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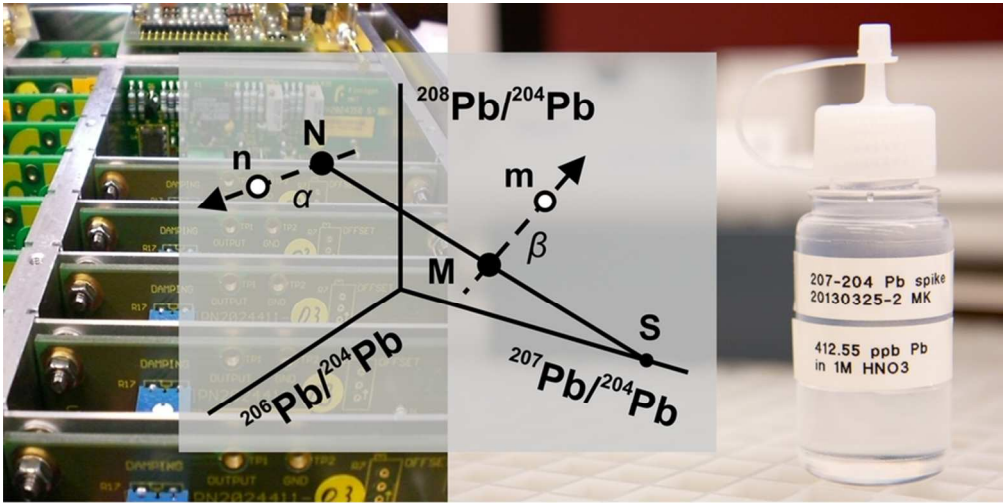


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The use of a 1013 Ohm amplifier to increase the ^{204}Pb signal enables high-precision, double spike Pb isotope data to be obtained for ng-size Pb samples

39x19mm (600 x 600 DPI)

Pb isotope analysis of ng size samples by TIMS equipped with a $10^{13} \Omega$ resistor using a ^{207}Pb - ^{204}Pb double spike

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ABSTRACT

The use of the double spike technique to correct for instrumental mass fractionation has yielded high precision results for lead isotope measurements by thermal ionisation mass spectrometry (TIMS), but the applicability to ng size Pb samples is hampered by the small size of the ^{204}Pb ion beam in the natural isotope composition analysis. To overcome this limitation, we successfully demonstrate the application of a $10^{13} \Omega$ resistor in the Faraday cup amplifier feedback loop used for the collection of ^{204}Pb in combination with a newly produced ^{207}Pb - ^{204}Pb double spike to correct for instrumental mass fractionation. The use of a $10^{13} \Omega$ resistor for the collection of the small ^{204}Pb ion beam leads to a tenfold improvement in the signal-to-noise ratio, but necessitates an external gain correction using a secondary standard and careful monitoring of the ion beam intensity. SRM 981 aliquots of 5 ng display unparalleled reproducibility of 90-125 ppm (2 SD) and are in excellent agreement with recommended values: $^{206}\text{Pb}/^{204}\text{Pb} = 16.9404 \pm 0.0016$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4977 \pm 0.0019$ and $^{208}\text{Pb}/^{204}\text{Pb} = 36.7193 \pm 0.0042$ (2 SD, $n = 22$). Comparable high quality data have been obtained for 5 ng aliquots of geological reference materials AGV-1 and BCR-1 (e.g. $^{206}\text{Pb}/^{204}\text{Pb} = 18.9399 \pm 0.0011$ and 18.8208 ± 0.0011 respectively), indicating that analytical blank contribution is negligible for sample sizes down to 5 ng. With further reduction in, or precise correction for, analytical blanks, the combination of the double spike technique with high-resistance amplifiers has the potential to produce highly accurate and precise (<200 ppm) Pb isotope data for samples below the ng level. This methodology will open a range of research possibilities presently impeded by the low amount of Pb available for analysis.

1. Introduction

Lead isotopes are a powerful geochemical tool to investigate a wide variety of geological and environmental processes. In addition, the combination of the decay chains of ^{238}U , ^{235}U and ^{232}Th , producing ^{206}Pb , ^{207}Pb and ^{208}Pb respectively, represents one of the most robust geochronological tools available. Recent improvements in clean lab technology have pushed analytical procedure blanks down to and below the pg level, thereby enabling precise measurement of ng quantities of lead, for instance for microsampling of volcanic minerals¹ or provenance studies². The accuracy of lead isotope measurements, however, is severely hampered by the difficulty in correcting for instrumental mass fractionation³. In contrast with other radiogenic isotope systems such as Sr, Nd, Hf and Os, no stable isotope pair with an accepted constant ratio is available to correct for instrumental mass fractionation as only ^{204}Pb is not produced by radioactive decay. In the last decades, multiple approaches have been proposed to overcome this problem. Reasonably accurate correction for instrumental mass fractionation in multi-collector inductively-coupled plasma mass spectrometry (MC-ICPMS) measurements can be achieved through sample-standard bracketing or TI-spiking³⁻⁵. Disadvantages of MC-ICPMS, however, are a higher background, isobaric interference of ^{204}Hg from the Ar plasma, memory effects and large instrumental mass fractionation³. In addition, the ion yield is up to an order of magnitude lower compared to thermal ionisation mass spectrometry (TIMS)^{3, 6}. Due to the high ion yield that is achievable with TIMS (up to 10 %^{7, 8}), this is the most suitable method for measurement of ng or smaller sized lead samples⁹⁻¹¹. Arguably the most accurate method to correct for instrumental mass fractionation in TIMS measurements is the use of the double spike method^{3, 6}. In contrast with isotope dilution, the double spike technique is not used

to determine absolute element concentrations, but offers a mathematical solution to correct for instrumental mass fractionation (see section 2). The conventional lead double spike technique, employing a double spike consisting of two stable isotopes of lead (e.g. ^{207}Pb - ^{204}Pb), has proven to be highly accurate and reproducible for large (>10 ng) sample sizes for both TIMS^{6, 12} and MC-ICPMS^{4, 5}. Its application to small (<10 ng) sample sizes, however, is hampered by two problems: i) two measurements are required per sample: an unspiked and a spiked analysis. At least 20 % of the total sample is required for the spiked analysis, and hence less sample is available for the natural analysis, thereby limiting the total ion beam size; and ii) the precision of the measurement is largely controlled by the small size of the ^{204}Pb ion beam in the natural run, which comprises only ~1.4 % of the total lead. The first problem can be overcome by the use of a ^{202}Pb - ^{205}Pb spike, which eliminates the need for two mass spectrometric measurements and is not influenced by the uncertainty on the small ^{204}Pb ion beam^{11, 13}, but this technique has its own intrinsic weaknesses. A ^{202}Pb - ^{205}Pb spike is radioactive, is not commercially available and suffers from interference by BaPO_2^+ and organic molecules. In addition, the problem of low ^{204}Pb remains when $^{208}\text{Pb}/^{204}\text{Pb}$ data are desired and is compounded by the fact that typically small ^{202}Pb and ^{205}Pb ion beams are measured due to the expense of the spike. An elegant way to circumvent the problem of the small ^{204}Pb ion beam is the use of two double spikes¹⁴. In this technique, the natural sample is first spiked with a ^{204}Pb - ^{205}Pb spike to augment the ^{204}Pb ion beam intensity, after which a ^{207}Pb - ^{204}Pb spike is used to correct for instrumental mass fractionation. The use of two spikes, however, introduces an additional source of error and organic molecular interference cannot be monitored at mass 205. Hence, a conventional double spike technique is expected to produce superior results once the limitation of the small ^{204}Pb ion beam is overcome. In this paper, we investigate the use of an amplifier fitted with a state-of-the-art $10^{13} \Omega$ resistor in the feedback loop for the collection of the small ^{204}Pb ion beam. Compared to default $10^{11} \Omega$ resistors, the use of a high-resistance $10^{13} \Omega$ resistor results in a 100 times higher signal intensity while the noise increases with a factor of only $\sqrt{100}$, and thus a tenfold improvement in the signal to noise ratio¹⁵. This allows the measurement of ion currents that are in the range normally covered by ion counting using a secondary electron multiplier (SEM), thereby taking advantage of the superior stability of a Faraday detector compared to SEM. The successful application of multiple $10^{13} \Omega$ resistors has been demonstrated for the measurement of sub-ng Sr and Nd samples^{15, 16}, but has not been investigated previously for Pb isotopes. We present an analytical protocol for the precise measurement of ng size Pb samples using a newly produced ^{207}Pb - ^{204}Pb double spike in combination with a $10^{13} \Omega$ resistor. The protocol is evaluated with NIST standard reference material (SRM) 981 and USGS reference materials AGV-1 and BCR-1.

2. Principles of the double spike technique

The use of the double spike technique to correct for instrumental mass fractionation is applicable to any element with at least four isotopes. It was first proposed by Dodson¹⁷ and is now regularly used to obtain high-precision isotope data for many elements, including Pb, Fe, Zn, Os etc.¹⁸. The fundamentals of the double spike technique have been discussed extensively in the literature^{5, 6, 17-19} and only a short summary is provided here. Two mass spectrometric measurements are required per sample, one for the unspiked sample (the natural analysis) and one for a mixture of the sample with a double spike (the spiked analysis). In four isotope space, these two measurements define three lines (Figure 1): a mixing line between the sample and the double spike, on which the mixture is located, and two mass fractionation vectors that displace the measured compositions from the true, mass fractionation corrected compositions. Provided that the composition of the double spike is well known, the nine equations that define the three lines can be solved to yield the mass fractionation factor α for the natural run and hence the mass fractionation corrected composition of the sample. Note that the absolute concentration of the double spike is not an input parameter and does not need to be precisely constrained.

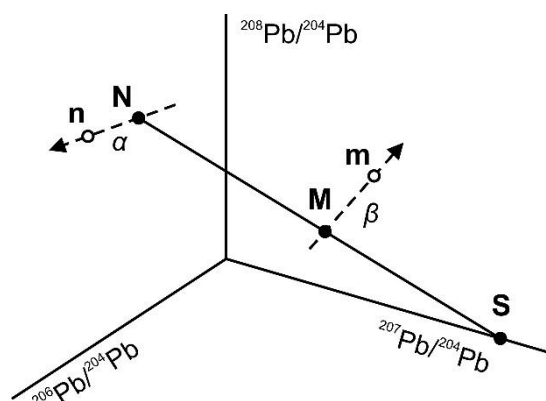


Figure 1. Principles of the double spike method. The combination of two measurements per sample, the natural analysis (N) and the spiked analysis (mixture – M), allows the construction of three lines in four isotope space: i) a mixing line N-M-S between the sample and the double spike (S); ii) a mass fractionation vector N-n for the natural run; and iii) a mass fractionation vector M-m for the spiked run. The mass fractionation vectors displace the measured composition (n, m) from the true composition (N, M) of the sample and the mixture. In four isotope space, this results in nine equations with nine unknowns, and hence the system can be solved for the composition of the sample (N). Note that the mass fractionation vectors form a vector field when an exponential law is applied. The figure is not to scale and does not represent the true composition of the double spike.

3. Analytical techniques

3.1. The VUA ^{207}Pb - ^{204}Pb double spike

A ^{207}Pb - ^{204}Pb double spike was made at the VU University Amsterdam (VUA Pb DS) from ^{204}Pb and ^{207}Pb single spikes obtained from Oak Ridge National Laboratory. An optimal double spike composition was calculated using the double spike toolbox¹⁸ and was designed to introduce minimal error magnification on $^{207}\text{Pb}/^{204}\text{Pb}$. The VUA Pb DS has a $^{207}\text{Pb}/^{204}\text{Pb}$ of 0.79086 ± 7 (Table 2), which allows large flexibility in the sample–double spike ratio without significantly increasing the error magnification. The isotope composition of the VUA Pb DS was calibrated against standard reference material NIST SRM 982 using the isotope ratios reported by Thirlwall⁴.

3.2. Ion-exchange chemistry

Single aliquots of USGS reference materials AGV-1 and BCR-1 used in this study were digested using PTFE Parr bombs and subsequently dissolved in 0.7M HBr. Double sub-boiling distilled reagents were used for sample dissolution and ion-exchange chemistry to ensure low blank levels. All PTFE and PFA laboratory equipment is cleaned by sub-boiling in pro-analysis quality ~ 6 M HNO_3 and ~ 6 M HCl for two hours each, followed by two 4–7 day leaching steps at 130°C with double distilled 6 M $\text{HCl}/1\text{--}2$ M HF and 0.25 M HBr respectively. Laboratory equipment that has contained the Pb double spike is reused at least once for any other purpose (e.g. Sr or Nd isotope analysis) before being reconsidered for Pb again to minimise double spike memory effects. For the purification of Pb, a double column pass anion-exchange technique was employed with disposable polyethylene pipette-tip columns fitted with a polyethylene filter (mesh $35\ \mu\text{m}$). The columns were loaded with 50 μl of Bio-Rad® AG 1-X8 200–400 mesh resin and cleaned three times with alternating 1.5 ml 1 M HF , 6.5 M HCl and milli-Q water before conditioning with 0.7 M HBr . Subsequently, 0.5 ml aliquots of the sample solutions dissolved in 0.7M HBr , corresponding to the desired amount of Pb (typically 75 ng Pb for regular samples and 5 ng for the small standards used in this study), were loaded onto the columns. The matrix was washed out with 1 ml 0.7 M HBr followed by a rinse with 0.15 ml 3.0 M HCl and elution of the Pb fraction was accomplished with 0.4 ml 6.5 M HCl . The Pb fractions were dried down while the columns were conditioned with 0.7 M HBr . Subsequently, the Pb fractions were re-dissolved in 0.5 ml 0.7 M HBr , loaded onto the same columns and Pb was extracted as in the first column pass. The purified Pb fractions were dried down and

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3 nitrated twice with 2 drops of concentrated HNO_3 to eliminate organic material. Over the 1.5 years of this
4 study, total procedural blanks, including sample destruction in PTFE Parr bombs, were 5-13 pg, but have
5 stabilized at 6 ± 1 pg Pb after implementation of the rigorous column cleaning procedure described above.
6 Columns blanks are 3-6 pg, suggesting that the ion-exchange chemistry is the largest contributor to the total
7 procedural blank.
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11 *3.3. Mass spectrometry*

12 Samples and standards were measured for isotope composition by TIMS using a Thermo Scientific TRITON *Plus*
13 instrument. A summary of the analytical method is shown in Table 1. For the natural analysis, the samples were
14 re-dissolved in 3 μl 10 % HNO_3 before loading on outgassed zone-refined rhenium filaments. First, 1.5 μl of
15 silica gel prepared by the method of Gerstenberger & Haase⁷ was loaded to which 2 μl (i.e., two-thirds) of the
16 sample was added drop by drop. The solution was evaporated at 1.0 A to allow effective mixing of the lead
17 with the silica gel. Subsequently, the filament current was increased to 2.0 A to fuse the silica gel and
18 evaporate excess H_3PO_4 from the silica gel. An aliquot of the VUA Pb DS and ~0.5 ml dilute HNO_3 were added to
19 the remaining one-third of the samples, which were left to equilibrate overnight at 120 °C to ensure effective
20 sample-spike homogenisation. Ideally, an amount of double spike Pb equivalent to the remaining amount of
21 sample Pb was added, but the sample-spike ratio can be varied up to an order of magnitude without
22 significantly increasing the error magnification. The spiked Pb fractions were dried down and loaded similarly to
23 the natural analysis except that the complete sample was loaded. Loading blanks are systematically <150 fg and
24 therefore differential loading blanks between the natural and spiked runs are assumed to be negligible.
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27 For the analysis of the unspiked samples larger than 5 ng Pb and all spiked analyses, regular $10^{11} \Omega$
28 resistors were used. Samples were heated to obtain a slightly growing ion beam in the temperature range
29 1160-1230 °C. After beam optimization, data were acquired in static multi-collector mode in six to eight blocks
30 of 20 cycles each without the use of the Triton's amplifier rotation option (see Table 1). A baseline
31 measurement of 32 s was performed in between blocks by defocusing the ion beam. An amplifier gain
32 calibration was performed at least daily. For the analysis of unspiked samples, a regular sample size of ca. 50 ng
33 will yield a stable ^{208}Pb beam with an intensity of $4-7 \times 10^{-11}$ A that can easily be maintained for the duration of
34 a measurement (roughly 30 minutes) in the temperature range 1160-1240 °C. Measurements obtained at a
35 filament temperature in excess of 1250 °C display a decrease in $^{207}\text{Pb}/^{204}\text{Pb}$ of up to 150 ppm while $^{206}\text{Pb}/^{204}\text{Pb}$
36 and $^{208}\text{Pb}/^{204}\text{Pb}$ are unaffected. Similar anomalous behaviour of ^{207}Pb on TIMS has been discussed in detail by
37 Thirlwall⁶ and Doucelance and Manhès²⁰, who concluded that isobaric interference was not the cause of the
38 ^{207}Pb anomaly. Our results also show no evidence of isobaric interference in this temperature range. Organic
39 molecular interference is monitored at mass 205, but an observable signal at $T > 1130$ °C was present in less
40 than 1 % of the analyses and was usually absent above 1180 °C. Hence, the origin of the anomalous behaviour
41 of ^{207}Pb remains unresolved, but is likely a nuclear effect^{21, 22}. Rather than applying a correction for the
42 anomalous behaviour of ^{207}Pb , we exclude any data acquired at $T > 1250$ °C. For the unspiked analysis of
43 sample sizes ≤ 5 ng Pb, a $10^{13} \Omega$ resistor is used for the detection of ^{204}Pb in combination with regular $10^{11} \Omega$
44 resistors for the other isotopes. As it is not possible to calibrate the gain factor of the $10^{13} \Omega$ resistor directly, an
45 external reference solution is measured at least daily¹⁵, as will be discussed in detail in section 4.2. A 660 s
46 baseline measurement is carried out during sample warm-up¹⁵ to save acquisition time, and after beam
47 optimization data are acquired continuously for 200-400 cycles. A detailed discussion of measurement
48 conditions is provided in section 4.2.
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Faraday cup isotope	cup configuration				
	L2 ^{204}Pb	L1 $^{205}\text{organics}$	C ^{206}Pb	H1 ^{207}Pb	H2 ^{208}Pb
		N-runs >5 ng Pb S-runs		N-runs <5 ng Pb	
resistor Faraday cup L2 (^{204}Pb)		$10^{11} \Omega$		$10^{13} \Omega$	
resistor other Faraday cups		$10^{11} \Omega$		$10^{11} \Omega$	
baseline (defocused beam)		32 s - every block		660 s - during warm-up	
gain calibration		software routine		external correction to in-house	
data acquisition		6-8 blocks of 20 cycles		2-4 blocks of 100 cycles	
integration time		8.389 s		8.389 s	
idle time		3 s		10 s	
run temperature		1160-1240 °C		1160-1240 °C	

Table 1. Analytical details of the measurements on a Thermo Scientific TRITON Plus TIMS.

3.4. Data reduction

By employing the exponential law to correct for mass fractionation, the double spike inversion cannot be solved algebraically and has to be processed individually per sample in an offline spreadsheet. First, the natural and spiked data were subjected to an artificial mass fractionation correction to the average $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of the first block of the unspiked analysis. This allows a realistic estimate of the analytical uncertainties to be made⁶ and, as the same correction was applied to both the natural and spiked data, this artificial correction will cancel out during the subsequent double spike inversion. The corrected data were subjected to a 2-sigma outlier test and a variance-covariance matrix of these data was used for algebraic error propagation. Average $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the natural and spiked analysis were entered in the double spike inversion, following the solution presented by Rudge et al.¹⁸. To correct for instrumental mass fractionation according to the exponential law, the double spike equation was solved iteratively using a Newton-Raphson method and a linear fractionation correction as a first approximation. Uncertainties were propagated algebraically^{18, 23}, taking into account the strong error correlation ($r > 0.90$) between $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. The error magnification factor (defined as 2 SE uncertainty of the double spike corrected $^{206}\text{Pb}/^{204}\text{Pb}$ ratio over the artificially corrected $^{206}\text{Pb}/^{204}\text{Pb}$ ratio) is dependant predominantly on the precision of the spiked run, but was almost always less than 1.20.

4. Results and discussion

4.1. Reproducibility of 75 ng standards with the double spike technique

Repeated analyses of standard reference material (SRM) 981 were used to assess the reproducibility (2 standard deviation of the results acquired during the 1.5 years of this study) of the double spike method. All analyses of SRM 981 represent an individual double spike measurement: a 75 ng aliquot of SRM 981 was evaporated in a clean PFA vial and was loaded, measured and spiked in an identical way as samples. We argue that this approach allows a more realistic estimate to be made of the performance of the double spike technique rather than using a single spiked SRM 981 measurement to correct all standard measurements. The data acquired for SRM 981 over the last 1.5 years display excellent reproducibility (51, 59 and 69 ppm 2 SD for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ respectively) and are in perfect agreement with recommended values (Figure 2 and Table 2). To test the reproducibility of the analytical procedure with geological matrices, USGS reference materials AGV-1 and BCR-1 were periodically included as unknowns in sample sets measured over the course of this study. These reference materials were selected on the basis of their superior homogeneity compared to AGV-2, BCR-2 and other “-2” USGS standards, which are characterized by significant Pb isotope

inhomogeneity^{5, 24}. Nevertheless, we opted for processing aliquots of a single dissolution of AGV-1 and BCR-1 to eliminate any doubt with regard to standard inhomogeneity in order to assess the reproducibility of the ion-exchange and mass spectrometric procedures. Results obtained for AGV-1 and BCR-1 are shown in Figure 3 and Table 2. The reproducibility for both standards is comparable to SRM 981 and the results agree within analytical uncertainty with published MC-ICPMS double spike corrected⁵ and MC-ICPMS TI-corrected²⁵ data. Hence, we conclude that the results obtained for AGV-1 and BCR-1 are of the same high quality as the SRM 981 data and that the chemical purification procedure has no effect on the accuracy and reproducibility of the Pb isotope data.

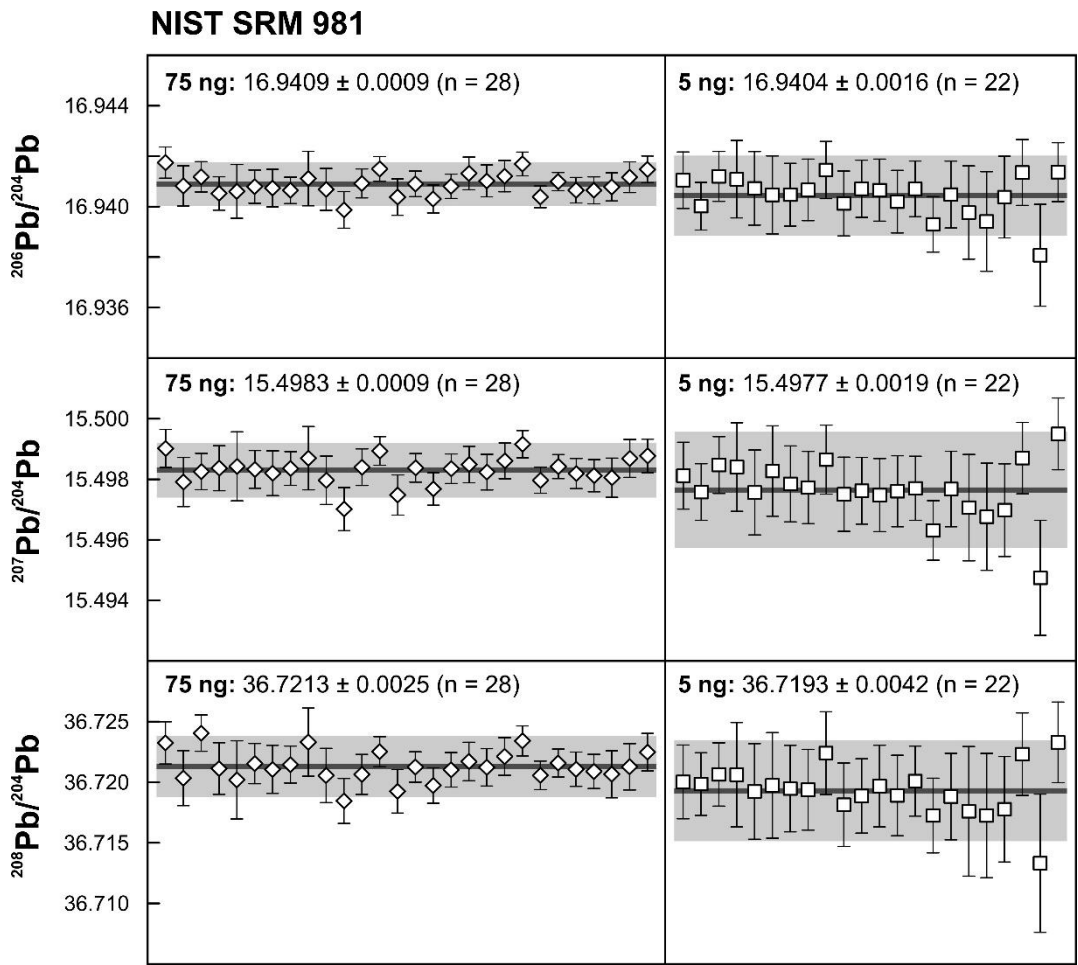


Figure 2. Results for the repeated analyses of NIST standard reference material 981 for 75 ng and 5 ng aliquots. The 5 ng data were acquired using a $10^{13} \Omega$ resistor in the Faraday cup amplifier feedback loop for the collection of ^{204}Pb . Error bars are propagated internal precision (2 standard error), shaded field indicates 2 standard deviation (2 SD) around the mean.

4.2. Measurement of small Pb samples using a $10^{13} \Omega$ resistor

The internal precision (2 standard error) of lead isotope analyses using the double spike technique depends predominantly on the uncertainty in the measurement of ^{204}Pb in the natural run. The low ^{204}Pb signal intensity is the main limiting factor in the successful application of the double spike technique to small lead samples. To potentially improve the precision, we evaluated the use of a $10^{13} \Omega$ resistor in the feedback loop of the Faraday cup amplifier for the detection of the small ^{204}Pb ion beam. The use of this high-resistance amplifier has proven to be superior to ion counting by SEM and default $10^{11} \Omega$ resistors at signal intensities between 3.2×10^{-15} and $2.5 \times 10^{-13} \text{ A}$ ¹⁵. Online calibration of the amplifier gain factor of the $10^{13} \Omega$ resistor through an internal reference current (3.33333 V on a $10^{11} \Omega$ resistor) is not possible. Therefore, the amplifier gain factor was

calculated through the measurement of a reference solution, in this case an in-house CPI Pb standard. The isotope composition of this reference solution has been determined through repeated double spike analysis of 75 ng aliquots ($^{206}\text{Pb}/^{204}\text{Pb} = 17.8996 \pm 0.0002$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.5645 \pm 0.0003$; $^{208}\text{Pb}/^{204}\text{Pb} = 38.0177 \pm 0.0009$; 2 SD, $n = 3$). During analytical sessions with the $10^{13} \Omega$ amplifier, the in-house CPI standard was measured at least daily using a $10^{13} \Omega$ resistor for ^{204}Pb . As ^{206}Pb and ^{208}Pb data are obtained on regular, gain corrected $10^{11} \Omega$ resistors, $^{208}\text{Pb}/^{206}\text{Pb}$ was used to correct for instrumental mass fractionation. Subsequently, the fractionation corrected $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios can be used to calculate the relative gain factor of the amplifier equipped with the $10^{13} \Omega$ resistor that was used for the collection of ^{204}Pb . The three independently calculated gain factors (relative to ^{206}Pb , ^{207}Pb and ^{208}Pb) were identical within error and the average calculated gain factor was inserted in the amplifier system table of the TRITON software such that the gain correction was performed online. The gain factor for the $10^{13} \Omega$ resistor was found to vary by less than 100 ppm (2 SD) over a 6 month period; day-by-day variation is even less (< 50 ppm 2 SD; Figure 4). Hence, we conclude that using an external reference solution to determine the gain factor of the $10^{13} \Omega$ resistor is reproducible and capable of producing results that are both accurate and precise.

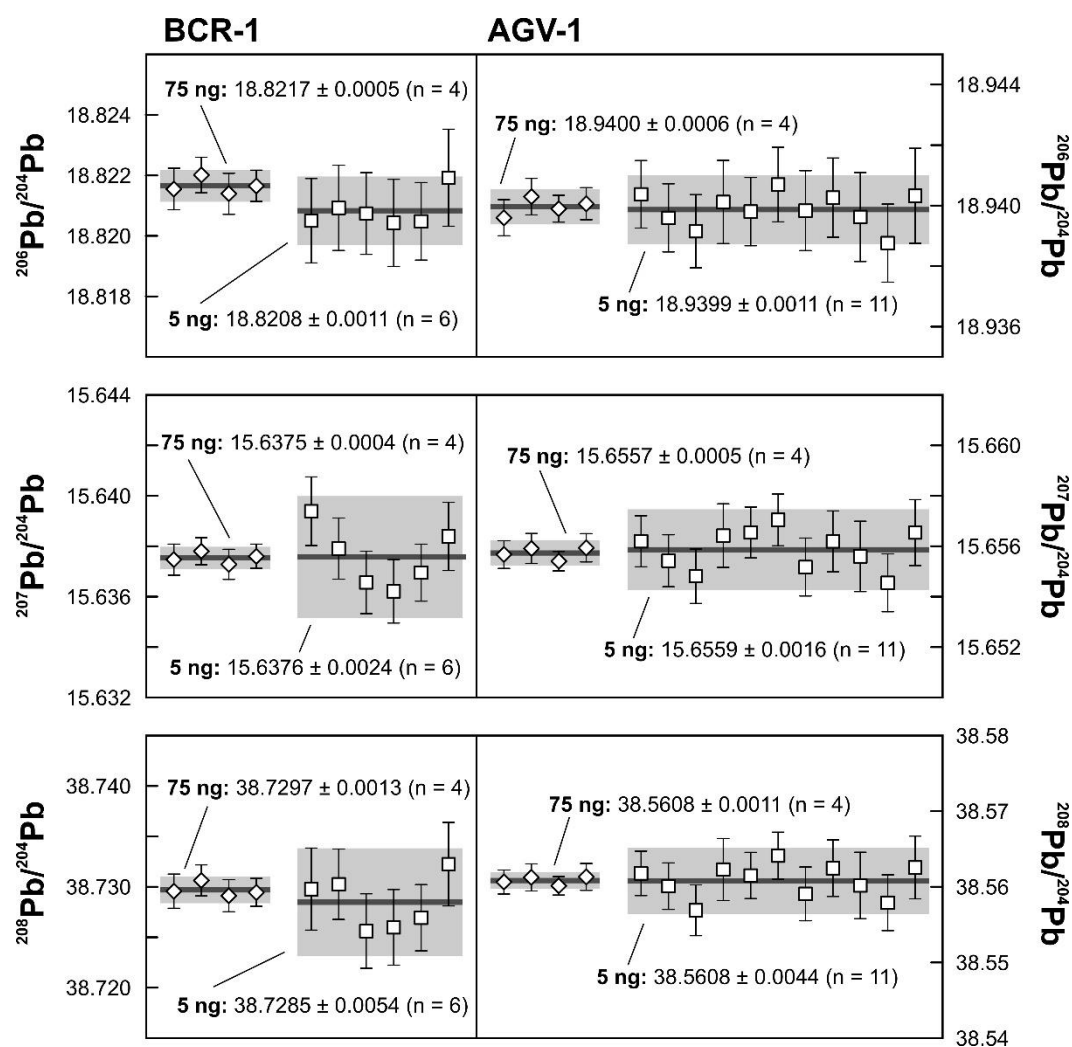


Figure 3. Results for the repeated analyses of USGS reference materials BCR-1 and AGV-1 for 75 ng and 5 ng aliquots. Error bars are 2 standard error (2 SE), shaded field indicates 2 standard deviation (2 SD) around the mean.

Study	Instrument	Ref.	²⁰⁶ Pb/ ²⁰⁴ Pb	2 SD	²⁰⁷ Pb/ ²⁰⁴ Pb	2 SD	²⁰⁸ Pb/ ²⁰⁴ Pb	2 SD
VUA Pb ²⁰⁷ Pb- ²⁰⁴ Pb DS			0.002346	0.000025	0.790861	0.000070	0.001977	0.000052
NIST SRM 981 - double spike								
This study - 75 ng (n = 28)	TIMS		16.9409	0.0009	15.4983	0.0009	36.7213	0.0025
This study - 5 ng (n = 22)	TIMS		16.9404	0.0016	15.4977	0.0019	36.7193	0.0042
NIST SRM 981 recommended value		3	16.9412	0.0003	15.4988	0.0006	36.7233	0.0013
Woodhead et al., 1995	TIMS	12	16.937	0.0040	15.492	0.0048	36.708	0.0128
Galer and Abouchami, 1998	TIMS ^A	26	16.9405	0.0015	15.4963	0.0016	36.7219	0.0044
Thirlwall, 2002	TIMS	4	16.9408	0.0021	15.498	0.0025	36.722	0.0080
Thirlwall, 2002	MC-ICPMS	4	16.9417	0.0029	15.4996	0.0031	36.724	0.0080
Kuritani and Nakamura, 2003	TIMS ^B	14	16.9414	0.0028	15.4992	0.0029	36.723	0.0075
Baker et al., 2004	MC-ICPMS	5	16.9416	0.0013	15.500	0.0015	36.7262	0.0031
Taylor et al., 2015	TIMS	3	16.9402	0.0027	15.4981	0.0027	36.7222	0.0075
Taylor et al., 2015	TIMS	3	16.9403	0.0029	15.500	0.0038	36.7224	0.0090
Taylor et al., 2015	MC-ICPMS	3	16.9415	0.0022	15.4985	0.0021	36.7212	0.0063
AGV-1								
This study - 75 ng (n = 4)	TIMS DS		18.940	0.0006	15.6557	0.0005	38.5608	0.0011
This study - 5 ng (n = 11)	TIMS DS		18.9399	0.0011	15.6559	0.0016	38.5608	0.0044
Woodhead and Hergt, 2000	TIMS DS ^C	28	18.942	0.001	15.659	0.003	38.566	0.007
Woodhead and Hergt, 2000	TIMS DS ^D	28	18.954	0.003	15.672	0.002	38.599	0.007
Kuritani and Nakamura, 2002	TIMS	27	18.938	0.003	15.650	0.004	38.554	0.019
Baker et al., 2004	MC-ICPMS DS	5	18.942	0.002	15.658	0.002	38.569	0.006
Weis et al., 2006	MC-ICPMS TI	25	18.9399	0.0063	15.6531	0.0038	38.5599	0.0096
BCR-1								
This study - 75 ng (n = 4)	TIMS DS		18.8217	0.0005	15.6375	0.0004	38.7297	0.0013
This study - 5 ng (n = 6)	TIMS DS		18.8208	0.0011	15.6376	0.0024	38.7285	0.0054
Woodhead and Hergt, 2000	TIMS-DS	28	18.814	0.006	15.630	0.005	38.703	0.015
Kuritani and Nakamura, 2002	TIMS	27	18.817	0.005	15.631	0.004	38.720	0.015
Baker et al., 2004	MC-ICPMS DS	5	18.822	0.003	15.639	0.003	38.739	0.008
Weis et al., 2006	MC-ICPMS TI	25	18.8225	0.0031	15.6363	0.0033	38.7321	0.0073

Table 2. Results for NIST SRM 981 and USGS reference materials AGV-1 and BCR-1 obtained with the lead double spike technique and the VUA Pb DS in comparison with published data^{3-5, 12, 14, 25-28}. Notes: ^A triple spike; ^B 2x double spike; ^C batch 61/13; ^D batch 20/3.

A complicating issue found when analysing with a combination of amplifiers with 10¹¹ and 10¹³ Ω resistors is the difference in signal response and decay times, which introduces a bias when the ion beam is unstable (Figure 5). For a growing ion beam, the longer response time of the amplifier with a 10¹³ Ω resistor causes the ²⁰⁴Pb signal intensity to lag behind, leading to relatively high ^{20x}Pb/²⁰⁴Pb. For a diminishing ion beam, the effect is opposite and leads to ^{20x}Pb/²⁰⁴Pb that are too low. The successful application of an amplifier with a 10¹³ Ω resistor therefore requires that the ion beam intensity is kept as stable as possible, with a maximum drift of 1.5 % in ion beam intensity per minute (Figure 5). This is easily achieved by carefully increasing or decreasing the filament current during data acquisition but requires careful monitoring of the ion beam stability. With these problems overcome, we tested the applicability of the double spike technique in combination with an amplifier with a 10¹³ Ω resistor for 5 ng aliquots of SRM 981, AGV-1 and BCR-1. Similar to the 75 ng data, all SRM 981 analyses represent individual aliquots, and in the case of AGV-1 and BCR-1 individual column passes, that were

treated as unknown samples. Typical sample loads of ~ 3.5 ng (i.e., two-thirds of the 5 ng aliquot) for the natural run yield a ^{208}Pb signal intensity of $3\text{--}6 \times 10^{-12}$ A, roughly ten times lower compared to typical 50 ng loads, which can be maintained for at least one hour in the temperature range 1170–1250 °C. This results in a ^{204}Pb ion beam intensity of $8\text{--}15 \times 10^{-14}$ A, in the range for which a 10^{13} Ω resistor has proven to be superior to ion-counting and regular 10^{11} Ω resistors¹⁵. Once a stable ion signal has been obtained, data are acquired continuously for 200 to 400 cycles (Table 1). Generally, data acquisition was terminated after 200 cycles as longer analyses did have a smaller internal precision (2 standard error) but the reproducibility did not improve.

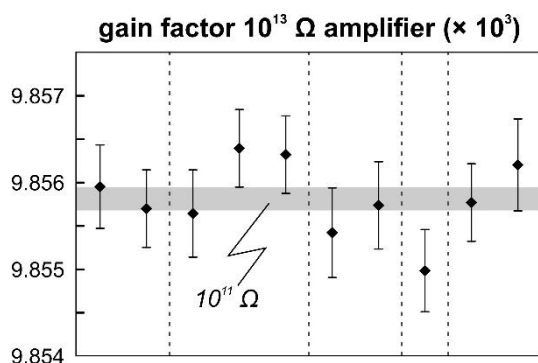


Figure 4. Variation in the gain factor of the 10^{13} Ω amplifier as determined through the measurement of the in-house CPI Pb reference solution over the six month period in which the technique was developed. The light grey field depicts the 2 SD range in the gain factor of the 10^{11} Ω amplifier that shows the largest variation during the same time period (a steady decrease in gain factor). Vertical dashed lines delineate the different analytical sessions (1–2 days). The gain factor of the 10^{13} Ω amplifier are roughly a factor 8 less reproducible compared to the default 10^{11} Ω amplifiers.

4.3. High-precision results for 5 ng standards

On the basis of the calculated Johnson-Nyquist noise of the 10^{11} and 10^{13} Ω resistors¹⁵, it is expected that the on average ten times lower signal intensity of the 5 ng SRM 981 standards will result in an internal precision (2 SE) that is only a factor 1.5 times worse compared to the 75 ng standards. The reproducibility and internal precision of the measurements of 5 ng aliquots of SRM 981 (Figure 3, Table 2) agree with this prediction and are comparable to the results obtained for the 75 ng aliquots. This is partly due to the longer data acquisition time for the analysis of the 5 ng standards, but predominantly the result of the use of the 10^{13} Ω resistor for the collection of the ^{204}Pb ion beam. In theory, the 10^{13} Ω resistor has a roughly ten times higher signal to noise ratio than default 10^{11} Ω resistors¹⁵, which should drastically improve the counting statistics of the ^{204}Pb ion beam and therefore the internal precision of $^{206}\text{Pb}/^{204}\text{Pb}$ data. We have compared data acquired for 3.5 ng SRM 981 aliquots with a 10^{13} Ω and a regular 10^{11} Ω resistor for the collection of ^{204}Pb . Typical internal precision for $^{206}\text{Pb}/^{204}\text{Pb}$ is ca. 70 ppm (2 SE) using a 10^{13} Ω resistor, which is over a factor two better than the ca. 160 ppm acquired with a 10^{11} Ω resistor. These results confirm that a higher internal precision can be achieved with a 10^{13} Ω resistor than with regular amplifiers for ion beam intensities $< 2.5 \times 10^{-13}$ A. We report a reproducibility of 90–125 ppm for the 5 ng aliquots of SRM 981, which is only a factor of ~ 1.8 worse than the 50–70 ppm obtained for 75 ng aliquots (Table 2). Considering that the precision and reproducibility are largely controlled by the uncertainty in the ~ 3.5 ng unspiked analysis, the 90–125 ppm reproducibility presents a marked improvement compared to the range of 170–900 ppm reported in previous studies for 2–5 ng Pb samples^{10, 11, 14, 27}. In addition, the excellent reproducibility indicates that the external gain correction and necessity of maintaining a stable ion beam inherent to the use of a 10^{13} Ω resistor do not introduce a bias nor have an adverse effect on the reproducibility.

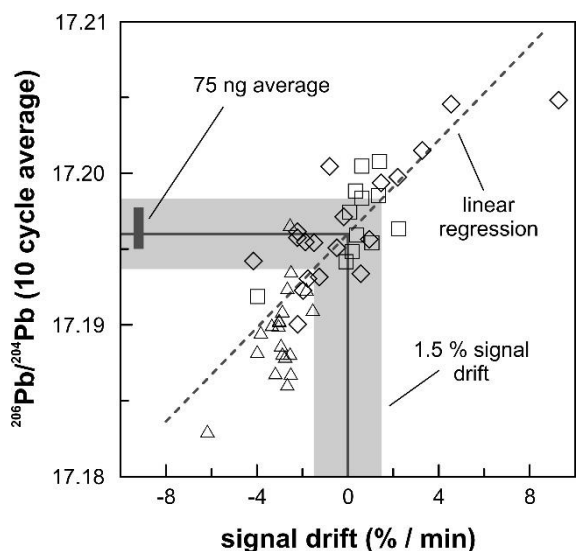


Figure 5. The effect of the longer signal response and decay times for the amplifier equipped with the $10^{13} \Omega$ resistor shown for three analyses of SRM 981 in which signal intensity was intentionally made to vary (each symbol represents a different analysis). The 10 cycle average $^{206}\text{Pb}/^{204}\text{Pb}$ is corrected for instrumental mass fractionation to an arbitrary but fixed value for $^{208}\text{Pb}/^{206}\text{Pb}$. The longer response time results in a relatively higher $^{206}\text{Pb}/^{204}\text{Pb}$ when the ion beam was growing (positive drift of the Pb signal) and vice versa for a diminishing ion beam. The dark grey bar denotes the average for 75 ng SRM 981 aliquots; the light grey field comprises 1.5 % drift in the signal intensity per minute, which is considered to be the maximum drift allowed for the measurement of samples and standards.

To evaluate the effect of the ion exchange procedure used for samples with a geological matrix on the analytical results, 5 ng aliquots of a single dissolution of BCR-1 and AGV-1 were processed. Given the typical column blank levels of 3-6 pg, the contribution by the analytical blank is expected not be of influence in the results. This is confirmed by the results for these USGS reference materials, which are in good agreement with results obtained on 75 ng aliquots and published values (Figure 3, Table 2). Typical internal precision and reproducibility for AGV-1 and BCR-1 are similar to the 5 ng SRM 981 results, indicating that analytical blanks are negligible for sample sizes down to 5 ng.

Preliminary tests indicate sample sizes much less than 5 ng can also be measured successfully using a $10^{13} \Omega$ resistor for the collection of ^{204}Pb . The internal precision for 2 ng, 500 pg and 200 pg sample loads of SRM 981 is not significantly worse than for ~ 3.5 ng aliquots, despite lower signal intensities, provided that a stable ion beam can be maintained for 200-400 cycles. For example, for a 200 pg SRM 981 standard, a ^{204}Pb ion current of $\sim 3 \times 10^{-14}$ A can easily be maintained for ca. 1 hour, resulting in an internal precision of 120 ppm (2 SE) for $^{206}\text{Pb}/^{204}\text{Pb}$. The limiting factor in obtaining precise and accurate results for < 5 ng samples, however, is the analytical blank. We have limited this study to sample sizes 1000 times larger than the currently lowest achievable blank level of ~ 5 pg. Clearly, introducing a blank correction could overcome this limitation, but an accurate blank correction requires that the isotope composition of the analytical blank is well known, which might be problematic when memory effect of laboratory equipment is the largest contributor. Nevertheless, with a further reduction in blank levels and the implementation of an analytical blank correction, the double spike procedure in combination with a $10^{13} \Omega$ resistor for ^{204}Pb has the potential to produce precise and accurate measurements of sample sizes down to or even below 1 ng. Internal precision and reproducibility are on par with or even better than other those obtained with a ^{202}Pb - ^{205}Pb spike¹¹. The main advantages of the use of a ^{207}Pb - ^{204}Pb double spike in combination with a $10^{13} \Omega$ resistor, when compared to a ^{202}Pb - ^{205}Pb spike, are the wider availability of the spike and higher reproducibility when accurate $^{206}\text{Pb}/^{204}\text{Pb}$ data are desired. In comparison with the standard TIMS approach of applying a constant instrumental mass fractionation correction of typically 0.06-0.15 % per a.m.u.^{3,9}, the double spike technique has proven to be superior in terms

of accuracy and reproducibility³. Therefore, the disadvantage of sacrificing 20-35 % of the total amount of sample for the spiked analysis is easily compensated by the greatly enhanced reproducibility.

5. Conclusions

This study demonstrates the successful application of the double spike technique to obtain high-precision lead isotope data for ng size samples. Repeated analyses of 75 ng aliquots of SRM 981, using a newly developed ²⁰⁷Pb-²⁰⁴Pb double spike to correct for instrumental mass fractionation, are highly reproducible (50-70 ppm) and in excellent agreement with recommended values. The use of a 10¹³ Ω resistor in the Faraday cup amplifier feedback loop allows the accurate and precise measurement of ion currents <2.5 × 10⁻¹³ A and thereby enables the measurement of the small ²⁰⁴Pb ion beam in sample sizes ≤5 ng. Minor complications that are intrinsic to the use of a 10¹³ Ω resistor include the necessity of an external gain calibration and stable ion beam, but these have been overcome. Results for 5 ng SRM 981 aliquots obtained with a 10¹³ Ω amplifier for the collection of ²⁰⁴Pb are accurate and show unparalleled reproducibility of 90 ppm (2 SD) for ²⁰⁶Pb/²⁰⁴Pb. Similar reproducibility is achieved for 5 ng aliquots of USGS reference materials AGV-1 and BCR-1, indicating that sample matrix and ion exchange procedure have no adverse effect on data quality and that the analytical blank contribution is negligible for sample sizes down to 5 ng. With further reductions in blank levels, the double spike technique in combination with a 10¹³ Ω resistor for the collection of ²⁰⁴Pb allows high-precision Pb isotope data to be obtained when sub-ng quantities of Pb are available. This new analytical achievement has the potential to open a range of possibilities for research in cosmochemistry, high-precision U-Pb dating and microsampling of geological and archaeological materials.

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