

# Direct determination of lead isotope ratios in rainwater using inductively coupled plasma mass spectrometry<sup>†</sup>

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Inductively coupled plasma mass spectrometry (ICP-MS) is a suitable method for the direct determination of Pb isotope ratios in rainwater. The interaction of several instrumental bias factors are corrected by systematic measurement of an external reference standard solution (NIST SRM 981), and external precision is determined independently on the standard solution, a reference solution and five natural rainwater samples previously analysed for Pb isotope ratios by thermal ionization mass spectrometry (TIMS). External precisions of 0.50, 0.50, 0.70 and 0.30% (all given as  $2\sigma$ ) are achieved for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$ , respectively, within a wide concentration range (2–50 ppb). The bias between the measured and expected value is always below the external precision. The precision of the ICP-MS data is sufficient to solve environmental problems such as the origin of Pb contamination present in rainwater from the French Massif Central where at least four components are clearly involved in the rainwater Pb budget: gasoline, a natural and an industrial component, and an unknown Pb-enriched radiogenic component.

**Keywords:** Lead isotope ratio; inductively coupled plasma mass spectrometry; rainwater; French Massif Central

A procedure using ICP-MS analysis and involving no prior chemical treatment is proposed as an alternative to TIMS (thermal ionization mass spectrometry) for determining Pb isotope ratios in rainwater. In the earth sciences, where Pb isotope ratios are commonly used to identify the origin of metals of economic interest stored in base-metal sulfide deposits, the studied material is a solid (*e.g.*, sulfide) and the external precision (repeated analysis of the same sample having undergone independent Pb separation) obtained by TIMS in this case is 0.12, 0.16, 0.22 and 0.05% for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$ , respectively, after Pb separation, all  $2\sigma$ .<sup>1</sup> With rainwater, however, which normally has a low Pb concentration (2–10 ppb), the TIMS method requires a large volume to be concentrated and for the Pb to be purified. The chemical preparation is time consuming and blank control is crucial since only the minimum amount of Pb can be loaded on the filament with no opportunity for duplicate analyses. Owing to these limitations, the external precision of this method is significantly poorer. Finally, the Pb isotope system has the specific feature of having no stable isotope pairs for ‘in-run’ checking of the mass discrimination phenomenon related to the actual measuring method,

which makes the precision of the TIMS method more than one order of magnitude less than that obtained for other isotope systems used in geochemistry (Sr, Nd, *etc.*). All these factors make ICP-MS, which requires no prior separation, a potential alternative method for the rapid acquisition of Pb isotope ratios with a competitive precision.

The aim of the present work was to make the external precision of the ICP-MS technique as close as possible to the internal precision. The external precision and accuracy was quantified using different reference solutions—a Pb reference SPEX solution and five rainwater solutions—all of which were precisely analysed for their Pb isotope ratios using TIMS. These reference solutions represent a fairly large range of naturally occurring isotope ratios, which makes the method appropriate for solving environmental problems.

In addition to the analytical study, rainwater samples from the French Massif Central were studied in order to characterize the signature of Pb contamination.

## EXPERIMENTAL

### Instrumentation

The determinations were made at the joint BRGM–INSU–LPS Laboratory at Saclay, using a VG PlasmaQuad 2 Plus ICP-MS instrument equipped with a peristaltic pump. The spray chamber and interface were cooled to 10 °C and the instrument was operated according to the conditions presented in Table 1. The detector dead time was optimized at 30 ns and the discriminator level was 25. The masses used were 204, 206, 207, 208 and 202 to correct for  $^{204}\text{Hg}$  isobaric interference, and  $^{187}\text{Re}$  (10 ppb) for normalization of blank subtraction. It was demonstrated that any memory effect is avoided with a wash time of 3 min. Monitoring on  $^{208}\text{Pb}$  is suggested to be sure of eliminating any residual Pb from the previous sample.

### Materials and methods

An automatic precipitation sampler, designed and constructed by BRGM,<sup>2</sup> was used for collecting the wet precipitations for trace metal and Pb isotope analyses, and typical ppb sampling procedures were followed because of the low levels of trace metals commonly encountered in rainwaters, which involved taking precautions to avoid contamination. The collector was cleaned in the laboratory by storing in ultrapure water of pH 2 and then conditioning in ultrapure water for a minimum of several weeks. The collector blanks never exceeded 0.5 ng for Pb, which is negligible. The sampling site was in the middle of the French Massif Central, far from any dirt road or other source of pollution, with no trees or rock outcrops in the

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**Table 1** ICP-MS operating conditions**Instrument:**

VG Elemental PlasmaQuad 2 Plus  
Normal continuous nebulization (Meinhard)

**Plasma:**

Plasma gas Argon  
Forward power 1350 W  
Reflected power <2 W  
Nebulizer gas flow 0.86 l min<sup>-1</sup>  
Auxiliary gas flow 0.8 l min<sup>-1</sup>  
Coolant gas flow 14 l min<sup>-1</sup>  
Spray chamber water-cooled at 10 °C

**Mass spectrometer:**

Vacuum stage 1, interface 2.0 hPa  
Vacuum stage 2, intermediate <10<sup>-4</sup> hPa  
Vacuum stage 3, analyzer <2 × 10<sup>-6</sup> hPa  
Nickel sampler  
Nickel skimmer

**Acquisition parameters:**

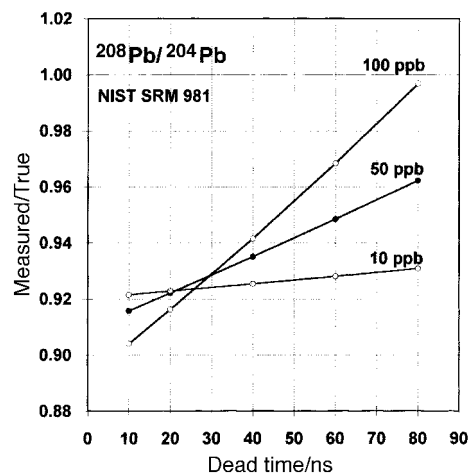
Full quantitative 'peak-jumping' mode  
Measurement mode Multi  
Measurements per peak 3 points  
Dwell time 30 ms (150 ms for 204)  
Integration time 25 s  
Replicates 16  
Ion collection Pulse counting mode  
To optimize counting times 'skip' regions were set between 10 and 150 u

vicinity of the collector. The Mediterranean is 300 km to the south and the Atlantic Ocean is 380 km to the west; the nearest towns, Clermont-Ferrand and Issoire, are 15 km to the north-west and 14 km to the south, respectively.

Samples were removed every month, except during periods of very high precipitation when they were removed every 15 d. For trace metal determinations, all samples were filtered through a pre-washed 0.2 µm Millipore PVDF filter with a pre-cleaned Nalgene apparatus and a 250 ml aliquot of the filtered rain sample was placed in an acid-washed Nalgene poly(propylene) bottle that had been cleaned with ultrapure water of pH 2 and conditioned with ultrapure water for a minimum of several weeks. The sample was then acidified to pH 2 with re-distilled, concentrated HNO<sub>3</sub>.

**RESULTS AND DISCUSSION**

Probably owing to an unsatisfactory linearity of the Channetron detector, it was apparently not possible to optimize sufficiently the dead time value for all the range of counts s<sup>-1</sup>, or for all the <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, <sup>208</sup>Pb/<sup>204</sup>Pb ratios, to obtain a precision better than 1% (2σ). A more suitable value (30 ns) was therefore defined that is sufficient for <sup>207</sup>Pb/<sup>206</sup>Pb determination considering that this ratio is close to 1 and gives the same range of counts s<sup>-1</sup> for both masses. Thus, the mass bias factor could not be determined either by systematic bias measurement on a standard or by an internal measurement after addition and determination of the <sup>205</sup>Tl/<sup>203</sup>Tl ratio.<sup>3-5</sup> In fact, for a given sample, the Pb/Pb ratios appeared to be dependent on the intensity of the 204, 206, 207 and 208 peaks, i.e., Pb/Pb ratios vary with sample dilution, despite the choice of the optimum dead time value (e.g., 30 ns). Fig. 1 shows that three curves obtained at three concentrations and recalculated at various dead time values do not intersect at a single point defining the most suitable dead time, defined as  $N_{\text{true}} = N_{\text{measured}} / (1 - \tau \cdot N_{\text{measured}})$ , where  $\tau$  = dead time (in ns). Moreover, the addition of 10 ppb Tl to correct the mass bias tentatively does not seem to be efficient; to illustrate this, the same solution containing 10 ppb of Pb (NIST SRM 981) and

**Fig. 1** Dead time correction curve for the <sup>208</sup>Pb/<sup>204</sup>Pb ratio at various concentrations in NIST SRM 981.

10 ppb of Tl was recorded successively five times in order to obtain similar counts s<sup>-1</sup> for <sup>203</sup>Tl (79 601 ± 247) and <sup>206</sup>Pb (70 136 ± 186) and similar counts s<sup>-1</sup> for <sup>205</sup>Tl (190 259 ± 800) and <sup>208</sup>Pb (147 815 ± 478). Hence, the influence of the dead time is negligible at this concentration and also it should be identical for <sup>203</sup>Tl and <sup>206</sup>Pb on the one hand, and for <sup>205</sup>Tl and <sup>208</sup>Pb on the other. The obtained <sup>205</sup>Tl/<sup>203</sup>Tl ratio was 2.3902 (±0.65%) instead of the expected value of 2.3871, which corresponds to a mass bias of +0.07% per atomic mass unit (u), whereas the <sup>208</sup>Pb/<sup>206</sup>Pb ratio was 2.1076 (±0.45%) instead of 2.1681, which corresponds to a mass bias of -1.4% per u. The uncertainty on dead time determination cannot take account of the observed mass bias, probably because Tl and Pb do not behave similarly in ICP-MS during ionization or in the quadrupole. Consequently, the best approach for routine Pb/Pb analysis is first to determine the concentrations of the unknown sample solutions and then to dilute/concentrate them to obtain the same concentration as the NIST SRM 981 solution and so avoid the uncertainty due to the lack of precision in the dead time factor. This normalization to the reference isotope standard solution (external standard) corrected the mass bias due to the differential transmission of ions of different mass from the sampling to the electron multiplier (including the interface region of the ICP-MS system, the quadrupole mass filter and the electron multiplier itself).

**Internal precision**

The internal precision corresponds to the instrumental error or 'in-run' error. It was measured on NIST SRM 981, a Pb reference SPEX solution, and several rainwater samples all diluted to obtain Pb concentrations ranging from 2–50 ppb. It is taken as twice the standard error (SE = 1σ) for  $n = 16$  runs giving an analysis  $2\sigma_m = 2\sigma/\sqrt{n}$ . This reflects the stability of a set of 16 runs, but cannot be used to compare the results of two samples. Table 2 shows that the internal error of the <sup>207</sup>Pb/<sup>206</sup>Pb ratio has slightly lower values than the internal error of the three other ratios. It also clearly shows that the precision improves with increasing concentration.

**External precision**

The external precision, or reproducibility, is defined as two standard deviations (2σ) of the average values of isotope ratios of repeated analyses of the same sample during various data acquisitions. To be representative it must be calculated on a standard and on natural samples. Table 3 shows the external precision measured on NIST SRM 981 over a period of 1 d

**Table 2** Average internal precision ( $2\sigma_m$ ) for various concentrations of various standard solutions and rainwater samples

Concentration (ppb)	Number of measurements	$^{206}\text{Pb}/^{204}\text{Pb}$ (%)	$^{207}\text{Pb}/^{204}\text{Pb}$ (%)	$^{208}\text{Pb}/^{204}\text{Pb}$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$ (%)
2	9	0.59	0.61	0.62	0.42
4	23	0.39	0.39	0.37	0.28
10	13	0.28	0.28	0.27	0.21
20	18	0.22	0.20	0.17	0.15
50	18	0.13	0.14	0.14	0.11

**Table 3** External precision on NIST SRM 981

Concentration (ppb)	Number of measurements	$^{206}\text{Pb}/^{204}\text{Pb}$ (%)	$^{207}\text{Pb}/^{204}\text{Pb}$ (%)	$^{208}\text{Pb}/^{204}\text{Pb}$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$ (%)
2	5	0.96	0.64	0.64	0.46
4	10	0.46	0.44	0.40	0.30
10	6	0.26	0.36	0.54	0.22
20	9	0.44	0.42	0.94	0.30
50	9	0.32	0.22	0.50	0.16
Average ( $2\sigma$ )	39	0.49	0.42	0.60	0.29

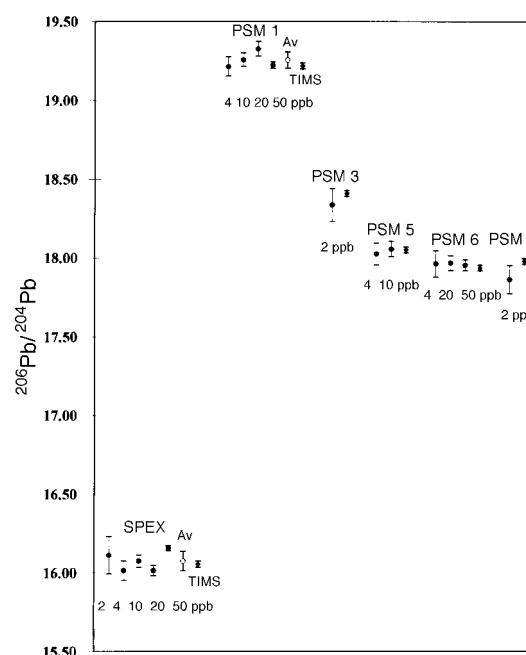
after blank subtraction and  $^{204}\text{Hg}$  correction. External precision is less dependent than internal precision on the Pb content of the solution, but both vary in the same range.

The external precision is better defined than the internal precision on unknown samples analysed on different days. The isotope ratios of the unknown rainwater samples and the SPEX standard were corrected for instrumental mass bias using NIST SRM 981 as the external standard. Table 4 gives the average external precision ( $2\sigma$ ) on the reference solution (SPEX) and rainwater samples (PSM 1 and 15) at various concentrations (2, 4, 10, 20 and 50 ppb) after blank subtraction and  $^{204}\text{Hg}$  correction (Figs. 2 and 3). The external precision using NIST SRM 981 and the natural solution is similar.

Considering the reproducibility obtained for NIST SRM 981, the SPEX solution and the two rainwater samples (PSM 1 and PSM 15) at different concentrations (2–50 ppb), it is assumed that an external precision ( $2\sigma$ ) of 0.50, 0.50, 0.70 and 0.30% is achieved for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$ , respectively, using ICP-MS for concentrations equal to, or above, 4 ppb. Note that the average external precision on the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio for sample PSM 1 is abnormally high (0.72%) due to one value, out of four, obtained at low concentration (4 ppb).

### Accuracy

To check whether the Pb isotope ratios of unknown samples are true within the previously defined external precision ( $2\sigma$ ), the same sample was analysed by a reference method (*i.e.*, TIMS). The observed average analytical bias for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  was, respectively, 0.26, 0.27, 0.17 and 0.15%, based on five rainwater samples and the reference SPEX solution (Table 5)—the accuracy is thus within the respective  $2\sigma$  estimated external precisions of 0.50, 0.50, 0.70 and 0.30%. The accuracy and precision of the ICP-MS isotope data are illustrated by comparing the isotope

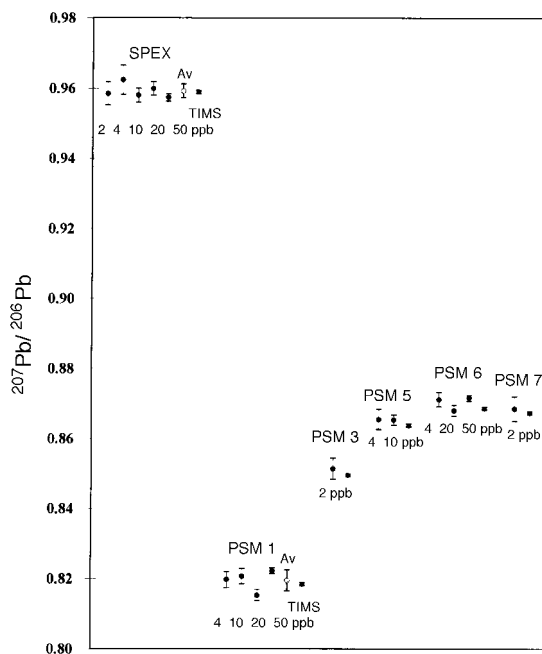


**Fig. 2**  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio for a SPEX reference solution and five rainwater samples analysed at various concentrations. The error bar for individual analyses corresponds to the ICP-MS internal precision of the measurement ( $2\sigma_m$ ). Average ICP-MS values and reference TIMS data ( $2\sigma$ ) are also plotted.

data plots of ICP-MS and TIMS (Figs. 4 and 5); good correlation lines are achieved in the ICP-MS *versus* TIMS plot for  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  isotope ratios, demonstrating that the quality of the ICP-MS data is sufficiently good to solve environmental problems.

**Table 4** Average external precision ( $2\sigma$ ) on a reference solution (SPEX) and rainwater samples (PSM 1 and 15)

Sample	Number of measurements	$^{206}\text{Pb}/^{204}\text{Pb}$ (%)	$^{207}\text{Pb}/^{204}\text{Pb}$ (%)	$^{208}\text{Pb}/^{204}\text{Pb}$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$ (%)
SPEX	5	0.76	0.48	0.86	0.42
PSM 1	4	0.54	0.38	0.60	0.72
PSM 15	4	0.68	0.70	1.12	0.34
Average ( $2\sigma$ )	13	0.66	0.52	0.86	0.50

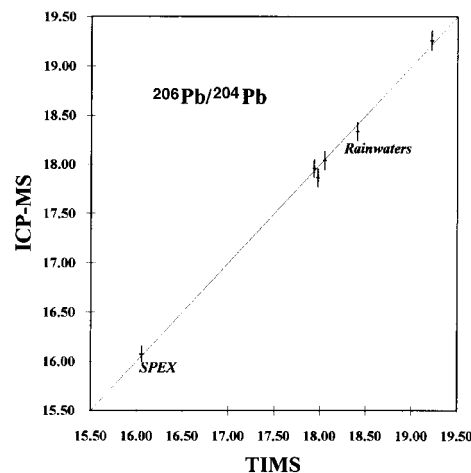


**Fig. 3**  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio for a SPEX reference solution and five rainwater samples analysed at various concentrations. The error bar for individual analyses corresponds to the ICP-MS internal precision of the measurements ( $2\sigma_m$ ). Average ICP-MS values and reference TMS data ( $2\sigma$ ) are also plotted.

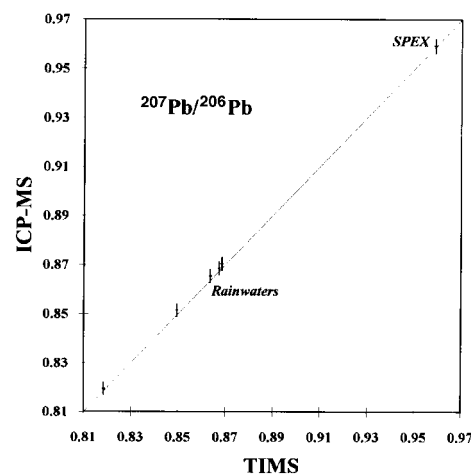
#### Lead isotope signature of rainwater

The isotopic composition of rainwater collected over the French Massif Central ranges from 17.74 (PSM 14) to 19.26 (PSM 1) for  $^{206}\text{Pb}/^{204}\text{Pb}$ , from 15.51 to 15.78 for  $^{207}\text{Pb}/^{204}\text{Pb}$  and from 37.42 to 38.63 for  $^{208}\text{Pb}/^{204}\text{Pb}$  (Table 6). The results have been plotted in classical isotope correlations (Fig. 6), which show good relationships for the rainwater data in the  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{208}\text{Pb}/^{204}\text{Pb}$  plots: the two regression equations are  $^{207}\text{Pb}/^{204}\text{Pb} = 13.20 + 0.13 \text{ }^{206}\text{Pb}/^{204}\text{Pb}$  ( $R=0.86$ ) and  $^{208}\text{Pb}/^{204}\text{Pb} = 23.35 + 0.80 \text{ }^{206}\text{Pb}/^{204}\text{Pb}$  ( $R=0.93$ ), which could reflect binary mixing. Taken overall, our data show higher Pb isotope ratios in the Massif Central rainwaters than was measured in Parisian rainwater,<sup>5</sup> which plot with the lower isotope ratios. The isotopic signatures of the rainwaters are more radiogenic than the gasoline signature,<sup>6</sup> less radiogenic than the unpolluted river sediment signature (which corresponds to an average natural signature<sup>7</sup>) and also less radiogenic than the industrial signature.<sup>8</sup> Note that isotope data for gasoline, unpolluted river sediments and the industrial field are not included in the regression calculation. Sample PSM 1 exhibits a high  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio (Table 6 and Fig. 6) and clearly lies outside these relationships, implying that a three-component model with a mixing of Pb from gasoline, nature and industry cannot alone explain the data set; the presence of a fourth, more radiogenic and Pb-enriched component, is required.

In order to test a model involving mixing between more than two pure components it is convenient to use the isotope



**Fig. 4** Plot of ICP-MS versus TMS data for the same  $^{206}\text{Pb}/^{204}\text{Pb}$  isotope ratio from rainwater samples and the SPEX solution. All the data (within the analytical error  $2\sigma$ ) plot on the theoretical correlation line.



**Fig. 5** Plot of ICP-MS versus TMS data for the same  $^{207}\text{Pb}/^{206}\text{Pb}$  isotope ratio from rainwater samples and the SPEX solution. All the data (within the analytical error  $2\sigma$ ) plot on the theoretical correlation line.

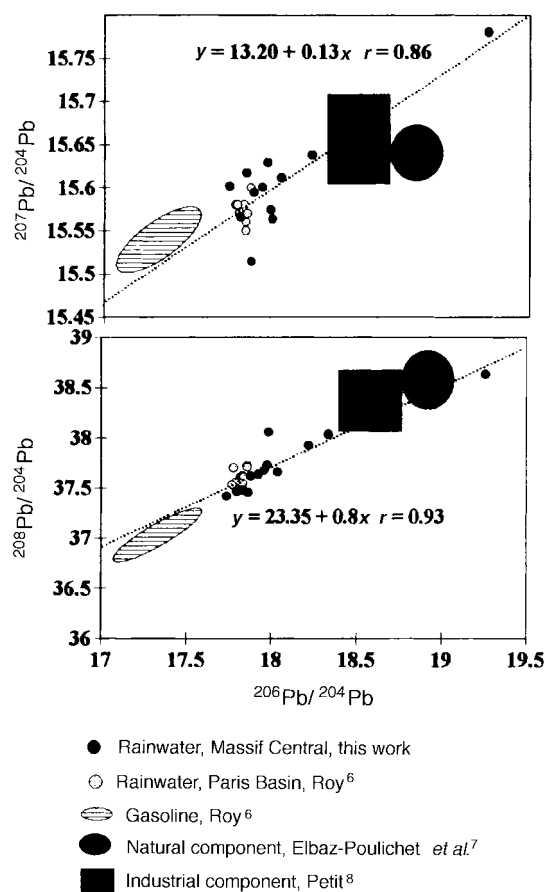
ratio versus the reverse of the concentration of the corresponding element, which gives a mixing line for mixing between two pure components. When plotted on a  $^{206}\text{Pb}/^{204}\text{Pb} = f(1/\text{Pb})$  diagram (Fig. 7), the rainwater data from the French Massif Central fall between at least three pure components: one with the lowest radiogenic Pb ( $^{206}\text{Pb}/^{204}\text{Pb} \approx 17.30$ ) and a relatively high Pb content; the second being highly radiogenic and very rich in Pb (unknown domain); and the third with an intermediate  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio around 18.50 and a low Pb content (probably a combination of an industrial and a natural component). That probably a minimum of four components are involved is confirmed by other elemental data sets,<sup>2</sup> and our

**Table 5** Assessment of accuracy using an unknown SPEX solution (previously measured with TMS) determined after blank subtraction,  $^{204}\text{Hg}$  correction and NIST SRM 981 normalization at five concentrations (2, 4, 10, 20 and 50 ppb)

Sample	Number of measurements	$^{206}\text{Pb}/^{204}\text{Pb}$ $\pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$ $\pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb}$ $\pm 2\sigma$	$^{207}\text{Pb}/^{206}\text{Pb}$ $\pm 2\sigma$
SPEX:					
ICP-MS	5	$16.074 \pm 0.080$	$15.419 \pm 0.077$	$35.745 \pm 0.250$	$0.95924 \pm 0.00288$
TMS		$16.055 \pm 0.019$	$15.396 \pm 0.025$	$35.724 \pm 0.079$	$0.95898 \pm 0.00050$
Bias		+0.12%	+0.16%	+0.06%	+0.03%

**Table 6** ICP-MS determination of Pb isotope ratios in rainwater (sample PSM 4 was determined by TIMS)

Sample	Concentration (ppb)	$^{206}\text{Pb}/^{204}\text{Pb}$ $\pm 0.090$ ( $2\sigma$ )	$^{207}\text{Pb}/^{204}\text{Pb}$ $\pm 0.078$ ( $2\sigma$ )	$^{208}\text{Pb}/^{204}\text{Pb}$ $\pm 0.265$ ( $2\sigma$ )	$^{207}\text{Pb}/^{206}\text{Pb}$ $\pm 0.00260$ ( $2\sigma$ )
PSM 1	465	19.257	15.781	38.632	0.81948
PSM 3	2.46	18.336	15.611	38.037	0.85136
PSM 4	1.22	18.229	15.618	37.559	0.85676
PSM 5	15.5	18.040	15.612	37.659	0.86538
PSM 6	64.0	17.960	15.629	37.675	0.87025
PSM 7	1.95	17.863	15.514	37.459	0.86849
PSM 9	4.54	17.800	15.566	37.463	0.87448
PSM 10	61.3	17.985	15.564	38.061	0.86536
PSM 11	50.0	18.220	15.638	37.927	0.85831
PSM 12	5.03	17.976	15.575	37.730	0.86643
PSM 13	8.70	17.927	15.600	37.637	0.87727
PSM 14	20.0	17.735	15.601	37.416	0.87969
PSM 15	49.0	17.835	15.617	37.476	0.87567
PSM 16	40.0	17.879	15.594	37.621	0.87221

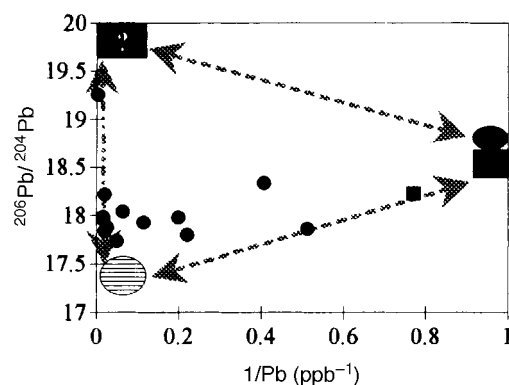


**Fig. 6** Pb isotope diagrams for rainwater from the French Massif Central (ICP-MS) compared with rainwater from the Paris Basin and indicating the gasoline-, industrial- and natural-component fields.

current research is focused on identifying this fourth pure component.

## CONCLUSIONS

Routine ICP-MS measurements and normalization to NIST SRM 981 allow a precise and accurate Pb isotope ratio determination in rainwater. An external precision ( $2\sigma$ ) of 0.50, 0.50, 0.70 and 0.30% is obtained for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$ , respectively, for concentrations



**Fig. 7** Plot of  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio versus  $1/\text{Pb}$  for rainwater from the French Massif Central (ICP-MS) showing that at least three components are involved in the rainwater budget (symbols as in Fig. 6).

equal to, or above, 4 ppb. Whenever possible, a concentration around 10 ppb is recommended to obtain precise Pb isotope ratios and easily eliminate possible contamination and/or memory effects. Thus, ICP-MS is a competitive method for measuring Pb isotope ratios in natural water in order to solve environmental problems.

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## REFERENCES

- 1 Pomiès, C., Cocherie, A., Guerrot, C., Marcoux, E., and Lancelot, J., *Chem. Geol.*, 1998, **144**, 137.
- 2 Negrel, Ph., and Roy, S., *Appl. Geochem.*, in the press.
- 3 Longerich, H. P., Fryer, B. J., and Strong, D. F., *Spectrochim. Acta, Part B*, 1987, **42**, 39.
- 4 Ketterer, M. E., Peters, M. J., and Tisdale, P. J., *J. Anal. At. Spectrom.*, 1991, **6**, 439.
- 5 Begley, I. S., and Sharp, B. L., *J. Anal. At. Spectrom.*, 1997, **12**, 395.
- 6 Roy, S., PhD Thesis, University of Paris VII, 1996.
- 7 Elbaz-Poulichet, F., Holliger, P., Huang, W. W., and Martin, J. M., *Nature (London)*, 1984, **308**, 409.
- 8 Petit, D., PhD Thesis, University of Bruxelles, 1977.

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