

Optimisation of a current generation ICP-QMS and benchmarking against MC-ICP-MS spectrometry for the determination of lead isotope ratios in environmental samples

Abida Usman^{a,b}, E. Louise Ander^b, Elizabeth H. Bailey^a, Simon Nelms^c, Vanessa Pashley^b, Scott D. Young^a and Simon R. Chenery^b

Abstract

The precision and accuracy of lead (Pb) isotope measurements obtained from quadrupole-based mass spectrometers (ICP-QMS) are considered to be limited by a number of factors originating in different components of the instruments. In this study, experimental and instrumental protocols were optimised for determining lead isotope ratios in urban soil digests. Experimental measures included individual dilution of all samples and isotopic standards (SRM-981, NIST) to a single Pb concentration intended to produce an intensity which was high enough to negate blanks and interferences but low enough to ensure the detector operated only in pulse counting mode. Instrumental protocols included batch dead time correction, optimisation of dwell time and the number of scans employed and correction of mass discrimination by sequential application of both internal ($^{203}\text{Tl}/^{205}\text{Tl}$ ratio) and external (SRM-981, NIST) standards.

This optimised methodology was benchmarked against multi-collector mass spectrometer (MC-ICP-MS) measurements of Pb isotope ratios using replicate digest solutions of the same soil; but after these had been subjected to Pb separation using an ion-exchange procedure. On the assumption that MC-ICP-MS measurements are more accurate, small additive and multiplicative differences were observed in only the 4th decimal place. ANOVA was used to compare the precisions of the two techniques demonstrating equal precisions c. 0.08% for $^{207}\text{Pb}/^{206}\text{Pb}$, suggesting a sample heterogeneity limitation. By contrast, for $^{207}\text{Pb}/^{204}\text{Pb}$, the worst-case ratio, ICP-QMS had a 10-fold poorer precision, despite negligible interference from ^{204}Hg , implying an instrumental limitation. The study concludes that ICP-QMS can provide valuable source apportionment information for most Pb isotope ratios but further efforts should focus on improving assay of the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio.

Keywords: ICP-QMS, MC-ICP-MS, lead isotopes, soil, parameter optimisation

Introduction

Lead isotopes can be measured by a range of mass spectrometry techniques. Until fairly recently, thermal ionization mass spectrometry (TIMS) was the preferred choice for precise (0.001-0.01% RSD) measurement of Pb isotope abundances (1, 2). However, TIMS involves laborious sample preparation steps, such as separation of the analyte from the matrix into a highly purified form, involving extensive chemical treatment, and stringent optimisation of vaporisation and ionisation conditions of samples, with long analysis times (~45 minutes). These measurements are not only time consuming but also incur cost, rendering TIMS unsuitable when analysing large numbers of samples (3, 4). Inductively coupled plasma mass spectrometers (ICP-MS) are more appropriate for routine use with large sample numbers and are operationally simpler than TIMS (5); sample introduction is at atmospheric pressure and ionization of most elements is readily achieved. They are widely used for multi-element and isotopic analysis and are routinely capable of a precision (<0.05% RSD) comparable to that of TIMS for Pb isotopes. The term 'ICP-MS' covers a range of instruments which differ in their mass filter and detector systems. These include; those that are quadrupole-based (ICP-QMS) or high resolution, magnetic sector field-based (HR-ICP-MS) and those which can utilize single-collector (SC), multi-collector (MC), array detector (AD) or 'time-of-flight' (TOF) detectors (4, 6).

Quadrupole-based inductively coupled plasma - mass spectrometers (ICP-QMS) are the most commonly used ICP-MS instruments principally because they are relatively inexpensive to produce and support, and are fast and simple in terms of sample preparation, handling and operation. As a result, the number and availability of ICP-QMS instruments far outweigh MC-ICP-MS. However, in isotope studies, specifically when high precision ratio measurements are required, MC-ICP-MS is preferred over ICP-QMS and is considered the benchmark for accurate and precise isotope data (7). This is principally due to simultaneous measurement of all relevant isotopes, which effectively cancels out the effects of 'plasma flicker', and the flat-topped peaks produced in MC-ICP-MS, with their inherent resistance to instrument drift. This is in contrast to sequential measurement of isotopes on leptokurtic peaks in ICP-QMS (8-10). The sequential nature of the analysis in any single collector instrument renders the technique susceptible to variations in, for example, sample aerosol transport, RF power fluctuations and physical perturbations within the plasma itself (plasma flicker). In essence, any signal instability results in non-sample related variation in relative isotope abundances from one microsecond to the next. To achieve the ultimate high accuracy and precision that MC-ICP-MS is capable of, does pose some extra constraints, these include the need to separate the element of interest not just to ensure minimising any spectral interferences but also to minimise matrix effects,

including mass bias. However, this is rarely used in ICP-QMS studies as the aims in particularly environmental research require the analysis of large numbers of samples, in the minimum time.

The accuracy and precision of isotopic ratios measured through ICP-QMS are considered limited by 'noise' (variation in signal intensity). This originates from varying conditions throughout the ion pathway, including the ion source (i.e. sample introduction system and the plasma itself), the interface region, the collision/reaction cell (if used), the quadrupole mass filter and the detector (9, 11). Variation in the efficiency of nebulisation and sample transport produces low frequency noise (12); as a result it is common in MC-ICP-MS studies to use manual sample introduction with naturally aspirating nebulisers. In the ICP ion source, noise is produced due to 'plasma flicker' that is caused by changes in energy transfer from plasma to analyte atoms. In addition to mainly random fluctuation caused by these instrumental factors, variation in 'mass bias' is a major source of systematic error, responsible for deviation of measured intensity ratios from true isotopic ratios (5, 13). The largest mass discrimination effect in ICP-MS is observed due to space charge effects (9), which occur between the plasma torch and the skimmer cone, and cause differential deflection of lighter ions (11, 14). Thus the ratio of heavier to lighter isotopes increases in the ion beam passing through the skimmer cone (15); therefore it is common in high precision isotope ratio studies to separate the element of interest to minimise these effects. Woodhead (16) , used this variability in mass bias with matrix to propose an improved Tl bias correction by "calibrating" the small difference in mass bias for Tl and Pb. It also has been reported that mass discrimination induced by space charge effects should be minimal in magnetic sector instruments due to high accelerating voltages however this is not always the case compared to the low extraction voltages, behind the skimmer cone, in a quadrupole instrument. Heumann, Gallus (15) showed that mass discrimination for bromine isotopes was smaller than for a quadrupole but was still significant leading to the suggestion that discrimination can occur between the plasma torch and the skimmer cone. Random noise originating in the ICP ion source and quadrupole mass filter is also responsible for imprecision in measuring isotope ratios because of the sequential measurement required in ICP-QMS and, to a lesser extent, single collector HR-ICP-MS.

In ICP-QMS, a discrete dynode detector is normally used which necessitates a compromise between employing large analyte concentrations to improve the counting statistics of minor isotopes while working below the point at which the detector trips to analogue mode for major isotopes. This may push the intensities of high abundance isotopes into the zone in which the detector dead time correction has a significant effect. Therefore, accurate *dead time correction* is necessary for precise measurement of isotopic ratios especially when very different isotope abundances are involved (e.g.

$^{208}\text{Pb}/^{204}\text{Pb}$) (15). The age of the detector is also considered an important factor in influencing dead time (8, 10, 17, 18).

Different strategies have been employed for precise determination of Pb isotopes using different types of mass spectrometers. To minimise low frequency noise sources, Furuta (19), Begley and Sharp (11) and Monna, Loizeau (20) all recommended cycling the ICP-QMS as rapidly as possible through the measured masses. Quétel, Thomas (9) used a factorial design approach to investigate the simultaneous effects of different factors (dwell time, number of sweeps/replicates, number of replicates/analysis and time factor) on the precise determination of Pb isotopes, including ^{204}Pb . To reduce the effects of mass bias in multi-collector, quadrupole and other mass spectrometers Ingle, Sharp (21) demonstrated mass bias correction by modelling the underlying instrument response function in MC-ICP-MS. Reuer, Boyle (22) revealed the importance of both external and internal correction for mass bias in MC-ICP-MS to improve measurements of Pb isotopes in natural samples, i.e. marine carbonates and sea water. Simultaneous assessment of several optimising parameters have also been undertaken in some studies. For regular monitoring of dead time and mass discrimination, Appelblad and Baxter (13) presented a linear model for the simultaneous determination of dead time and mass bias correction factor in double focusing sector field mass spectrometry (SF-ICP-MS) for regular monitoring of dead time and mass discrimination. This had the advantage of utilizing more time on the isotopes of interest. Different methods for calculating accurate detector dead times have also been demonstrated to improve the accuracy of isotopic ratios (10, 17).

In this study, the ability of a current-generation ICP-QMS instrument to determine Pb isotope ratios in urban soil samples was tested through a comparison with MC-ICP-MS analysis. The primary aim of this study was to refine protocols intended to maximise the accuracy and precision of ICP-QMS determination of Pb isotope ratios to enable soil Pb source apportionment. The optimised methodology was benchmarked against MC-ICP-MS measurements on the same sample material.

Experimental

Preparation of samples

Composite urban surface (0-15 cm) soil samples (n=11) from a range of sites in Wolverhampton and Nottingham were used. These had been sampled previously as part of a Natural Environmental Research Council (NERC) project, under the URGENT programme, conducted by a research consortium from Imperial College, London, NERC Isotope Geosciences Laboratory, British Geological Survey and University of Nottingham between 1999 and 2002 (Table 1).

Table 1 Soil samples from Nottingham (Ng) and Wolverhampton (Wv)

Sample	Total Pb content mg kg ⁻¹	Land use	Grid ref
Ng2	385	Churchyard	455280 338770
Ng5	434	Domestic garden	457360 342370
Ng7	340	Grassland (imported)	458500 339110
Ng8	339	Grassland (racecourse)	459710 339170
Ng9	146	Vegetated colliery spoil heap	453570 344310
Ng12	893	Disused factory	455760 338550
Wv2	47.6	Grassland (Golf course)	388450 300860
Wv12	134	Grassland	388240 295750
Wv19	40.6	Grassland	395150 299140
Wv21	27.9	Brownfield	393960 299860
Wv29	271	Deciduous woodland	391680 300080

Soil samples were air-dried and sieved to <2 mm and a small subsample of the archived soil (c. 2.0 g in triplicate) was ground in an agate ball mill (Model PM400, Retsch GmbH & Co., Germany). Complete digestion of 0.2 g samples was achieved in PFA vials in a 48-place Teflon-coated graphite block digester (Model A3, Analysco Ltd, Chipping Norton, UK) using a mixed acid digestion process i.e., HNO₃ (68%), HClO₄ (70%) and HF (70%). The dried digestate was dissolved in 68% HNO₃ and diluted to 50 mL with Milli-Q water (18.2 MΩ cm). Prior to analysis of total Pb concentration by ICP-QMS a further 1:10 dilution with 2% HNO₃ was undertaken. Internal standards were introduced to the sample stream via a separate T-line including Ge (50 µg L⁻¹), Rh (20 µg L⁻¹) and Ir (10 µg L⁻¹) in 2% HNO₃ and multi-element standards (0, 20, 40, 100 µg L⁻¹) were used to determine the Pb concentration (CLMS-2; CertPrep™). Three procedural blanks were also included in each digestion batch for quality assurance. All samples were analysed with the ICP-QMS operating in 'kinetic energy discrimination' (KED) mode, with He as the cell gas, to eliminate polyatomic interferences e.g. ¹⁹¹Ir¹⁶O, ¹⁶⁷Er⁴⁰O and ²⁰⁶Pb¹H on ²⁰⁷Pb.

(i) Dilution of samples for Pb isotopes measurement (ICP-QMS)

The precision of Pb isotope ratio measurements generally improves with increasing Pb concentration as counting statistics improve (19). However, at high concentrations the ion counter detector used with the ICP-QMS employed in this study trips to an analogue signal, resulting in non-linearity caused

by measuring isotopes in different detector modes, with added uncertainty due to the application of a gain correction between the two detector types (20, 23). Thus, individually tailored dilutions of each sample digest were carried out, with 2% HNO₃, using previously quantified total concentrations of Pb. The objective was to work with near identical concentrations (~15 µg L⁻¹) of all samples and reference materials (SRM-981, NIST Pb wire). This approach had the advantages of (i) reducing the effect of any error in the dead time correction factor and (ii) ensuring that the intensity of the ²⁰⁴Pb signal was as high as possible (c. 27 X 10³ cps) while keeping the ²⁰⁸Pb signal below the detector trip point (c. 1 X 10⁶ cps). The blank contribution for each isotope although subtracted during analysis was only 0.76% of the sample Pb and had an insignificant effect on results.

(ii) Lead separation method for Pb isotope measurement by MC-ICP-MS.

Variations in mass bias and small interferences are known to impact on data quality in MC-ICP-MS isotope ratio determinations (24). Therefore, prior to the measurement of Pb isotopes in soil digests, a preliminary separation of Pb was performed using an anion exchange (AG1-X80) column (25). Aliquots, containing an estimated 200 ng of Pb from each digest, were heated overnight to dryness in PFA vials on a hotplate. An aliquot of HBr (2 mL) was then added to each vial and left overnight again to solubilise the sample. Sample Pb was separated using anion exchange resin columns (2 mL, AG1-X80). The resin was pre-cleaned with MQ quality (>18 MΩ cm) water followed by 6 M HCl and then equilibrated by washing the column with 2 mL 1 M HBr. All samples were then passed through individual columns adsorbing the sample Pb as PbBr₄²⁻ ions. Major cations were then eluted from the columns with further HBr. The sample Pb was then eluted using 8 mL of 6 M HCl back into its original vial. Concentrated nitric acid (0.2 mL) was added to each vial as an oxidising agent and the contents evaporated to dryness on a hotplate, overnight, at 90°C. Prior to analysis by MC-ICP-MS each sample was diluted to c.5-10 ng mL⁻¹ and spiked with Tl (c. 5-10 ng mL⁻¹) for instrumental mass bias correction with the aim of achieving less than the maximum 10V signal on ²⁰⁸Pb and ²⁰⁵Tl.

Instrumentation and optimisation procedures

ICP-QMS

At the University of Nottingham Pb isotope ratios were determined by current generation ICP-QMS (Model iCAP Q; Thermo Scientific, Bremen, Germany). All samples were analysed with the ICP-QMS operating in 'kinetic energy discrimination' (KED) mode, with He as the cell gas, to reduce potential polyatomic interferences. Additionally, in the past it has been suggested that the use of a collision gas may "thermalize" the ion beam and improve isotope ratio precision (26). Samples were introduced from an autosampler incorporating an ASXpress™ rapid uptake module (Cetac ASX-520, Teledyne Technologies Inc., Omaha, NE, USA), with a 5 mL sample loop, through a perfluoroalkoxy (PFA)

Microflow PFA-ST nebuliser (Thermo Fisher Scientific, Bremen, Germany). The typical operational parameters selected for measurement of Pb isotopic ratios are given in Table 2. The settle/idle time was not optimised as this is hard-wired into the software of this instrument and not readily available to the user.

Table 2 Operational parameters selected for measurement of Pb isotopic ratios using ICP-QMS

Detector acquisition mode	Pulse counting mode
Dead time	36.8 ns
Dwell time	10 ms
Number of runs	10
Number of scans	10000
Isotopes measured	^{202}Hg , ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{203}Tl and ^{205}Tl
Points per peak	1
Number of replicates	3
Analysis time per sample	16 minutes

MC-ICP-MS

Lead isotope analysis was conducted at the NERC Isotope Geosciences Laboratory (BGS, Keyworth, U.K.) using a Nu Instruments, Nu Plasma, MC-ICP-MS (Multi-Collector Inductively Coupled Plasma Mass Spectrometer). Prior to analysis, each sample was spiked with a Thallium (Tl) solution, to enable correction of instrument induced mass bias. Samples were then introduced into the instrument via an ESI PFA50 nebuliser attached to a de-solvating unit, (Nu Instruments DSN 100). For each sample, five ratios were simultaneously measured ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$) using the instruments array of Faraday detectors. The collector configuration used is illustrated in Table 3. Each individual acquisition consisted of 3 blocks of 25 cycles, with a 5-second integration time per cycle, following a 60 second de-focused baseline (c. 7 min. per acquisition). The measured Tl ratio was used to make an exponential correction for instrument induced mass bias effects on both Pb and Hg isotopes, based on an assumed $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of 2.3890. Hg was measured at amu 202 and a proportionate amount subtracted from the ion beam at amu 204, based on an assumed $^{204}\text{Hg}/^{202}\text{Hg}$ ratio of 0.229883.

The precision and accuracy of the method was assessed through repeat analysis of a SRM-981, NIST Pb reference solution, (also spiked with Tl). The average values obtained for each of the mass bias corrected SRM-981, NIST ratios were then compared to the known values for this reference material (27): $^{206}\text{Pb}/^{204}\text{Pb} = 16.9417 \pm 29$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4996 \pm 31$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.724 \pm 09$, $^{207}\text{Pb}/^{206}\text{Pb} = 0.91488 \pm 08$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677 \pm 24$; Precision = ppm \pm 2sd. All sample data were subsequently normalised according to the relative deviation of the measured reference values from the true values.

The analytical errors for each of the sample ratios were propagated relative to the reproducibility of the SRM-981, NIST to take into account the errors associated with the normalisation process.

Table 3 Configuration of the Nu Plasma HR 'Zircon' collector block, used for Pb isotope analysis

High 4	High 3	High 2	High 1	Axial	Low 1	Low 2
²⁰⁸ Pb	²⁰⁷ Pb	²⁰⁶ Pb	²⁰⁵ Tl*2	²⁰⁴ Pb ²⁰⁴ Hg	²⁰³ Tl*2	²⁰² Hg*1

*1 Measured to allow for the correction of the isobaric interference of ²⁰⁴Hg on ²⁰⁴Pb.

*2 Measured to allow for the correction of instrumental mass bias.

Procedures for optimising measurement of Pb isotopes using ICP-QMS

Evaluation of detector dead time correction factor

A dead time correction factor (dtcf) was determined, according to a method described by Nelms, Quétel (17), for the isotopic ratios: ²⁰⁴Pb/²⁰⁸Pb, ²⁰⁶Pb/²⁰⁸Pb and ²⁰⁷Pb/²⁰⁸Pb. Values of dtcf were measured from intensity ratios determined across a range of Pb standard solutions (i.e. 0, 2, 4, 6, 8....22 µg L⁻¹) prepared from SRM-981, NIST in 2% HNO₃. Data from samples providing higher count rates for ²⁰⁸Pb were used so that the detector was more likely to be close to saturation; we also wanted to investigate the validity of measurements up to the point where the detector tripped to analogue signals.

The dtcf was initially set to zero ns. An isobaric correction factor for ²⁰⁴Hg was determined from measurement of the signal at m/z = 202 (²⁰²Hg). This correction was negligible for samples as Hg would be efficiently evaporated from the sample solutions during the high temperatures of the digestion procedure. Intensity values (cps) were measured using a quadrupole dwell time of 10 ms with 200 sweeps and 20 separate integrations to give 4000 quadrupole visits to each isotope per sample and a total signal integration time per isotope of 40 seconds. Initially, a blank correction was made to all raw Pb isotope intensities (I_{sample} – I_{blank}). Sample intensity values were corrected using Eq. 1, following optimisation of the dtcf value (28).

$$I_{\text{corr}} = \frac{(I_{\text{sample}} - I_{\text{blank}})}{1 - (I_{\text{sample}} - I_{\text{blank}})\text{dtcf} \cdot 10^{-9}} \quad (1)$$

The value of dtcf was optimised by determining the slope of individual isotope intensity ratios (i.e. $^{204}\text{Pb}/^{208}\text{Pb}$) against the intensity signal for ^{208}Pb (cps) and varying the value of dtcf until the value of the slope squared (slope^2) was minimised. This was undertaken using the Microsoft Excel *Solver* function. The optimised values of dead time calculated for Pb isotopic ratios were 37.4, 36.7 and 36.3 ns for $^{204}\text{Pb}/^{208}\text{Pb}$, $^{206}\text{Pb}/^{208}\text{Pb}$ and $^{207}\text{Pb}/^{208}\text{Pb}$ ratios respectively. The values of dtcf calculated did not change systematically with mass difference between the isotopes and they were independent of mass and analyte concentration as illustrated in Fig. 1 for the isotopic ratio $^{204}\text{Pb}/^{208}\text{Pb}$. An average value of dead time correction was calculated (i.e., 36.8 ns) and set within the instrument software. Values of dead time were in good agreement with previous studies (20, 29) and close to the manufacturer's factory-set value of 40 ns. Subsequently, all analytical sessions were preceded by measurement and re-setting of detector dead-time.

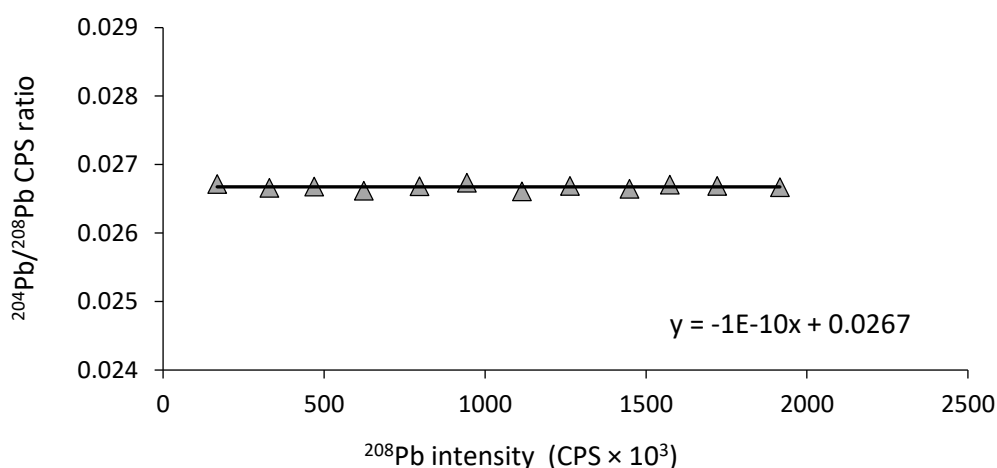


Figure 1. Isotopic count ratios (CR) $^{204}\text{Pb}/^{208}\text{Pb}$ vs ^{208}Pb intensity measurements (cps) at the optimised value of dtcf.

Mass bias correction

Prior to mass bias correction, Pb isotope intensities were corrected for an isobaric interference from ^{204}Hg , through measurement of ^{202}Hg , and for operational blanks. The resulting data was then corrected for mass bias using both *proxy internal* and *external* standards. Thallium ($2\text{ }\mu\text{g L}^{-1}$) was used as an internal standard because its isotopic masses (i.e., ^{203}Tl and ^{205}Tl) are sufficiently close to those of the Pb isotopes that it can be used as a proxy for continuous monitoring of mass discrimination in individual samples (22). Thallium was continuously delivered to the nebulizer on a separate line and the bias per unit mass (ϵ) determined from the measured $^{205}\text{Tl}/^{203}\text{Tl}$, when compared to the known, 'true', value for this ratio i.e., 2.3871 (1).

Three equations (i.e., linear, power and exponential models; equations 2-4 below) are generally used to estimate the mass discrimination correction factor (or 'K-factor') for a pair of Pb isotopes when Tl is used as an internal standard (15, 30). Most previous studies conducted using MC-ICP-MS have favoured a power (Eq 3.) or exponential (Eq 4.) equation over a linear relation (Eq. 2) on grounds of precision for internal standardisation (1, 15, 30). However, a linear model (Eq. 2) is more commonly used for mass discrimination correction for quadrupole mass analysers as this has been found to be a sufficiently accurate model as their precision is rarely good enough to discriminate between models (31).

$$K = 1 + (\Delta m \varepsilon) \quad (2)$$

$$K = (1 + \varepsilon)^{\Delta m} \quad (3)$$

$$K = \exp(\Delta m \varepsilon) \quad (4)$$

In equations 2 – 4, Δm is the mass difference between two Pb isotopes; K is the K-factor for the ratio of those two isotopes and ε is the bias per unit mass determined for the ratio $^{205}\text{Tl}/^{203}\text{Tl}$. Preliminary data for Pb isotopes were processed using the linear (Eq. 2), power (Eq. 3) and exponential (Eq. 4) equations to assess the difference in mass bias correction factor, but very similar results were observed using the three approaches. Therefore, the simplest linear correction was used in this study and applied to all samples and the NIST SRM-981 Pb reference material.

Thallium-corrected data was then further normalised using the NIST SRM-981 Pb reference material to allow for any element-specific drift in instrument sensitivity during the experiment. The refined K-factor for each sample was calculated using interpolated values of the K-factor for SRM-981, NIST samples ($15 \mu\text{g L}^{-1}$) run every 10th sample. The magnitude of the K-factor correction using Tl varied between 0.5% for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio to 2% for the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio, reflecting the greater correction for mass bias for wider spaced isotopes. The subsequent SRM-981 K-factor corrections varied between 0.25% and 0.5% and were not mass dependent, probably reflecting differences in Pb-Tl responses, that others have addressed using artificially modified Tl isotope ratios. A table of these K-factors for both correction stages are given in Electronic Appendix Table 1.

Quadrupole dwell time

Improvement in precision of Pb isotope ratio determinations can be achieved by decreasing the quadrupole dwell time in order to reduce low frequency noise in the plasma (11), but this may result in inaccurately jumping to the mass peak maximum at extremely fast scanning rates (low dwell times) (19) and additionally becomes a state of diminishing returns as the quadrupole settle time becomes large relative to the data acquisition time. This suggests that there should be an optimum isotope

dwelt time at which counting precision is greatest. The influence of quadrupole dwelt time was tested using a solution of SRM-981, NIST ($5 \mu\text{g L}^{-1}$) spiked with Tl ($1 \mu\text{g L}^{-1}$). The test solution was aspirated directly and the precision of Pb isotopic ratio measurements (% RDS) determined for a range of dwell times. Ten separate integrations were set with the number of sweeps changed inversely to increasing isotope dwell time (1-15 ms) to retain a constant overall signal acquisition time. Values of %RSD for individual Pb isotopic ratios were plotted against dwell time.

Figure 2 shows that the variation in precision across the range of dwell times was neither systematic nor significantly different between dwell times, with the single outlier of ^{204}Pb ratios at 9 ms. It was therefore decided to retain a dwell time of 10 ms for further studies as suggested in the literature (32).

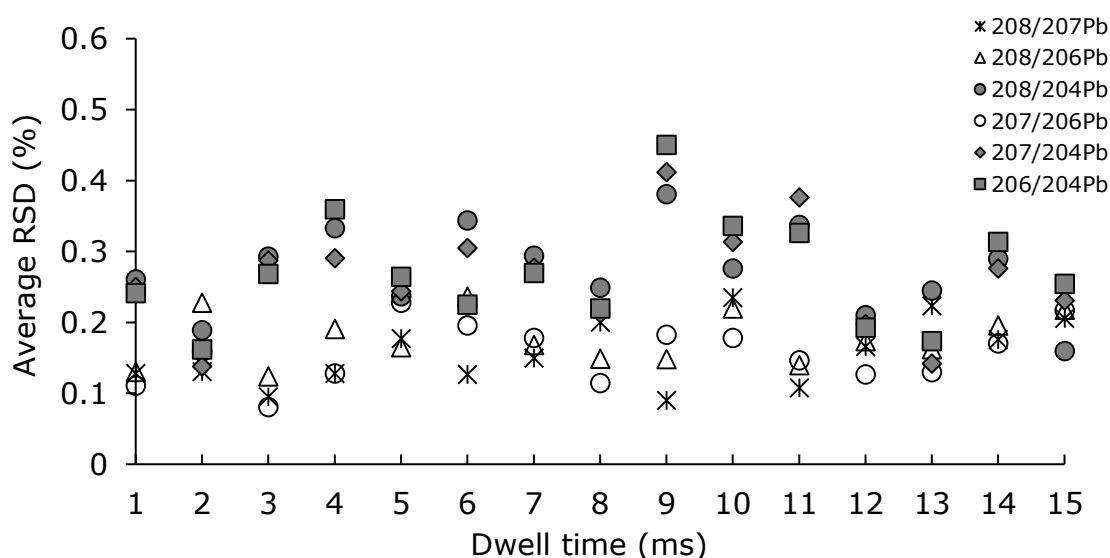


Figure 2. Average residual standard deviation expressed as a proportion (%) of Pb isotope ratios against dwell time (ms) whilst retaining a constant total acquisition time.

Optimising the number of scans (quadrupole peak visits)

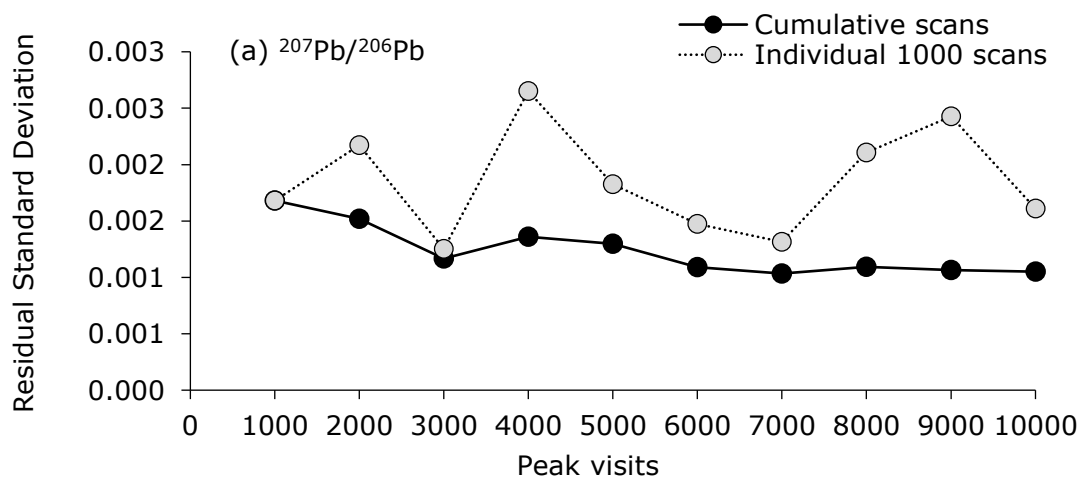
To optimise the number of scans (peak visits by the quadrupole), 10 separate runs with 1000 scans per run was selected and the number of points per peak was set to one (dwell time 10 ms). The total analysis time for each sample (SRM-981, NIST) was approximately 16 minutes. To determine the effects of the number of scans on Pb isotopic ratios determination, each of the 10 runs of 1000 scans was processed (i) separately and (ii) cumulatively i.e. using 1000, 2000 scans etc. A comparison of the resulting data is shown in Fig 3. The error for different Pb isotopic ratios (i.e., $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$) was assessed by comparing residual standard deviation values against the multi-

collector data. Results were calculated by taking 10 measurements of 1000 peak visits and calculating the residual standard deviation from those 10 values. Residual standard deviation (RSD) was calculated from multi-collector data Eq. 5,

$$RSD = \sqrt{\frac{\sum (IR_{MC} - IR_{Quad})^2}{df}} \quad 5$$

where IR_{MC} and IR_{Quad} are isotope ratio measurements from the multi-collector and quadrupole instruments and df represents degrees of freedom.

The data processed using individual groups of 1000 scans showed relatively high and variable residual standard deviation values for all isotopic ratios (grey circles). By contrast, data processed in a cumulative way showed better precision and consistency for all three isotopic ratios. Precision generally increased with increasing number of scans as shown in Fig 3. (a-d). For the current study we decided to use 10,000 scans to try to minimise variation due to counting statistics, although Fig .3 suggests this could potentially be reduced to 6000 scans to save time without significant loss of precision. For example, if the precision of the ratios is solely based on counting (Poissonian) based statistics, then the standard deviation of the number of counts measured is the square root of the mean number of counts. This would result in a $\sqrt{10} = 3.162$ improvement in ratio precision, when using 10,000 ratios rather than 1,000. Whereas acquiring 10,000 ratios rather than 6,000 would produce a more modest precision improvement of $\sqrt{(10,000/6,000)} = 1.291$. This potentially being swamped by other normally distributed noise sources.



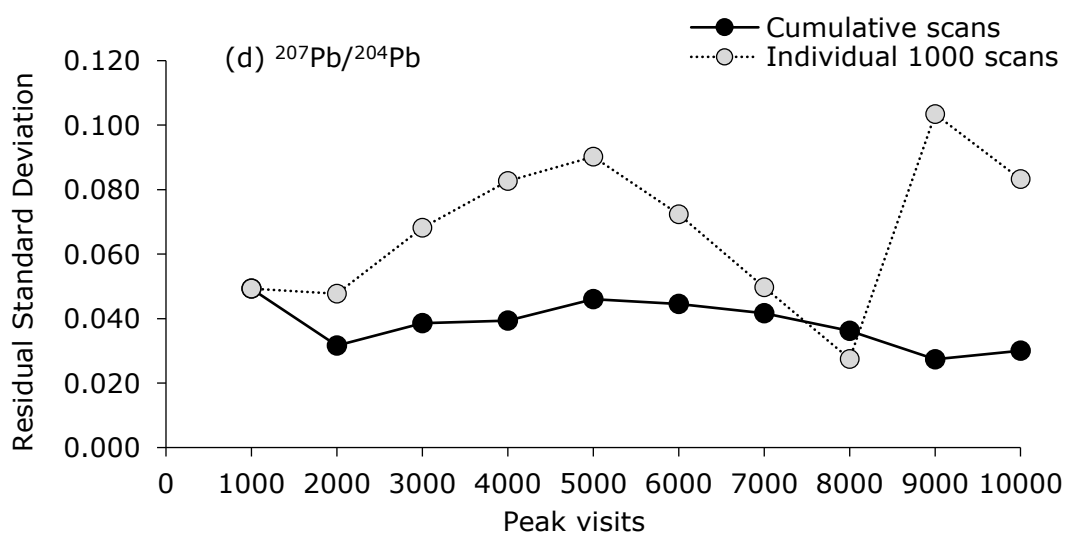
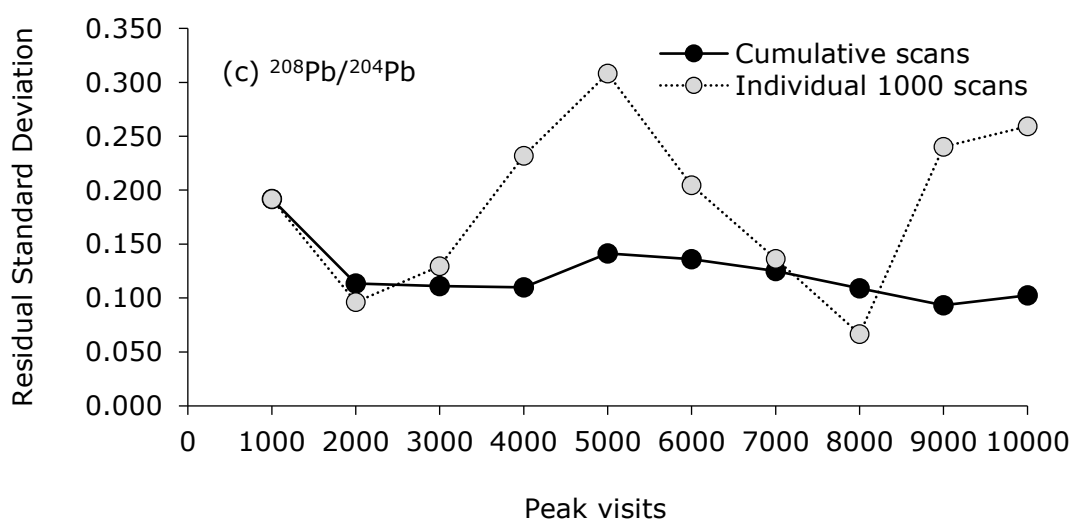
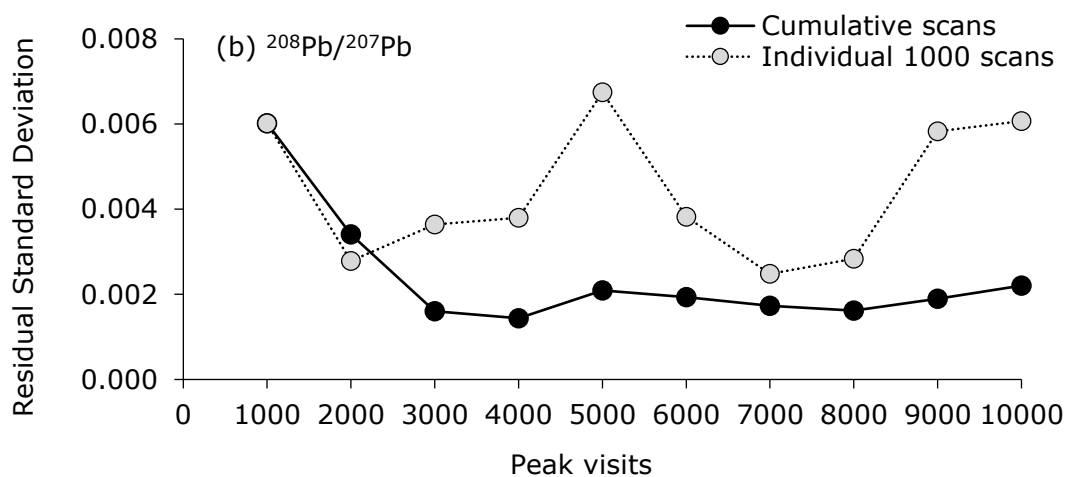
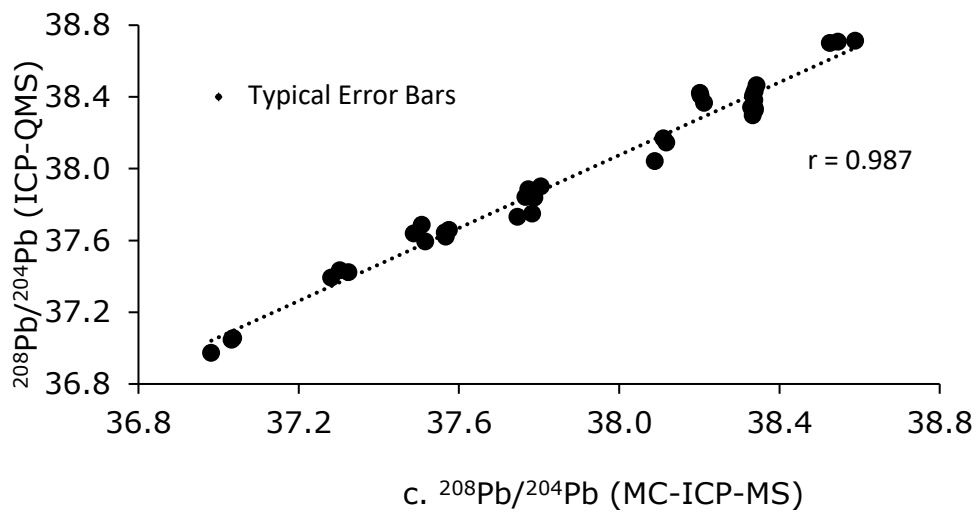
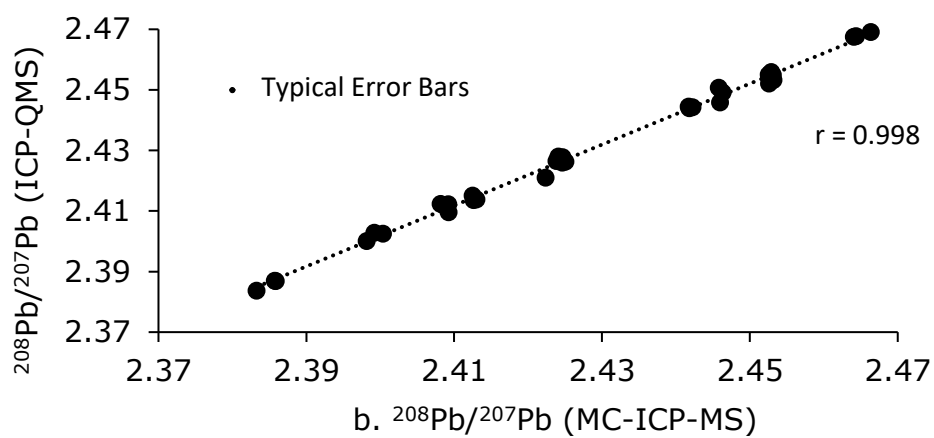
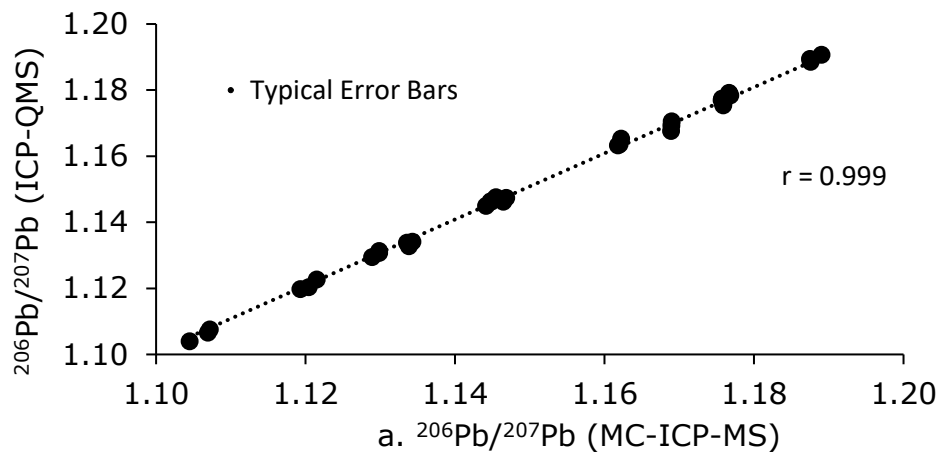


Figure 3. Values of residual standard deviation, comparing ICP-QMS with MC-ICP-MS, for Pb isotope ratios (a) $^{207}\text{Pb}/^{206}\text{Pb}$, (b) $^{208}\text{Pb}/^{207}\text{Pb}$, (c) $^{208}\text{Pb}/^{204}\text{Pb}$, and (d) $^{207}\text{Pb}/^{204}\text{Pb}$ against the number of quadrupole scans (peak visits).

Results and discussion

Comparison of Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$) measured by ICP-QMS and MC-ICP-MS

Following optimisation of the Pb isotopic ratios measurement protocol, the processed data for diluted soil sample digests analysed with ICP-QMS (10,000 scans) were compared to equivalent data for chemically separated Pb measured by MC-ICP-MS. Each of the 3 digestions for an individual sample were treated as a separate data point to achieve the most direct comparison of the two techniques. An excellent correlation ($r=0.999$ and $r=0.998$; $n=36$) was observed for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotopic ratios with slope values of 1.0008 and 1.0006 respectively shown in Fig 4. (a and b). The correlation observed for the $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratio was also good, albeit a little weaker than for the other ratios (Fig 4. c; $r=0.987$, slope=1.0017). This is understandable given that: (i) there is a greater dependence on mass bias because of the mass difference of 4 amu; (ii) ^{204}Pb (isotopic abundance = 1.4%) produces a lower signal giving poorer counting statistics; (iii) the large difference in isotopic abundance results in increased vulnerability to errors in dead time correction and (iv) the need for Hg correction on ^{204}Pb , which further compromises the measurement uncertainty. Of these potential effects, the dominant and unavoidable one will be number (ii), poorer statistics from the isotopic abundance of ^{204}Pb c.1.4% compared to the next smallest isotope ^{207}Pb c.22.1%; this being a factor of c.3.4. All of the other effects are either minimised by optimisation, (i) and (iii), or, in the case of (iv), insignificant for samples prepared in the current study by HF digestion.



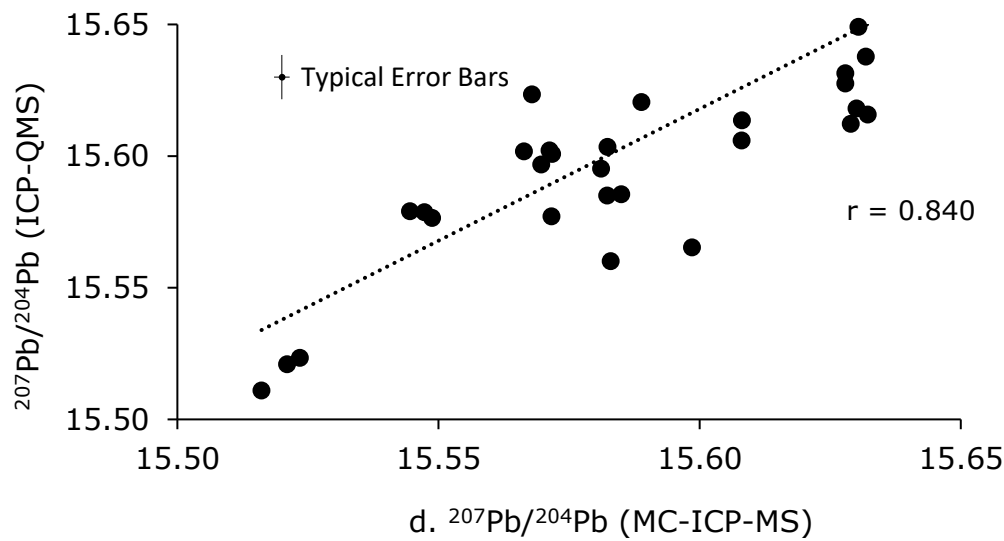


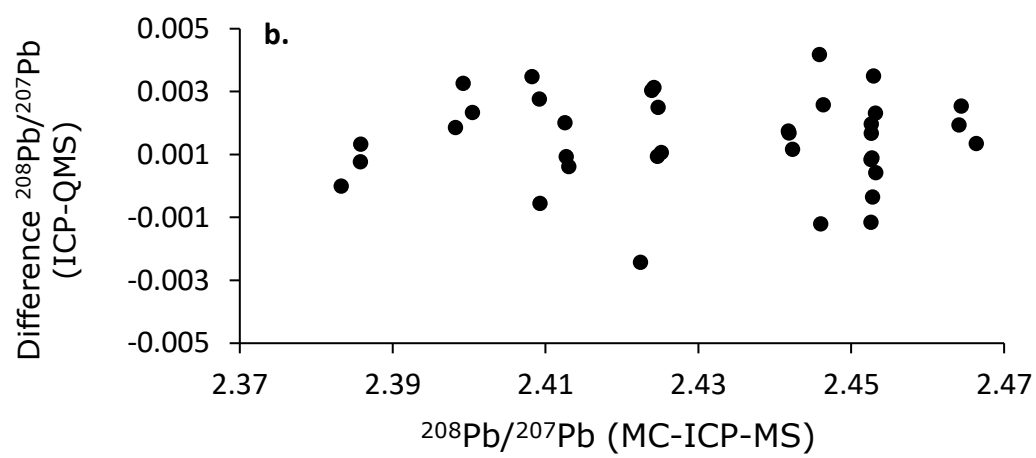
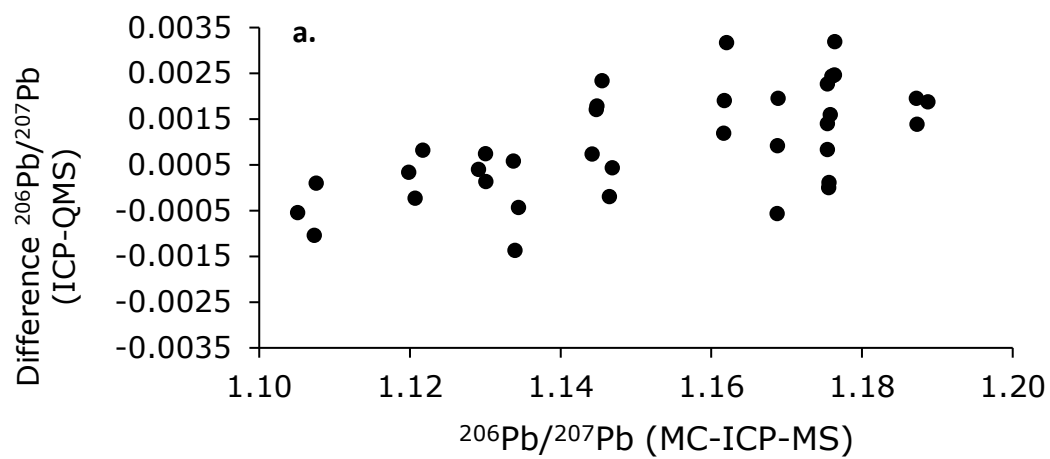
Figure 4. Correlation of Pb isotope ratios (a) $^{206}\text{Pb}/^{207}\text{Pb}$, (b) $^{208}\text{Pb}/^{207}\text{Pb}$, (c) $^{208}\text{Pb}/^{204}\text{Pb}$ and (d) $^{207}\text{Pb}/^{204}\text{Pb}$ measured using quadrupole (ICP-QMS) and multi-collector (MC-ICP-MS) instruments.

With such strong correlations it is instructive to examine the difference between the accuracy/precision of the benchmark MC-ICP-MS and the ICP-QMS data (Fig 5. a- d), assuming that the MC-ICP-MS has no error for the purposes of this comparison. There may be two sources of error between the datasets: *additive* i.e. a simple offset value constant for all samples, and *multiplicative* i.e. a change in value proportional to the isotope ratio measured. For $^{206}\text{Pb}/^{207}\text{Pb}$ (Fig. 5a) there was a clear increase in error with increasing isotopic ratio, indicating a multiplicative bias between ICP-QMS and MC-ICP-MS. For $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ this was not apparent. A regression analysis of ICP-QMS on MC-ICP-MS was made and tested for significance of the slope being different to 1 for all ratios shown in Table 4. All slope values were statistically different from 1 except $^{208}\text{Pb}/^{206}\text{Pb}$; however only in the 4th significant figure. To account for the effect of the very narrow range of isotope ratio values, an intercept between the ICP-QMS and MC-ICP-MS data was estimated by correcting the ICP-QMS data for the slope, then calculating the difference between the two data sets. The median difference was calculated (Table 4) to avoid outliers biasing the estimate. In terms of impact, the offset for $^{208}\text{Pb}/^{204}\text{Pb}$ ratio was the most significant with an absolute value of 0.02, equivalent to approximately 0.04% of the median $^{208}\text{Pb}/^{204}\text{Pb}$ ratio.

As each original soil sample was digested and analysed separately 3 times there was an opportunity to test 'fitness for purpose' for the whole method from digestion to ICP-QMS and MC-ICP-MS measurement. This was achieved using analysis of variance (ANOVA) to separate the total variance of the dataset into the analytical variance and the true variance between samples; where the analytical variance is a combination of the digestion variance and the measurement variance.

In evaluating the quality of data produced by the two techniques the first comparison is the within-sample analytical precision (as measured by RSD %) of the ICP-QMS with that of MC-ICP-MS (Table 5). If we assume that the MC-ICP-MS inherently has a better measurement precision but with the within sample precision essentially being equal between the techniques, then we must assume that the digestion process has limited our analytical precision. For example, for $^{207}\text{Pb}/^{206}\text{Pb}$ values of RSD for ICP-QMS and MC-ICP-MS were 0.09% and 0.07%, respectively, which suggests the data were digestion heterogeneity limited. By contrast, for $^{207}\text{Pb}/^{204}\text{Pb}$ the greater values for ICP-QMS (0.13%) compared to MC-ICP-MS (0.02%) suggests that the precision is limited by instrumental factors. This is supported by quantifying if within sample variance is different between ICP-QMS and MC-ICP-MS using the F-statistic. This statistic demonstrated that there was no difference in precision between the two instruments for $^{207}\text{Pb}/^{206}\text{Pb}$; but very significant differences for $^{207}\text{Pb}/^{204}\text{Pb}$ (Table 5). This implies that there is no advantage in using MC-ICP-MS, and chemical separation of Pb, for determination of $^{207}\text{Pb}/^{206}\text{Pb}$ ratios but the converse is true for $^{207}\text{Pb}/^{204}\text{Pb}$. This is qualified by consideration of the mass of Pb required for this comparison. In the current study, typical of many environmental investigations, the mass available is not a limiting factor and the equivalence of capability for $^{207}\text{Pb}/^{206}\text{Pb}$ ratios holds. However, in other applications where the mass of Pb available may be limited, the greater sensitivity of the MC-ICP-MS (a factor of 5-10 fold), provides a clear advantage, even for $^{207}\text{Pb}/^{206}\text{Pb}$ ratios.

The ANOVA, via the F-statistic, can be further used to test, for each isotope ratio, the power of the analytical technique to discriminate between samples. The greater the ratio of the “between samples” variance and the “within sample” variance which is the F-statistic, the better the discrimination i.e. when the ratio falls below the F_{crit} value we have no discrimination. For $^{207}\text{Pb}/^{206}\text{Pb}$, a variance ratio of 615 for ICP-QMS implies that we can readily discriminate between samples; for $^{207}\text{Pb}/^{204}\text{Pb}$ with a variance ratio of 6, this was not the case, as this is barely above the F_{crit} of 2.78. Thus, values of $^{207}\text{Pb}/^{204}\text{Pb}$ ratio measured by ICP-QMS (the lowest F-value), will have little resolving power between samples and any further analytical improvements should focus on determination of this isotopic ratio. By comparison, the variance ratios for these isotope ratios by MC-ICP-MS were 1123 and 137 respectively, suggesting that MC-ICP-MS can be readily used for all isotope ratios to differentiate between samples.



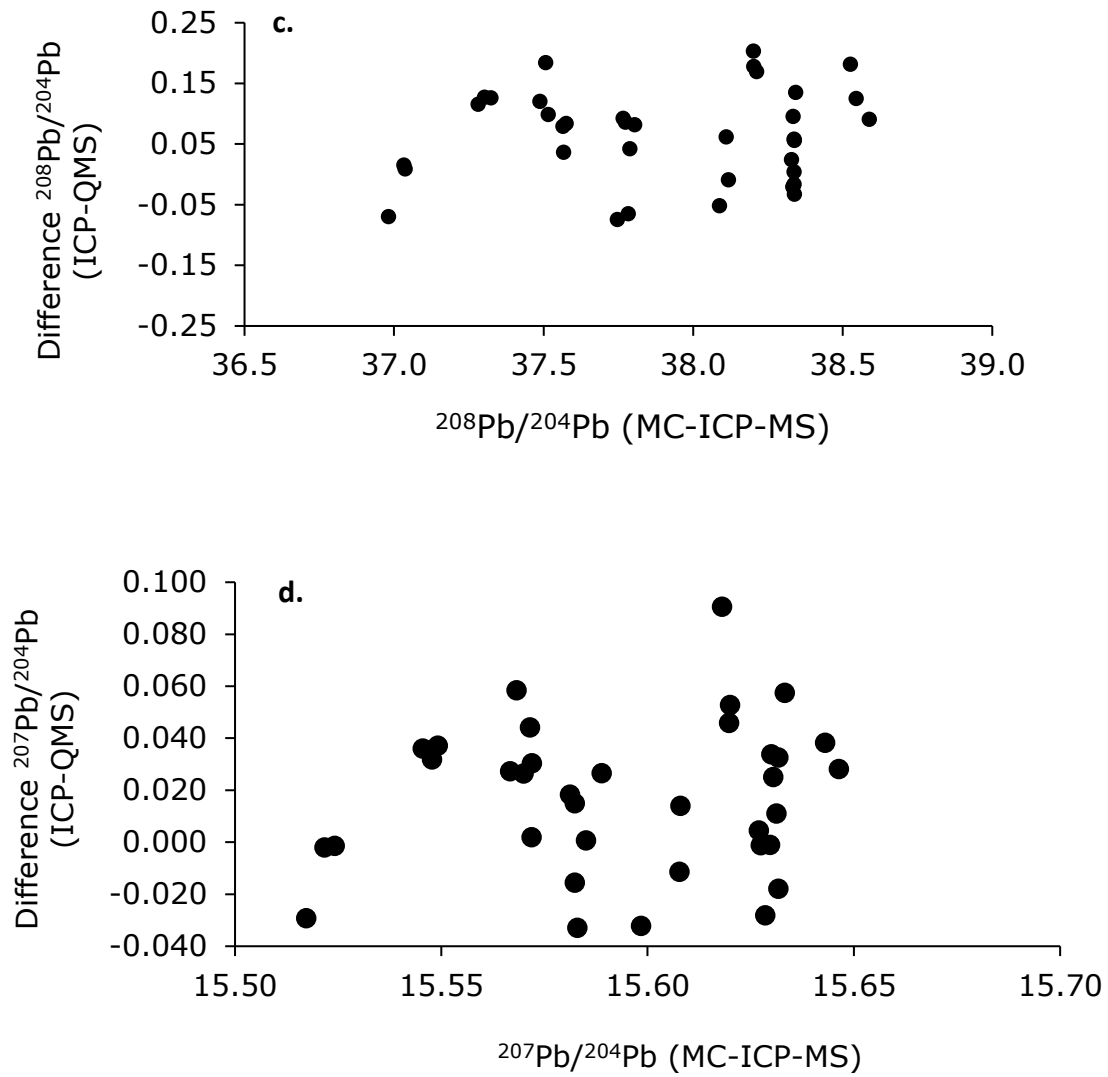


Figure 5. Difference between the benchmark MC-ICP-MS data and the difference between ICP-QMS and MC-ICP-MS (a) $^{206}\text{Pb}/^{207}\text{Pb}$, (b) $^{208}\text{Pb}/^{207}\text{Pb}$, (c) $^{208}\text{Pb}/^{204}\text{Pb}$ and (d) $^{207}\text{Pb}/^{204}\text{Pb}$.

Table 4 Evaluation of significance of slope (multiplicative) and offset (additive) when regressing the difference between measured ICP-QMS and MC-ICP-MS against MC-ICP-MS ratios, showing the significant differences occurring in the offset for $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios.

Ratio	Slope	95% Confidence interval	Median Offset
$^{207}\text{Pb}/^{206}\text{Pb}$	0.9992	0.0003	0.00007
$^{206}\text{Pb}/^{207}\text{Pb}$	1.0009	0.0003	-0.0001
$^{208}\text{Pb}/^{206}\text{Pb}$	0.9998	0.0004	0.0001
$^{208}\text{Pb}/^{207}\text{Pb}$	1.0006	0.0002	0.0002
$^{206}\text{Pb}/^{204}\text{Pb}$	1.0019	0.0006	0.0008
$^{207}\text{Pb}/^{204}\text{Pb}$	1.0011	0.0006	0.0045
$^{208}\text{Pb}/^{204}\text{Pb}$	1.0017	0.0007	0.02

Table 5 Statistical comparison of within sample measurement precision with between sample precision and evaluation for Pb isotope ratios determined both by ICP-QMS and MC-ICP-MS. Note: the greater the F-statistic is over the critical F value, the greater the power of the measurement to discriminate true sample variation from analytical 'noise'.

		$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
MC-ICP-MS	Within sample RSD%	0.07	0.03	0.08	0.02	0.05	0.07	0.03
MC-ICP-MS	Between sample RSD%	2.27	1.21	2.48	0.24	1.28	2.25	1.04
ICP-QMS	Within sample RSD%	0.09	0.08	0.14	0.13	0.16	0.09	0.08
ICP-QMS	Between sample RSD%	2.34	1.28	2.58	0.31	1.32	2.31	1.04
F_{crit} 1-tail 95% (10df,10df) = 2.98	Within sample F-stat MC -ICP-MS v ICP-QMS	1.94	6.11	3.35	37.30	10.34	2.00	5.40
F_{crit} 1-tail 95% (22df,10df) = 2.78	Between v Within sample F-stat ICP-QMS	615	237	322	6	67	625	167
F_{crit} 1-tail 95% (22df,10df) = 2.78	Between v Within sample F-stat MC-ICP-MS	1123	1302	1001	137	653	1180	902

Comparison of Binary plots

Binary plots were used to attempt soil Pb source apportionment for the three sets of data derived from (i) MC-ICP-MS, (ii) ICP-QMS measured using 10,000 scans, and (iii) ICP-QMS using just the first run of 1,000 scans as an example of acquisition parameters used previously in the literature (33). The first comparison was made using a conventional binary plot ($^{208}\text{Pb}/^{207}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$) as shown in Fig. 6. The MC-ICP-MS data (dark circles) all fell on a single straight trend line, expected from a simple 2 isotopic end-member system. Similarly, data analysed by ICP-QMS with 10,000 scans (grey circles) fell very close to the multi-collector data. By contrast, data from ICP-QMS using 1000 scans (white circles) clearly deviated from the multi-collector data and the single mixing line in the binary plot. The standard error at each data point ($n=3$) was also large compared to ICP-QMS data analysed using 10,000 scans where reproducibility was very high.

A further comparison was made using a second binary plot (Fig. 7) involving the ^{204}Pb isotope ($^{208}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$) in an attempt to identify the presence of further end member sources not revealed by Fig. 6; as Ellam (34) has pointed out plots based only on $^{206,207,208}\text{Pb}$ ratio have a limited ability to discriminate more than 2 end-members. Again, all data points determined by MC-ICP-MS fell on a single straight mixing line, providing no evidence of a 'third source' of Pb. The data determined by ICP-QMS using 10000 scans (grey circles) again fell very close to the multi-collector data. However, a few points visibly deviated from the single mixing line and the standard errors were very small, suggesting a small systematic deviation. The largest systematic deviations and standard errors ($n=3$) were observed for ICP-QMS data using 1,000 scans (white circles). It is clear that although a straight line through the data would indicate 2 dominant sources, the substantial scatter around the mixing line could be erroneously interpreted as indicating multiple (> 2) sources of Pb in the current dataset. This highlights the necessity for longer total acquisition time than previously reported (33, 35) and a fuller understanding of causes of error in determination of Pb isotope ratios.

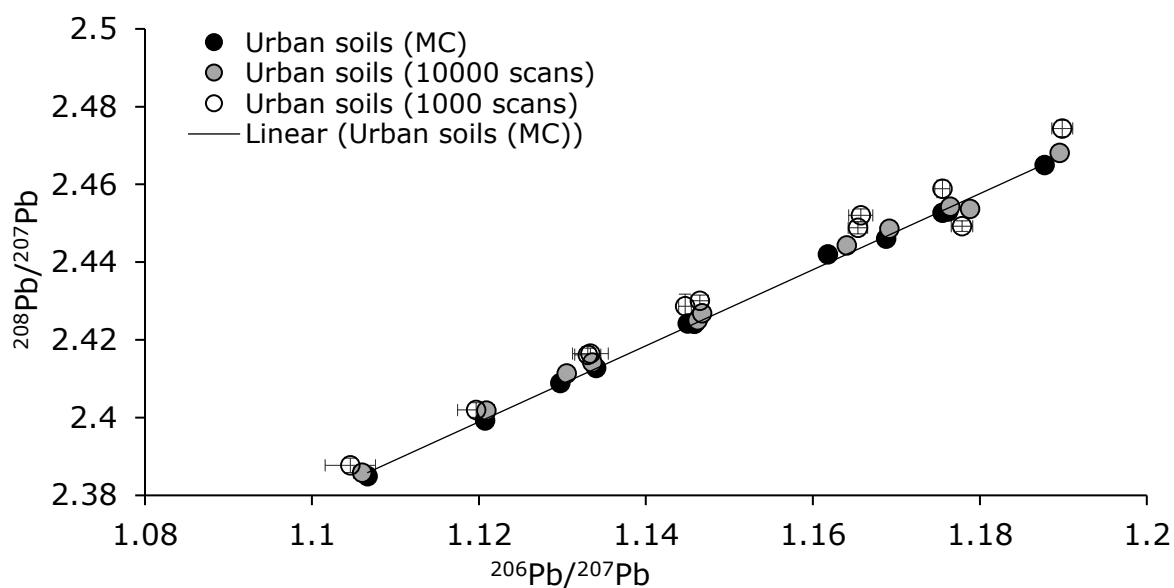


Figure 6. A binary plot using isotopic ratios $^{208}\text{Pb}/^{207}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ for data derived from MC-ICP-MS and ICP-QMS with either 10,000 or 1,000 scans. Note error bars for MC-ICP-MS and ICP-QMS (10000 scans) are smaller than symbols for most samples.

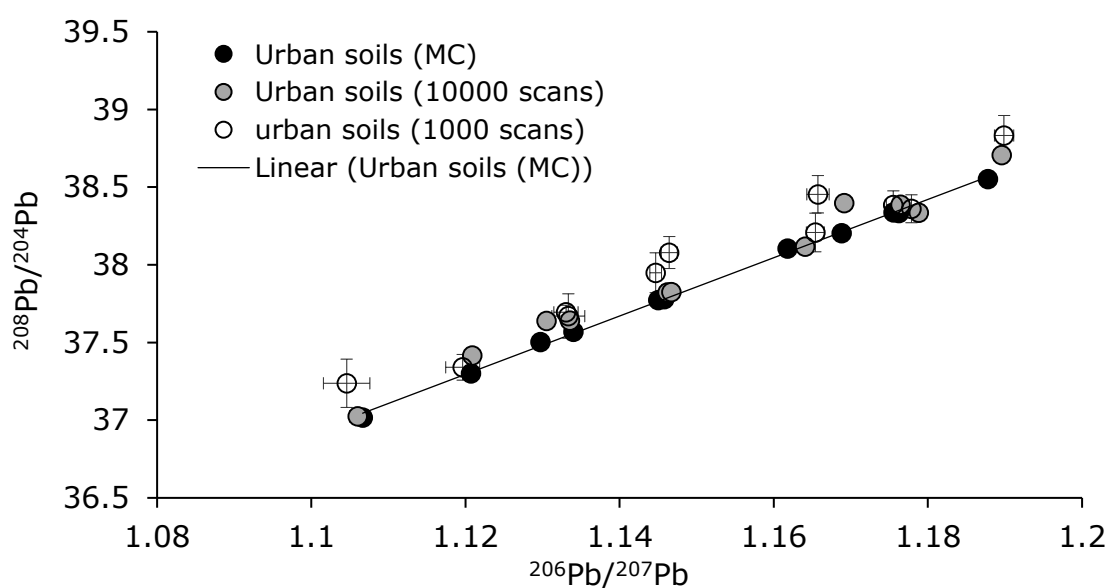


Figure 7. A binary plot using isotopic ratios $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ for data derived from MC-ICP-MS and ICP-QMS with either 10,000 or 1,000 scans.

Conclusions

The use of ICP-QMS for the determination of lead isotope ratios in environmental samples rather than TIMS or MC-ICP-MS is a highly attractive approach. Advantages include greater sample throughput, both as a result of sample introduction at atmospheric pressure and the possibility of avoiding separation of Pb from its matrix. This permits larger scale, more representative and cost-effective applications and has led to its adoption in many laboratories and resulted in numerous publications. Recently, Gulson et al (36) have called into question the quality of data produced by ICP-QMS and conclusions drawn from such data. However, it may be argued that this is not an inherent limitation of the ICP-QMS technique but a lack of attention to detail in making measurements and an understanding of the 'fitness for purpose' of chosen methodologies.

Therefore, in this study a protocol is refined for accurate and precise determination of Pb isotope ratios in urban soils using current-generation ICP-QMS. The operating parameters optimised were; individual dilution of soil samples to a single Pb concentration (15 ug L^{-1}), identical to that of an external isotope standard (SRM-981, NIST), determination of dead time correction factor ($\text{dtcf} = 36.8 \text{ ns}$), optimisation of quadrupole dwell time (10 ms), number of scans per sample and use of both internal (TI) and external (SRM-981, NIST) mass bias correction. No dependency of measurement precision on isotope dwell time, was observed compared to that observed in studies with previous generations of ICP-QMS instrument. High reproducibility was observed for data where the number of scans was increased to 10,000 (total analyte time per sample = 16 min). This developed protocol was further compared to Pb isotopic ratios data measured through MC-ICP-MS using the same soil sample digests. An excellent correlation was observed for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios ($r = 0.999$ and $r = 0.998$, $n = 35$). The correlation observed for $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratio was also strong but weaker than for other ratios ($r=0.987$).

Analysis of Variance (ANOVA) was used to test 'fitness for purpose' for the whole method from digestion of samples to ICP-QMS and MC-ICP-MS measurement. No statistical difference was observed for $^{207}\text{Pb}/^{206}\text{Pb}$ (ICP-QMS RSD 0.09%; MC-ICP-MS 0.07%) whereas for determination of the $^{207}\text{Pb}/^{204}\text{Pb}$ isotope ratio (ICP-QMS 0.13%; MC-ICP-MS 0.02%) ICP-QMS appeared to be limited by instrumental factors. Comparison of measurement variance with that of the between-sample variance was also undertaken using the F-statistic. It was apparent that the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio determined through ICP-QMS (V.R. = 615) has excellent discriminating power between samples; by contrast utilising the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio (V.R. = 6) for Pb source apportionment would require further analytical improvements, for example a detector with a wider pulse counting dynamic range that would allow the accumulation of better counting statistics within a reasonable time-frame.

In summary, although ICP-QMS is not capable of the absolute precision or the full source discrimination power of MC-ICP-MS, it is clearly capable of providing 'fit-for-purpose' Pb isotope ratio data on environmental samples, such as soils, where sample heterogeneity can be a limiting factor.

Conflicts of interest

SN is an employee of Thermo Fisher Scientific but the study was independently designed and executed by the other authors.

Acknowledgements

A.U., L.A., V.P. and S.C. publish with the permission of the Director, British Geological Survey.

This paper was significantly improved by the constructive comments of the referees.

References

1. Weiss DJ, Kober B, Dolgoplova A, Gallagher K, Spiro B, Le Roux G, et al. Accurate and precise Pb isotope ratio measurements in environmental samples by MC-ICP-MS. *International Journal of Mass Spectrometry*. 2004;232(3):205-15.
2. Cheng H, Hu Y. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. *Environ Pollut*. 2010;158(5):1134-46.
3. Thirlwall M. Inappropriate tail corrections can cause large inaccuracy in isotope ratio determination by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*. 2001;16(10):1121-5.
4. Komárek M, Ettler V, Chrástný V, Mihaljevič M. Lead isotopes in environmental sciences: a review. *Environment International*. 2008;34(4):562-77.
5. Santos R, Machado MC, Ruiz I, Sato K, Vasconcelos M. Space charge and mass discrimination effects on lead isotope ratio measurements by ICP-QMS in environmental samples with high uranium content. *Journal of Analytical Atomic Spectrometry*. 2007;22(7):783-90.
6. Maréchal CN, Télouk P, Albarède F. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*. 1999;156(1):251-73.
7. Wu G, Zhu J-M, Tan D, Han G, Zhang L, Ren K. Accurate and precise determination of lead isotope composition in selected geochemical reference materials. *Acta Geochimica*. 2017;36(3):421-5.
8. Begley IS, Sharp BL. Characterisation and correction of instrumental bias in inductively coupled plasma quadrupole mass spectrometry for accurate measurement of lead isotope ratios. *Journal of Analytical Atomic Spectrometry*. 1997;12(4):395-402.
9. Quétel CR, Thomas B, Donard OF, Grousset FE. Factorial optimization of data acquisition factors for lead isotope ratio determination by inductively coupled plasma mass spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*. 1997;52(2):177-87.
10. Vanhaecke F, De Wannemacker G, Moens L, Dams R, Latkoczy C, Prohaska T, et al. Dependence of detector dead time on analyte mass number in inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*. 1998;13(6):567-71.

11. Begley IS, Sharp BL. Occurrence and reduction of noise in inductively coupled plasma mass spectrometry for enhanced precision in isotope ratio measurement. *Journal of Analytical Atomic Spectrometry*. 1994;9(3):171-6.
12. Carré M, Poussel E, Mermet J-M. Drift diagnostics in inductively coupled plasma atomic emission spectrometry. Plenary lecture. *Journal of Analytical Atomic Spectrometry*. 1992;7(6):791-7.
13. Appelblad PK, Baxter DC. A model for calculating dead time and mass discrimination correction factors from inductively coupled plasma mass spectrometry calibration curves. *Journal of Analytical Atomic Spectrometry*. 2000;15(5):557-60.
14. Gillson GR, Douglas DJ, Fulford JE, Halligan KW, Tanner SD. Nonspectroscopic interelement interferences in inductively coupled plasma mass spectrometry. *Analytical Chemistry*. 1988;60(14):1472-4.
15. Heumann KG, Gallus SM, Rädlinger G, Vogl J. Precision and accuracy in isotope ratio measurements by plasma source mass spectrometry. *Journal of Analytical Atomic Spectrometry*. 1998;13(9):1001-8.
16. Woodhead J. A simple method for obtaining highly accurate Pb isotope data by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*. 2002;17(10):1381-5.
17. Nelms SM, Quérel CR, Prohaska T, Vogl J, Taylor PD. Evaluation of detector dead time calculation models for ICP-MS. *Journal of Analytical Atomic Spectrometry*. 2001;16(4):333-8.
18. Richter S, Konegger-Kappel S, Boulyga S, Stadelmann G, Koepf A, Siegmund H. Linearity testing and dead-time determination for MC-ICP-MS ion counters using the IRMM-072 series of uranium isotope reference materials. *Journal of Analytical Atomic Spectrometry*. 2016;31(8):1647-57.
19. Furuta N. Optimization of the mass scanning rate for the determination of lead isotope ratios using an inductively coupled plasma mass spectrometer. *Journal of Analytical Atomic Spectrometry*. 1991;6(3):199-203.
20. Monna F, Loizeau J-L, Thomas B, Guéguen C, Favarger P-Y. Pb and Sr isotope measurements by inductively coupled plasma-mass spectrometer: efficient time management for precision improvement. *Spectrochimica Acta Part B: Atomic Spectroscopy*. 1998;53(9):1317-33.
21. Ingle CP, Sharp BL, Horstwood MS, Parrish RR, Lewis DJ. Instrument response functions, mass bias and matrix effects in isotope ratio measurements and semi-quantitative analysis by single and multi-collector ICP-MS. *Journal of Analytical Atomic Spectrometry*. 2003;18(3):219-29.
22. Reuer MK, Boyle EA, Grant BC. Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS. *Chemical Geology*. 2003;200(1):137-53.
23. Wu Z, Guo W, Jin L, Hu S. Effect of signal acquisition mode on isotope ratio precision and accuracy in ICP-quadrupole-MS analysis. *Microchemical Journal*. 2018;142:251-7.
24. Yang L. Accurate and precise determination of isotopic ratios by MC-ICP-MS: A review. *Mass Spectrometry Reviews*. 2009;28(6):990-1011.
25. Strelow FWE. Application of ion exchange chromatography to accurate determination of lead, uranium, and thorium in tantaloniobates. *Analytical Chemistry*. 1967;39(12):1454-5.
26. Bandura DR, Baranov VI, Tanner SD. Effect of collisional damping and reactions in a dynamic reaction cell on the precision of isotope ratio measurements Presented at the 26th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Vancouver, October 24–29, 1999. *Journal of Analytical Atomic Spectrometry*. 2000;15(8):921-8.
27. Thirlwall MF. Multicollector ICP-MS analysis of Pb isotopes using a ²⁰⁷Pb-²⁰⁴Pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization. *Chemical Geology*. 2002;184(3):255-79.
28. van Heuzen AA, Hoekstra T, van Wingerden B. Precision and accuracy attainable with isotope dilution analysis applied to inductively coupled plasma mass spectrometry: theory and experiments. *Journal of Analytical Atomic Spectrometry*. 1989;4(6):483-9.
29. Encinar JR, Alonso JIG, Sanz-Medel A, Main S, Turner PJ. A comparison between quadrupole, double focusing and multicollector ICP-MS instruments Part I. Evaluation of total combined

515 uncertainty for lead isotope ratio measurements. *Journal of Analytical Atomic Spectrometry*.
 516 2001;16(4):315-21.

517 30. Taylor PD, de Bièvre P, Walder AJ, Entwistle A. Validation of the analytical linearity and mass
 518 discrimination correction model exhibited by a multiple collector inductively coupled plasma mass
 519 spectrometer by means of a set of synthetic uranium isotope mixtures. *Journal of Analytical Atomic*
 520 *Spectrometry*. 1995;10(5):395-8.

521 31. Nelms SM, Beauchemin D. *Inductively coupled plasma mass spectrometry handbook*: Oxford,
 522 Boca Raton, FL; 2005.

523 32. Almeida CM, Vasconcelos MTS. ICP-MS determination of strontium isotope ratio in wine in
 524 order to be used as a fingerprint of its regional origin. *Journal of Analytical Atomic Spectrometry*.
 525 2001;16(6):607-11.

526 33. Mao L, Bailey EH, Chester J, Dean J, Ander EL, Chenery SR, et al. Lability of Pb in soil: effects of
 527 soil properties and contaminant source. *Environmental Chemistry*. 2014;11(6):690-701.

528 34. Ellam RM. The graphical presentation of lead isotope data for environmental source
 529 apportionment. *Sci Total Environ*. 2010;408(16):3490-2.

530 35. Shetaya W, Marzouk E, Mohamed E, Elkassas M, Bailey E, Young S. Lead in Egyptian soils:
 531 Origin, reactivity and bioavailability measured by stable isotope dilution. *Sci Total Environ*.
 532 2018;618:460-8.

533 36. Gulson B, Kamenov GD, Manton W, Rabinowitz M. Concerns about Quadrupole ICP-MS Lead
 534 Isotopic Data and Interpretations in the Environment and Health Fields. *International journal of*
 535 *environmental research and public health*. 2018;15(4):723.