS values from [16]; ²: lichens isotopic composition from [17]; ³: overbank sediments from [18] ; (-): not determined. The errors are given at 95 % confidence level.

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