

Optimising accuracy and precision of lead isotope measurement (^{206}Pb , ^{207}Pb , ^{208}Pb) in acid digests of peat with ICP-SMS using individual mass discrimination correction

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Using ICP-SMS, a robust analytical protocol for accurate and precise determination of the isotopic Pb composition (^{206}Pb , ^{207}Pb , ^{208}Pb) of acid digests of peat samples was developed. External precision better than 0.05% and 0.1% for Pb concentrations in the range of $1 \mu\text{g l}^{-1}$ and $0.1 \mu\text{g l}^{-1}$, respectively, were achieved for both $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. This precision has never before been achieved with ICP-SMS in a complex matrix containing such low concentrations of total Pb. Procedural Pb blank concentrations amounted to $0.003 \mu\text{g l}^{-1}$ and had no influence on the accuracy of the Pb isotope ratios. Corrections for mass discrimination were accomplished using the certified isotopic reference material SRM 981. However, mass discrimination was found to be non-systematic, and varied among the masses both with respect to magnitude and direction. To accommodate this phenomenon, an individual mass discrimination correction was applied to each ratio resulting in improved accuracy. Using this approach, the mass discrimination for both Pb isotope ratios was $<0.2\%$, compared to values on the order of $\pm 0.35\%$ if only a single Pb isotope ratio was used. The accuracy and precision of the ICP-SMS protocol was further evaluated using thermal ionisation mass spectrometry (TIMS) of selected samples and an in-house peat reference material. In general, the Pb isotope ratios determined using ICP-SMS deviated from the TIMS values by less than $<0.1\%$. Given the throughput of the ICP-SMS compared to the TIMS (which requires chemical separation of Pb), the approach described offers great promise for environmental studies to fingerprint the predominant sources of anthropogenic Pb. Two applications are presented here: a bog profile from the Black Forest (SW Germany) consisting of eight thousand years of peat accumulation, and a depth profile through a snowpack collected from the same site during the winter of 2003.

Introduction

Ombrotrophic (rain-fed) peat bogs receive metals exclusively from the atmosphere¹ and are gaining popularity as archives of atmospheric trace element deposition.² While a growing range of trace metals has been investigated,^{3–6} Pb has certainly attracted the most attention.^{3,7,8} Precise measurements of Pb isotope ratios using thermal ionisation mass spectrometry (TIMS) of peat cores age-dated using ^{210}Pb ^{8,9} and comparison with herbarium samples of *Sphagnum* moss¹⁰ have shown that Pb is effectively immobile in peat profiles, and that bogs provide faithful records of the atmospheric deposition of this element.⁷ Using the isotopic composition of Pb as a fingerprinting tool, age-dated peat profiles represent a potentially very powerful tool for the reconstruction of atmospheric fluxes and predominant sources of Pb and other trace metals.¹¹

For any given sample, thermal ionisation mass spectrometry (TIMS) provides the most accurate and precise measurements of Pb isotope ratios. However, TIMS analyses are laborious and time-consuming because the analyte (Pb) has to be separated from the sample matrix prior to analysis. Quadrupole ICP-MS (Q-ICP-MS) has been used to measure the isotopic composition of Pb in acid digests of peat and lichens in several studies,^{12,13} but accuracy and precision are poor compared to TIMS measurements; here, studies employing this technique are not discussed further. Multi-collector ICP-MS (MC-ICP-MS) may offer precision and accuracy comparable to TIMS, but this comparatively new method has not yet been applied to acid digests of peat.

Double focusing ICP-MS instruments with a magnetic sector

(ICP-SMS) have become an increasingly attractive alternative to TIMS for the accurate and precise determination of isotope ratios.^{14–23} The best precision ever reported for the determination of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios by ICP-SMS in its standard sample introduction configuration made of glass range from 0.03 to 0.05%.^{16,20,22,23} To achieve this precision, however, total Pb concentrations in the analyte solutions had to be between 5 and $50 \mu\text{g kg}^{-1}$. To date, because of the large dilution factors needed to overcome the effects of sample matrix and digestion reagents on instrument performance, in complex matrices only those samples with relatively high Pb concentrations could be analysed with acceptable precision (e.g. 0.05%). Using an ultrasonic nebulizer (USN) with a membrane desolvation unit can help to overcome this limitation.¹⁸ With the improved sensitivity of this instrumental set-up, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios with precision of 0.07% and 0.02%, respectively, could be determined in a synthetic water reference material (diluted 100-fold) with a total Pb concentration of $0.182 \mu\text{g l}^{-1}$.¹⁸ This achievement, however, required a sample volume of more than 20 ml and this could be a critical issue in some environmental studies when only a limited amount of sample is available. A tandem spray chamber arrangement (combination of a cyclone spray chamber and a Scott-type spray chamber) provides an intensity enhancement by a factor of two to four times and a more stable signal compared to conventional or USN sample aspiration, but has not found widespread use so far.¹⁹ At the $1 \mu\text{g l}^{-1}$ level, this sample introduction system provided precision ranging from 0.03 to 0.09% for $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in various diluted isotopic reference materials.¹⁹

Peat is a complex matrix containing very stable organic and inorganic (mineral) components which are resistant to decomposition even in the most aggressive digestion solutions. The present study was undertaken to further extend the application of Pb isotope ratio measurements by ICP-SMS and to improve the overall performance by addressing the following issues: (i) extension of Pb isotope ratio measurements using an HF-resistant sample introduction system (PFA nebulizer, PFA spray chamber, sapphire injector) to allow analysis of digestion solutions containing HF and HBF₄; these are necessary to completely destroy the Pb-bearing mineral grains in peat which are derived from atmospheric soil dust particles; (ii) optimisation of data acquisition parameters for obtaining the best possible precision; (iii) elucidation of precision achievable at Pb concentrations < 1 µg l⁻¹; (iv) comparison of the Pb isotope ratio determination with data obtained for the same set of samples using TIMS; and (v) application of the optimised analytical protocols to the determination of Pb isotope ratios in acid digests of selected peat samples from a German bog. Finally, the protocol is also applied to fresh snow samples containing ultralow concentrations of total Pb collected from the same site.

Experimental

Instrumentation

All sample manipulations and preparations of standards were performed under laminar flow clean air benches (class 100) to minimize potential risk of contamination. Sample digestions were performed in a clean laboratory of class 10 000.

Two hundred mg of dried, powdered peat samples were dissolved in 3 ml HNO₃ and 0.1 ml HBF₄ in PTFE digestion vessels (20 ml) in a microwave heated autoclave (ultraCLAVE II, MLS GmbH, Leutkirch, Germany) as described in detail elsewhere.^{24,25} Briefly, up to 40 samples were simultaneously heated to 240 °C within 75 min obtaining clear, homogeneous digestion solutions.

All ICP-MS measurements were carried out with an Element 2 ICP-SMS (Thermo Finnigan, Bremen, Germany) equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. The high resolution double focusing (reverse Nier–Johnson geometry) single collector ICP-MS instrument provides flat top peaks in the low resolution mode (*m/Δm* 300) which was used. A micro volume autosampler (ASX 100, Cetac Technologies, Omaha, NE, USA) and a HF resistant sample introduction kit consisting of a microflow PFA nebulizer, a PFA Scott-type double pass spray chamber and a sapphire injector tube were employed to transport the analytes into the plasma of the ICP-MS. The PFA spray chamber has an additional gas inlet which was flushed with about 0.1 l argon min⁻¹ to increase sensitivity and stability of this sample introduction setup. The dead time of the detector (13 ns) was determined following the manufacturer's instructions. Peat samples were diluted with 0.1% (v/v) high-purity HNO₃ to reach a total Pb concentration of about 1 µg l⁻¹ in the analyte solution; snow samples were directly analysed for both total lead concentration and Pb isotope ratios. Details on the ICP-MS operating conditions, the data acquisition and reduction parameters are summarised in Tables 1 and 2, respectively. Total Pb concentrations in solid peat samples were analysed by EMMA XRF.²⁶

Lead isotope ratio determination using TIMS were carried out on a MAT 261 (Thermo Finnigan) following well established analytical procedures.^{27,28}

Reagents and standards

For the preparation of all solutions, high purity water (18.2 MΩ cm) from a MilliQ-Element system designed for

Table 1 Operating conditions of the ICP-SMS

Forward power	1250 W
Coolant gas flow rate	16 l min ⁻¹
Auxiliary gas flow rate	~0.8–1.0 l min ⁻¹ , optimised daily ^a
Sample gas flow rate	~0.8–1.0 l min ⁻¹ , optimised daily ^a
Spare gas flow rate	~0.1 l min ⁻¹ , optimised daily ^a
Sample cone	Ni, 1.1 mm aperture id
Skimmer cone	Ni, 0.8 mm aperture id
Resolution	300 (<i>m/Δm</i>)
Sample uptake rate (pumped)	~0.1 ml min ⁻¹
Scan type	Fixed magnet with electric scan over small mass ranges
Ion sampling depth	Adjusted daily ^a
Ion lens settings	Adjusted when appropriate

^a Optimised in order to obtain a stable ²⁰⁸Pb signal (typically 700 000 cps for 1 µg l⁻¹) and the lowest possible oxide formation rate (see text for details).

Table 2 Data acquisition parameters for Pb isotope ratio measurements

Isotopes measured	²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb
Scan type	Magnet fixed at ²⁰⁶ Pb, electric scans over other masses (E-scan)
Mass scanning window	5%
Magnet settling time	1 ms (default minimum)
Dwell time per isotope	5 ms
Scan duration per scan	78 ms
Number of scans	1200
Total time per sample (5 replicates including uptake)	9 min 30 s
Sample uptake and equilibration time	100 s
Rinse time between sample and bracketing standard	1 min with 1% HNO ₃
Detector dead time	13 ns

ultra trace analysis (Millipore, Milford, MA, USA) was used. Nitric acid (65%, analytical-reagent grade, Merck, Darmstadt, Germany) was further purified by sub-boiling distillation (MLS GmbH). Other reagents for digestions were tetrafluoroboric acid solution (HBF₄, ~50%, purum, Fluka, Buchs, Switzerland) and hydrogen peroxide (30%, Baker analysed, J.T. Baker, Deventer, Holland).

Lead calibration solutions were prepared daily by appropriate dilution of a 10 mg l⁻¹ stock standard solution (Merck) with 0.14 mol l⁻¹ high-purity nitric acid. To correct for instrumental drifts and plasma fluctuations, all solutions analysed for total Pb were spiked with an indium solution (Merck) to a final concentration of 1 µg l⁻¹.

For isotopic analysis, the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 981 Common Lead Isotopic Standard was diluted to a Pb concentration of 250 µg g⁻¹ with 1% (v/v) high-purity HNO₃. This standard solution was further diluted to about 1 µg Pb l⁻¹ for daily analysis.

Collection of peat and snow samples

A 6 m long peat core was collected in the southern Black Forest (Germany) in June 2002 using a Ti Wardenaar and a Belarus corer using procedures similar to those described in detail elsewhere.³ Immediately after collection the core was wrapped in polyethylene foil and transferred into boxes for transport into the laboratory. On arrival in the laboratory, the peat core was frozen, subsequently cut into 1 cm slices using a band saw and further processed for analysis.

A snow profile was dug in the 70 cm snow pack located on the ombrogenic part of the above mentioned peat bog in February 2003. Each 10 cm layer was collected with PET gloves in virgin plastic bags previously “rinsed” with snow from the same level. Snow bags were kept frozen in an insulated box until their transfer for filtration in the laboratory. Snowmelt

was realized at room temperature overnight. Melt waters were filtered through 0.45 μm membranes (type HAWP, Millipore), collected in acid-cleaned polypropylene bottles and acidified with doubly distilled HNO_3 to reach a pH between 1 and 2.

Quality control

The accuracy of the isotope ratio measurements by ICP-SMS were assessed by measuring the certified Pb isotope standard SRM 981. As an independent check of the obtained accuracy, selected peat samples were also analysed for Pb isotope ratios using TIMS. In both cases (SRM 981 and TIMS) Pb isotope ratios determined by ICP-SMS generally agreed to within <0.1% of the "true" value.

Accuracy of the determination of total Pb in snow samples was ascertained by the determination of the Pb concentration in the riverine water reference material SLRS-2, National Research Council Canada, Ottawa, Canada (certified $0.129 \pm 0.011 \mu\text{g l}^{-1}$; found $0.137 \pm 0.011 \mu\text{g l}^{-1}$, $n = 9$); for the peat samples, the certified plant material GBW 07602 Bush Branches and Leaves, Institute of Geophysical and Geochemical Exploration, Langfang, China, (certified $7.1 \pm 0.7 \mu\text{g g}^{-1}$; found $7.2 \pm 0.7 \mu\text{g g}^{-1}$, $n = 6$).

Results and discussion

Data acquisition parameters

The data acquisition parameters for Pb isotope ratio measurements summarised in Table 2 were found to provide excellent performance of the ICP-MS instrument and were thus not further optimised. In fact, using 1200 scans per replicate with a dwell time of 5 ms per Pb isotope yielded comparable results to the best ever reported Pb isotope ratio measurements using a single collector ICP-MS instrument. Principal considerations for the appropriate selection of the number of scans, dwell time, mass integration window, *etc.* have been repeatedly reported in the recent literature.^{15–18,20,23}

Data reduction, processing, and statistical analyses

The voluminous set of ICP-MS signals acquired during each sample run requires careful and thoughtful data reduction. As outlined by Gwiazda *et al.* in some detail, the procedures employed to reduce the data acquired by the ICP-MS signals may significantly influence the precision of the final results.¹⁷ In the present study, the measurement sequence consisted of 5×1200 scans per sample. For data reduction, the 1200 scans per replicate were split into 6×200 scans which were used to calculate a mean Pb isotope ratio per replicate with a corresponding standard deviation; the *internal precision* (short term variability) is defined as the relative standard deviation (RSD) of this mean. Five replicates per sample were analysed without washing in between; this helped to keep measurement time to a minimum.

The results reported here are expressed as the mean of the means of all five replicates measured per sample, *i.e.* total of 6000 scans. The same holds true for the corresponding standard deviation and relative standard deviation; the RSD of this composite mean is defined as the *external precision* (long term variability). Before and after each sample the certified isotopic Pb standard solution was analysed twice to correct for mass discrimination drifts as outlined in detail below.

Applying the analytical scheme described above, four samples, including bracketing standards, can be analysed in about 1 h by ICP-SMS and will provide the accuracy and precision described below.

Precision

Precise determination of the isotopic composition of a sample is a major prerequisite for a meaningful interpretation of the results. In addition to the limitations set purely by Poisson (counting) statistics, precision of isotope ratio measurements obtainable by a single collector ICP-MS instrument is influenced by effects such as plasma flickering, fluctuations in the sample aspiration due to the peristaltic pump, *etc.* Therefore, the RSD of the isotope ratios for any given sample can only approach, but never achieve, that predicted by theoretical, idealized, considerations.

As mentioned above, the internal precision obtained from the isotope ratio measurement of a single sample (*i.e.* the RSD of 1200 scans) depends on the signal intensity. Fig. 1 is a composite graphic illustrating the dependence of the internal precision of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio on the concentration of total Pb (as indicated by the number of ^{206}Pb counts per second) accumulated throughout this study. Internal precision amounted to approximately 0.2% at a level of $0.5 \mu\text{g l}^{-1}$ total Pb in the analyte solution. In agreement with other researchers, the external precision, *i.e.* the RSD derived from five consecutive measurements of the same sample, was much better and approached 0.01% in some cases. However, on a routine basis, the protocol described here provided external precision of 0.05% for both $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios at total lead concentrations of $1 \mu\text{g l}^{-1}$.

Similarly low external precision ($\leq 0.1\%$) for Pb isotope ratio measurements have been reported in other kinds of samples using ICP-SMS.^{15,20} In these earlier studies, however, relatively high concentrations of total Pb (up to $50 \mu\text{g kg}^{-1}$) were required in the digestion solutions to achieve this performance. For lower Pb concentrations, an ultrasonic nebulizer with a membrane desolvation unit requiring a sample volume of about 20 ml was necessary to obtain comparable precision.¹⁸ In contrast, during the present investigation, external precision of 0.1% were achieved at concentrations of total Pb as low as $0.1 \mu\text{g l}^{-1}$. In fact, in the present study no sample contained more than $1 \mu\text{g l}^{-1}$ Pb. Using an HF resistant low flow PFA sample introduction system, five replicate measurements of each sample consumed less than 1 ml per sample. In other words, the protocol described here provides Pb isotope ratios at precision as good as or better than ever obtained using ICP-SMS, but at far lower ($10\times$ or more) concentrations of total Pb, and in much smaller sample volumes. Higher Pb concentrations than $2 \mu\text{g l}^{-1}$ were not considered in order not to "contaminate" the ICP-MS.

Five replicate measurements of a sample under the selected experimental conditions proved to be sufficient to provide the reported RSD. An attempt to increase the number of replicates

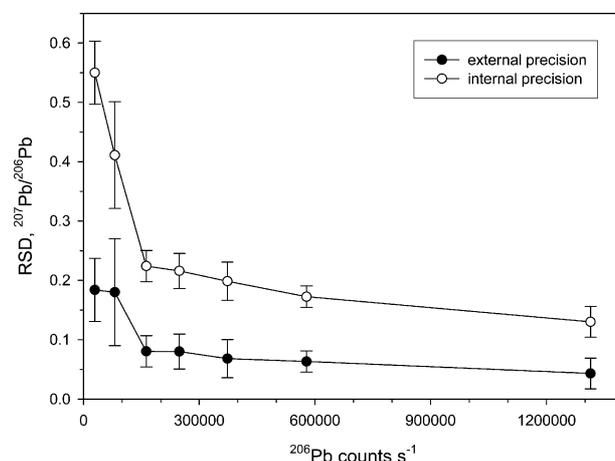


Fig. 1 Dependence of internal and external precision ($n = 5$) on the count rate of the ICP-SMS.

to up to 10 led to no further improvement of the precision of the Pb isotope ratio measurements. In summary, routine measurement of five replicate samples containing total Pb as little as $0.1 \mu\text{g l}^{-1}$ provides an external precision better than 0.1%.

Effect of sample dilution. Another important factor potentially influencing the precision of isotope ratio measurements was the dilution of the peat digests. When a minimum final dilution factor of 400 times of solid peat samples was applied, the obtained RSD was independent of the matrix. Below this value, RSD sometimes worsened depending on the matrix composition of the particular sample. Given the fact that the “cleanest” peat samples dating from pre-anthropogenic times (*ca.* six to nine thousand years old) typically contain 200 ng g^{-1} in the solid phase,⁷ a dilution factor of 400 times ensures that all acid digests will contain at least $0.5 \mu\text{g l}^{-1}$; this concentration of total Pb ensures that the external precision of the Pb isotope measurements of virtually all peat samples will exceed 0.1% (Fig. 1).

Instrument tuning. Tuning of the instrument (mainly torch position and gas flows) for best signal stability is another key point to obtain precise results. Experience has shown that it is not advisable to optimise instrumental parameters for maximum ^{115}In intensity and a smooth ^{115}In signal as is typically the case for elemental analyses, but rather to tune on Pb. Here, ^{208}Pb is preferred because it has the greatest natural abundance of all the Pb isotopes. At an initial stage of this study, the ICP-SMS was tuned on ^{115}In and the performance for Pb isotope ratio measurements was not acceptable. A closer look at this problem revealed that, although the ^{115}In signal was very stable, the time resolved signal for ^{208}Pb experienced considerable fluctuation. A perfectly stable signal obtained after optimisation of all gas flows using an In standard solution will not result in a stable Pb signal and *vice versa*. Therefore, the instrument was tuned for maximum stability and gain of the ^{208}Pb signal.

Formation of oxides. It should be also noted that the oxide formation rate after optimisation, established *via* monitoring the ratio of UO to U, ranged between 6–12%. This relatively high oxide formation rate is partly due to the use of the guard electrode increasing the oxide formation rate by about one order of magnitude which can have a potentially serious drawback.¹⁹ For example, polyatomic overlaps arising from Ar-based erbium and ytterbium interferences may negatively influence both precision and accuracy of all three Pb signals. The results of this study, however, revealed that this was not the case. Because of their comparatively low concentrations, other potential interferences originating from Os, Pt and Ir are very unlikely. In cases where oxide formation could be problematic, desolvating sample introduction systems, largely reducing the oxide formation rate, might be advantageous in that context.

Accuracy

Once the precision of the actual measurement has been optimised, the accuracy of the obtained isotope ratios largely depends on the determination of the detector dead time and the factor to be used for the mass discrimination correction. Both effects as well as adequate approaches to correctly quantify these two phenomena have been repeatedly discussed in the literature.^{15,21}

Detector dead time. Compared to ICP-quadrupole mass analyzers (50–80 ns), the detector dead time for ICP-SMS is distinctly lower (20–50 ns).^{15,16,18,20,22} For the Element 2, the detector dead time is even lower²¹ and in the case of our instrument, it amounts to only 13 ns. The determination of the

detector dead time is not critical for small isotope ratios such as the ratio between ^{206}Pb and ^{207}Pb which is more or less unity. However, if the ratio between the isotopes is 1:500, differences in dead time of only 1 ns may induce inaccuracies as large as 0.1%.²¹

Correction for mass discrimination. A distinctly larger influence on the accuracy of the results, however, can be attributed to the appropriate correction of the mass discrimination drift during a measurement sequence. “Mass discrimination”, often referred to as “mass bias”, is a measure of the deviation between the measured and true isotopic ratio. Two approaches are generally applied to correct for mass discrimination. *Internal mass discrimination* correction uses the drift of $^{203}\text{Tl}/^{205}\text{Tl}$, for example, to correct the Pb isotope ratios.^{14,18} This approach assumes, however, that the mass discrimination/mass unit is constant and therefore can be also applied to the correction of the determined Pb isotope ratios. A second problem with this approach is that Tl isotopes might fractionate differently during the measurement and thus might not perfectly match the behaviour of Pb; this could lead to a different mass discrimination for both elements. Additionally, spiking of Tl to all samples is necessary using this methodology. Moreover, time which could be spent on the acquisition of Pb counts is lost because the two Tl isotopes have to be monitored with great precision in every sample. Nevertheless, the mass discrimination is simultaneously determined together with corresponding Pb isotopes in each sample, which favours this approach.

External mass discrimination correction, using the certified isotopic lead standard reference material SRM 981, was applied throughout this study. Two replicates of SRM 981 were always measured before and after five replicate measurements of each sample. The Pb ratios of four replicates of SRM 981 (two before and two after each sample) were averaged and used to calculate the mass discrimination for the sample. The reason for always analysing two replicates of SRM 981 between real samples was to check for potential matrix effects of the sample which distinctly influenced the mass discrimination in the reference material. Generally, the two Pb isotope ratios of each of the two replicates of SRM 981 measured before and after a sample agreed within the standard deviation of their means. If a digest was insufficiently diluted thereby inducing serious matrix effects, a distinct drift of the mass discrimination determined before and after the sample was obvious. Such values were withdrawn and after appropriate dilution of the digest, the sample was measured once again yielding improved results. As mentioned before, a final dilution factor of approximately 400 was generally required to obtain accurate and precise results as well as a stable and robust performance of the instrument. Under these conditions, the sensitivity of ICP-SMS remained unchanged for at least 14 h. In contrast, previous studies¹⁶ have reported drifts in sensitivity as great as 10% or more in as little as 4 h; the experience obtained here suggests that these problems might have been caused by inadequate dilution of the sample. Other researchers did not comment on this important issue in detail^{16,20,22} but they probably used even greater dilution factors than we have used here, as they analysed samples of galena, soil, or copper alloys, all of which have very high Pb concentrations.

Mass discrimination for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. Common practice for correction of the mass discrimination is the calculation of a “mass discrimination/mass unit” using one Pb isotope ratio of a certified isotopic reference material. This mass discrimination/mass unit is considered constant (at least for some mass units) and is used to correct all measured isotope ratios. Reported values for this mass discrimination using ICP-SMS range from 0.2 to 0.75% per mass unit.^{15,20,22} To further improve the accuracy of the Pb isotope ratio measurements, we

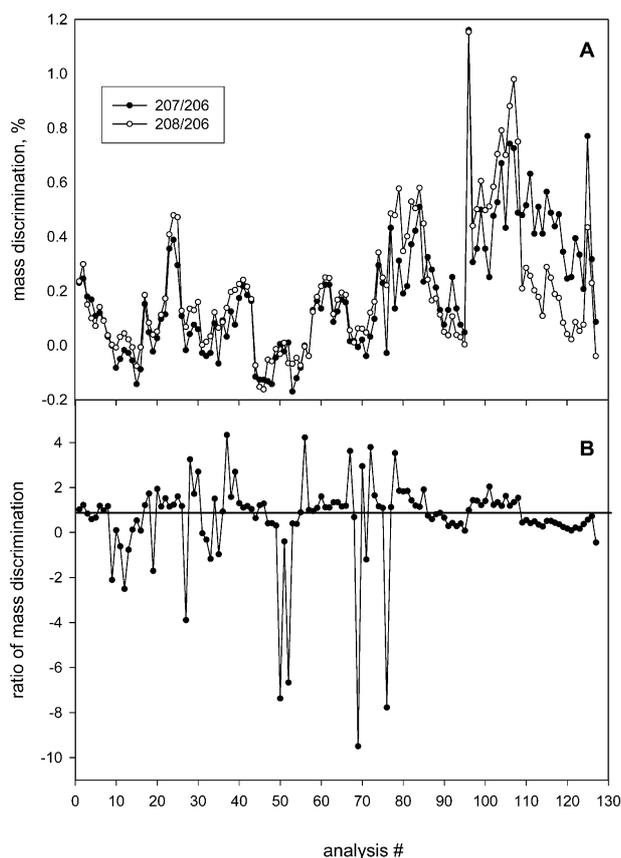


Fig. 2 A: Changes in the mass discrimination of the $^{207}\text{Pb}/^{206}\text{Pb}$ and the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio during several measurement sequences as determined on the certified isotopic reference material SRM 981. B: Ratio of the mass discrimination of the $^{207}\text{Pb}/^{206}\text{Pb}$ and the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio.

investigated this assumption in more detail. We calculated the mass discrimination for both the $^{207}\text{Pb}/^{206}\text{Pb}$ and the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio considering about 260 measurements of SRM 981 which have been measured between unknown samples. Fig. 2A highlights the mass discrimination drift during several measurement sequences obtained on different days. As can be clearly seen from this Figure, the mass discrimination of the two Pb isotope ratios largely follow each other, assuming that, at least at first glance, the commonly applied mass discrimination correction is accurate. Sometimes, however, the mass discrimination of the two Pb isotope ratios largely differ from each other. To illustrate this effect, the ratio of both mass discriminations was plotted in Fig. 2B. Ideally, the ratio should be unity if both Pb isotope ratios were affected in the same manner. The data in Fig. 2B shows that this is certainly not always the case. As is evident from this plot, many values are centred around unity but large deviations ranging from about 4 to -10 are observed. It should be stressed that these deviations from the ideal case are not caused by instances of poor instrument performance which might occur at random. In fact, even larger differences in the mass discrimination for both pairs of Pb ratios yielded accurate results as confirmed by TIMS analysis of identical samples (see below). Considering the results from the analysis of SRM 981 starting from #80 until the end of the sequence, it is evident that, even though the mass discrimination for the $^{207}\text{Pb}/^{206}\text{Pb}$ and the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio largely differ from each other, the ratio of the mass discrimination of the two ratios is centred around unity and thus an accurate correction of the mass discrimination drift can be applied to the samples. If only a single Pb isotope ratio for the calculation of the mass discrimination would have been considered, the deviation from the true value could be as large as $\pm 0.35\%$. On an average, the mass discrimination for both Pb isotope ratios was $< 0.2\%$, however, with standard

deviations of 0.2% . As it is convenient to calculate the mass discrimination correction factor for each Pb isotope ratio, uncorrected Pb isotope ratios of samples were corrected by the individual mass discrimination of the same ratio in the SRM 981 standard reference material.

Already in 1998, Woolard *et al.*¹⁵ reported non-systematic mass discrimination that varied between the masses in both magnitude and mass direction. They concluded that a well characterised Pb isotope standard should be used to individually correct the mass discrimination for each Pb isotope ratio to obtain highest possible accuracy of the results. This finding is strongly supported by our detailed investigations graphically summarised in Fig. 2. Unfortunately, it is not clear from the data presented in several earlier publications, whether or not authors applied individual mass discrimination corrections for each Pb isotope ratio. It seems, however, that most of these authors only used a single mass discrimination correction factor to correct all measured Pb isotope ratios because most of them report a mass discrimination per mass unit.

Warm-up time. A second effect, namely the necessary warm-up of the magnet by running the analysis method for about 2 h before beginning data collection, was not required with our ICP-SMS.^{11,13} The best performance with the Element 2 was already obtained after igniting the plasma and warming up the electronics for about 1 h. However, the number of pre-scans, which is normally set to 1 for concentration determinations, was set to 20 for isotope ratio measurements. Thus the magnet scans 20 times over the selected mass range before starting with the acquisition of data, thereby "conditioning" the magnet. This reduced warm-up time most probably is thanks to the new magnet and the fully thermostated analyser in the Element 2.

Regression models to calculate the mass discrimination factor. In agreement with other findings using the same ICP-SMS, a check of the three commonly applied models (linear, power law, exponential function) to calculate the mass discrimination correction factor revealed that all three models gave almost identical results.²¹ It is important to note here that the limited precision obtainable by single collector ICP-SMS is the reason why all three correction models yield the same Pb isotope ratios. The distinctly higher precision of MC-ICP-MS and TIMS allows the description of physical effects in the mass spectrometer such as fractionation and thus clearly shows the dependence of the results on the applied model. All Pb isotope ratios reported in this study have been corrected using the power law function.

Comparison with results obtained using TIMS

To help evaluate the potential of the analytical procedure quantitatively, several peat samples analysed in this study by ICP-SMS have also been measured using TIMS after chemical separation of the analytes from the peat matrix by common column chemistry.^{27,28} Additionally, the certified isotopic reference material SRM 981 has been analysed for quality control purposes. The results of this comparison are highlighted in Table 3. It is evident that external precision (RSD) obtainable by TIMS are as much as one order of magnitude lower than those of ICP-SMS. However, the precision of the lead isotope ratio determinations by ICP-SMS is generally $< 0.1\%$. Accuracy, established by comparison of the ICP-SMS data to the TIMS data, revealed that the deviation of the ICP-SMS results from the "true values" is generally $< 0.1\%$.

It should be noted that in two cases (OGS 1878P and LDW 23) the difference between ICP-SMS and TIMS for $^{207}\text{Pb}/^{206}\text{Pb}$ ratios was $> 0.1\%$, *i.e.* 0.16% and 0.14% , respectively (Table 3). The precision obtained by TIMS for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in these two samples was worse than usual and comparable to that obtained by ICP-SMS. As the latter method gave RSD of

Table 3 Comparison of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios determined in selected peat samples and the certified standard reference material SRM 981 by ICP-SMS and TIMS

Peat sample laboratory code	$^{207}\text{Pb}/^{206}\text{Pb}$			$^{208}\text{Pb}/^{206}\text{Pb}$			
	Mean	<i>s</i>	RSD (%)	Mean	<i>s</i>	RSD (%)	
OGS 1878P	ICP-SMS	0.8701	0.0003	0.04	2.1042	0.0003	0.02
	TIMS	0.8687	0.00037	0.04	2.1046	0.00013	0.006
	Deviation from TIMS	0.16%			-0.02%		
LDW 3	ICP-SMS	0.8559	0.0006	0.07	2.0971	0.0013	0.06
	TIMS	0.8566	0.00002	0.003	2.0986	0.00006	0.002
	Deviation from TIMS	-0.08%			-0.07%		
LDW 6	ICP-SMS	0.8524	0.0007	0.08	2.0914	0.0017	0.08
	TIMS	0.8522	0.00003	0.003	2.0895	0.00005	0.003
	Deviation from TIMS	0.02%			0.09%		
LDW 23	ICP-SMS	0.8490	0.0004	0.05	2.0864	0.0010	0.05
	TIMS	0.8478	0.00018	0.021	2.0847	0.00036	0.017
	Deviation from TIMS	0.14%			0.08%		
SRM 981	ICP-SMS	0.9144	0.0008	0.09	2.1672	0.0012	0.05
	certificate	0.91464	0.00033	0.036	2.1681	0.00033	0.015
	Deviation from certificate	0.03%			0.04%		

0.04% and 0.05%, respectively, TIMS data for these two Pb isotope ratios should be interpreted with some caution, as the quality of the data is poor compared to accuracy and precision of Pb isotope ratios obtained by geochronologists working with geological specimens.²⁷ In this context, however, it must be emphasised that the performance obtained using TIMS measurements employed “real world” samples of peat: this is a complex material containing a wide variety of both organic and inorganic components which are highly resistant to attack by oxidising, acidic digestion solutions. As a result, the comparative data given in Table 3 is not a reflection of the quality of Pb isotope data which can be obtained by TIMS generally, but does illustrate the complexity of the peat samples. The main reason for the limited precision may be due to organic matter which has survived the digestion of the peat samples, either interfering with the chemical separation of Pb on the ion exchange columns, or with the Re filament, giving unstable signals. Either way, the comparison with the TIMS data shows that ICP-SMS can provide excellent accuracy and precision for Pb isotope measurements in such difficult matrices as acid digests of peat.

Isotopic composition of Pb in a peat profile and snow profile

Peat profile. The Pb concentrations (obtained using the EMMA XRF²⁶) as well as the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of selected samples (obtained using ICP-SMS) from the peat core collected in the Black Forest (SW Germany) is shown *versus* depth in Fig. 3. The preliminary data set of the ongoing research presented here serves to demonstrate the potential of the analytical protocol and is not yet a complete record of atmospheric lead deposition.

Ignoring the deepest samples which are “contaminated” by mineral matter from the sediment underlying the bog, the profile shows that peat samples dating from pre-anthropogenic times (4390 to 770 BC) contain less than $1 \mu\text{g g}^{-1}$ Pb and have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the range 1.18 to 1.20 (Fig. 3). In contrast, there is a tremendous increase in Pb concentrations, and decrease in Pb isotope ratios, corresponding to the start of the Industrial Revolution in the second half of the 19th century, which is consistent with other records and due mainly to coal burning.^{3,4,7,8} The lowest ratio of $^{206}\text{Pb}/^{207}\text{Pb}$ in the profile (<1.14) indicates the maximum impact of leaded gasoline. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.143 established for the youngest peat sample (dating from 2002) is consistent with the corresponding ratio found in the snow samples (1.14–1.16) for the winter season 2002/2003 collected at the same site (see below). These most recent values are much less radiogenic than the samples dating from pre-anthropogenic times which shows

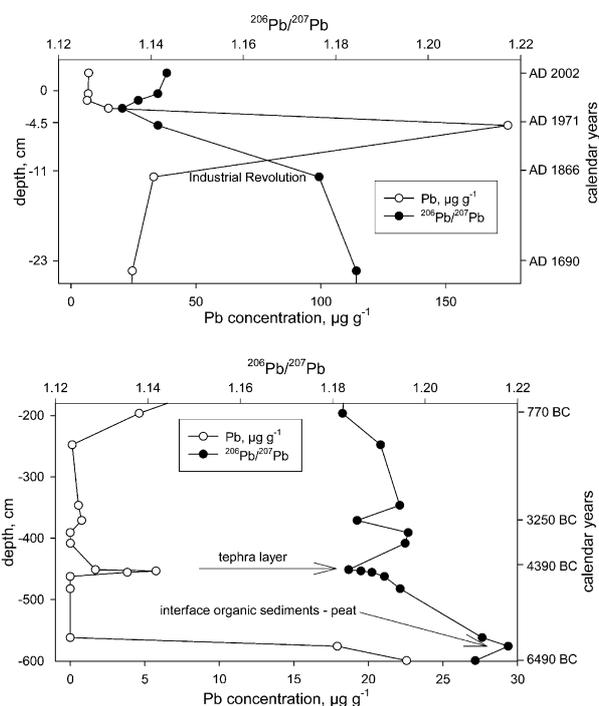


Fig. 3 Lead concentration and isotopic Pb composition ($^{206}\text{Pb}/^{207}\text{Pb}$) profile of a peat core collected in the Black Forest (SW Germany) in June 2002. Error bars indicating one standard deviation of the mean of $^{206}\text{Pb}/^{207}\text{Pb}$ data are smaller than the diameter of the data points in the figure.

unambiguously that there is *significant anthropogenic Pb contamination even today*, despite the ban on leaded gasoline in Europe. The tephra layer (volcanic eruption) found around 4390 BC in the peat profile is revealed by increased Pb concentrations and a distinct change in its isotopic composition, documenting a different predominant source of Pb. Clearly, the accuracy and precision of the Pb isotope ratio measurements obtained using ICP-SMS are not only sufficient for fingerprinting the predominant sources of Pb in modern, contaminated samples, but also for identifying much smaller, natural changes in atmospheric dust deposition, such as volcanic ash inputs. For most environmental applications, therefore, given the throughput of the ICP-SMS compared with the TIMS (which requires chemical separation of Pb), TIMS measurements are probably necessary only in those cases where the best possible accuracy and precision is needed.

It is important to note here that the Pb digestion blank was

mainly caused by the purity of the digestion acids (HNO_3 and HBF_4), but was very low ($0.003 \mu\text{g l}^{-1}$) and stable. As the digestion solutions analysed for Pb isotope ratios in this study ranged between 0.5 and $1.5 \mu\text{g Pb l}^{-1}$, no blank subtraction was performed prior to the determination of the Pb isotopic ratios. The agreement between ICP-SMS and TIMS data presented in Table 3 additionally justifies this approach.

Snow profile. The snow profile from the Black Forest (SW Germany) with a length of about 70 cm (10 cm increments) represents the snow fall of the winter period of 2002/2003. The snow was collected close to the site where the peat core was sampled in the year 2002. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and the total Pb concentration (determined by ICP-SMS) are plotted against depth in Fig. 4. The surface layer of the snow profile contained the highest Pb concentration ($1.6 \mu\text{g l}^{-1}$), with no clear tendency for the other snow samples. The lowest Pb concentrations in snow amounted to $0.088 \mu\text{g l}^{-1}$. These Pb concentrations are in good agreement with findings of Döring *et al.*²⁹ who reported Pb concentrations ranging from 0.02 to $5.5 \mu\text{g kg}^{-1}$ in snow samples from two high alpine sites. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the snow samples ranged from roughly 1.14 to 1.16 and is close to the values found for modern peat samples from the same site (see above). These $^{206}\text{Pb}/^{207}\text{Pb}$ ratios fit well into the range of 1.12 to 1.17 that was reported for 90 snow samples covering the years 1993–1996 from two alpine glaciers.²⁹ Other authors found $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ranging from 1.161–1.128 in snow samples from 15 remote locations in the French Alps during the period 11/98–04/99.³⁰ Because of the high sensitivity of the employed ICP-SMS instrument, the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios could be analysed with an external precision of 0.12% and 0.24%, respectively, in the snow sample with the lowest Pb concentration ($0.088 \mu\text{g l}^{-1}$). External precision of Pb isotope ratios in the other snow samples was $<0.1\%$. The procedural blank (including filtering of the snow samples) was very low amounting to $0.003 \mu\text{g l}^{-1}$ and thus was not considered for the Pb isotope ratio determination.

Conclusions

This study clearly demonstrated that the accuracy of Pb isotope ratio determination by ICP-SMS in acid digests of peat samples is comparable to TIMS analysis. Deviations of ICP-SMS results from the reference values obtained by TIMS are generally $<0.1\%$. Even though the precision obtained using TIMS is generally at least one order of magnitude superior to

that of ICP-SMS ($<0.1\%$ at sufficiently high count rates and dilution factor), many applications in earth and environmental sciences do not require such precision. In fact, the accuracy and precision of Pb isotope ratios obtained using ICP-SMS makes it a powerful tool for fingerprinting the predominant sources of anthropogenic Pb in environmental samples such as peat. Even natural, geological variations in atmospheric Pb deposition such as volcanic ash (tephra) are clearly seen using this approach. About 86% of the source discriminating power can be attributed to the ^{206}Pb , ^{207}Pb and ^{208}Pb isotopes.³¹ Thus, highly precise and accurate analytical data rather than a lack of ^{204}Pb data (where TIMS is certainly superior to ICP-MS), is the most critical issue with respect to unequivocal identification of Pb sources in most cases.³¹

Considering the speed of ICP-MS (four samples h^{-1} including bracketing standards), the analytical approach presented here is an excellent alternative to the distinctly more laborious and time-consuming TIMS methodology.

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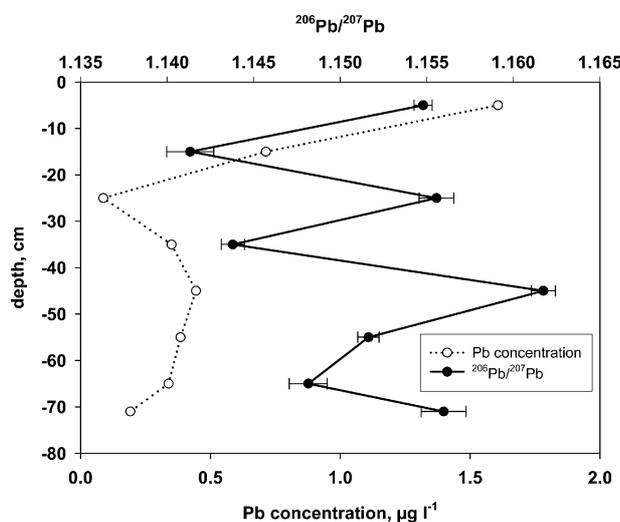


Fig. 4 Lead concentration and isotopic Pb composition ($^{206}\text{Pb}/^{207}\text{Pb}$) profile of a snow core collected in the Black Forest (SW Germany) in February 2003.

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