A new variable dispersion double-focusing plasma mass spectrometer with performance illustrated for Pb isotopes

N.S. Belshaw[a],*, P.A. Freedman[b], R.K. O'Nions[a], M. Frank[a], Y. Guo[a]

[a]*Department of Earth Sciences, Oxford University, Parks Rd, Oxford, OX1 3PR, UK*
[b]*Nu Instruments Ltd, Wrexham Industrial Estate, Wrexham, Wales, UK*

Abstract

A new generation multiple collector plasma source mass spectrometer (PSMS) produced by Nu Instruments Ltd is evaluated. The instrument has a double-focusing Nier–Johnson analyser with laminated magnet and a novel variable dispersion ion optical arrangement, enabling all masses to be located in the centre of the Faraday collectors of a fixed static array.

The performance of the instrument has been assessed through the analysis of NBS-981 Pb using a Tl doping technique with Faraday collector efficiencies and amplifier gains determined independently. A second method of analysis involves comparison of interspersed standard and sample Pb measurements with effective gains for each collector determined from the standards. In both cases the repetition of Pb isotope measurement is competetive with the thermal ionization mass spectrometry (TIMS) double-spike method. (Int J Mass Spectrom 181 (1998) 51–58) © 1998 Elsevier Science B.V.

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1. Introduction

The importance of the plasma source mass spectrometer (PSMS) as an analytical tool is now well established. It offers clear advantages as a rapid means of determining elemental and isotopic abundances in both liquids and solids. The inherent simplicity of the plasma source combined with its ability to ionise all elements has opened up new areas of mass spectrometric application and its success in measuring isotope ratios of elements with poor thermal ionization efficiencies have made it either preferable or a serious alternative to thermal ionisation mass spectrometry (TIMS). The performance of TIMS instruments in terms of analytical sensitivity, precision, and accuracy of isotope ratio measurement have been documented extensively over the last few decades but these aspects of the plasma source instruments are yet to be fully evaluated.

Previous studies (e.g. [1,2]) have compared PSMS and TIMS and emphasized the restriction of TIMS to elements with relatively low ionisation energy. In contrast, the plasma source is able to ionise elements with high ionization energies and samples may be presented to the mass spectrometer with minimal chemical preparation. Initial attempts to measure isotope ratios using plasma source instruments were made with quadrupole mass analysers and their accuracy was limited by the inherently poor peak shape

* Corresponding author.

and restricted analytical precisions to 0.1–0.5%. This situation underwent a dramatic improvement with the coupling of the plasma source to a multiple collector magnetic sector mass spectrometer [1,2]. The first instrument of this type was produced by Fisons Instruments and there are now some notable successes in the application of this instrument to problems in the geological sciences (e.g. [3–7]).

The purpose of this article is to describe the configuration of a new generation instrument that is also commercially produced by Nu Instruments, UK. The instrument is configured as a full double-focusing instrument in order to handle the ion energy spread that also includes a fast laminated magnet and a fixed multiple collector array coupled to a variable dispersion zoom lens system.

2. Instrument configuration

2.1. Source

The source of the instrument is similar to that used elsewhere (e.g. [1,2]) and comprises a Fassel-type ICP torch with automated radio frequency power matching. This configuration has been evaluated so far for aqueous samples using either a peristaltic pump and Meinhard nebuliser, or a microconcentric nebuliser. The interface region of the instrument consists of a water cooled Ni sampler cone located in front of a Ni skimmer cone operating at approximately 4 kV. These cones are followed by the extraction and transfer optics (Fig. 1). The extraction optics (Lens 1) arrange for the passage of a circular cross-section ion beam to a transfer assembly (Lens 2) in which the ion beam is converted from circular to slit geometry in order to meet the entrance requirements of the mass analyser. These extraction and transfer stages are housed in separately pumped chambers that are interconnected by small apertures that allow ions to pass from the plasma at atmospheric pressure into the analyser, but at the same time severely restrict the conductance of Ar gas. In this arrangement the ion-pumped mass analyser operates at $\sim 3 \times 10^{-9}$ mbar.
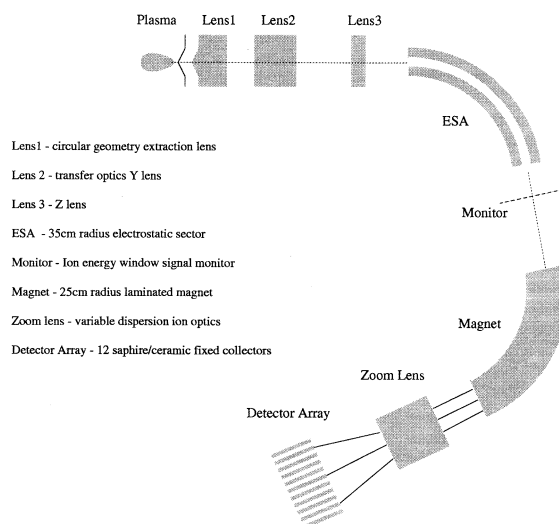

Fig. 1. Schematic layout of the variable dispersion PSMS. The mass spectrometer is a double-focusing Nier–Johnson arrangement with a fast-scanning, low heat dissipation laminated magnet. The detector array consists of 12 fixed Faraday collectors and three fixed ion counting channels. The mass dispersion of the ion beam is varied using a zoom lens system situated between the magnet and collector array. (Lens 1—circular geometry extraction lens; Lens 2—transfer optics *Y* lens; Lens 3—*Z* lens; ESA—35 cm radius electrostatic sector; Monitor—ion energy window signal monitor; Magnet—25 cm radius laminated magnet; Zoom lens—variable dispersion ion optics; Detector Array—12 saphire/ceramic fixed collectors.)

2.2 Spectrometer

The mass analyser (Fig. 1) is a Nier–Johnson double-focusing geometry with a 35 cm radius electrostatic sector followed by a 25 cm radius laminated magnet. Vertical or *Z* focusing in the analyser is achieved using both a long focal length lens before the electrostatic analyser (ESA) and the fringe field at the magnet exit pole. The detector array consists of 12 sapphire/ceramic Faraday collectors, with a fixed 2.5 mm spacing between them on the mass focal plane. The magnification of the final image is adjusted by a pair of quadrupole lenses that act as a zoom lens and focus ion beams optimally into the collectors (Fig. 1). At high mass, where the physical separation of adjacent masses is small, the ion beams are collected in adjacent collectors. At lower masses every second or higher order collector is used rather than imposing a large demagnification of the ion beam. Observation of

peak shape show that this approach introduces minimal aberrations. The multiple collector has three channels of ion counting using discrete dynode electron multipliers and a retardation filter for measurements at higher abundance sensitivity. The magnet is laminated and achieves high scan rates with low heat dissipation—the magnet has no special cooling and remains cool even at high mass.

This ion optical configuration offers advantages over mechanically adjustable multiple collectors, or a fixed static array of collectors without variable dispersion. Because magnetic/electrostatic switching is fast it is possible to measure the isotope composition of two or more elements on the same sample in the same analytical procedure with minimal loss of time. Such a procedure with mechanically adjustable collectors is too slow to be useful.

2.3. Electronics and control

The control and monitoring of the instrument is via an external PC that operates under WinNT or Unix. The computer is interfaced through an intelligent controller that handles real-time tasks including tuning of the rf plasma, monitoring of the source and the analyser pressures, and reading the collector signals. The analyses reported here were obtained using the Unix-based (Linux) software.

3. Analytical procedure

3.1. Background

Isotope ratios measured using plasma source instruments exhibit a large mass bias relative to accepted values that are the result of processes operating at the plasma spectrometer interface. These result in the preferential transmission of heavier ions by $\sim$1% per atomic mass unit in the Pb isotope mass range. This mass bias shows little time dependence under normal operating conditions, in contrast to the mass fractionation occurring in thermal ionisation where the isotope ratios show a small and time-dependent bias, usually towards the lighter isotopes. The correction procedures employed for mass fractionation effects in TIMS are also applicable to the discrimination effects in plasma source mass spectrometers. Thus, for the TIMS analysis of an element such as Sr or Nd the correction factor applied for discrimination may be derived from the measurement of the nonradiogenic isotope ratios such as $^{86/88}$Sr, $^{146/144}$Nd. A similar correction procedure is used here.

For Pb on the other hand, where only ^{204}Pb is without a radiogenic contribution, the optimal TIMS procedure is to use a double spike (e.g. [8–10]) or to limit fractionation through careful control of filament temperature. With the PSMS a different approach may be adopted by exploiting the chemical independence of the mass bias imposed on all species extracted from the plasma. The technique of Tl doping is used to obtain an estimate of the mass discrimination from the $^{205/203}$Tl ratio that is then applied to the isotopes of Pb. Measurements of standard materials have demonstrated that different elements with isotopes in a similar mass range may be used to derive valid correction factors, certainly at the precisions so far achieved [1–3]. An alternative measurement procedure is possible with a plasma source instrument similar to that used, for example, in carbon or oxygen stable isotope analysis. In this case samples are referenced to measurements of standards before and after the unknown, an approach that depends on either minimal or time-independent discrimination.

3.2. Experimental

In this article the capabilities of the new variable dispersion instrument have been assessed using NBS-981 and a sample of ferromanganese crust for which TIMS measurements of Pb isotopes are available. The repetition of Pb isotope ratio measurement has been assessed using two approaches: (1) Measurements of Tl-doped NBS-981 solutions were taken over a period of several weeks to determine the long-term stability and the repetition of isotope ratio measurement. Tl was added to standard Pb in a 1:1 concentration ratio to ensure similar signal levels for the major isotopes of Pb and Tl and minimise error propogation during mass bias correction. The gains of the Faraday col-

lectors were derived from a calibration using Ag isotopes. This calibration technique uses the quadrupole lenses to vary the mass dispersion to calibrate two adjacent Faraday collectors using ^{107}Ag and ^{109}Ag. This involves holding one isotope of Ag in a reference collector while simultaneously altering the magnet and zoom lenses to switch the other isotope between two other collectors to be calibrated. In this manner the relative gain factor between two collectors may be rapidly determined to precisions <20 ppm and the relative gains of all collectors in the array may be similarly determined. Ag is particularly useful for this calibration because it possesses two isotopes of similar abundance and the analyser setting required for the calibration routine is within the useful magnification range of the zoom lens; (2) measurements of Pb isotope ratios in NBS-981 solutions were taken from a series of runs carried out over a period of several weeks in order to assess the precision and accuracy of the system using the standard–sample–standard reference technique. In this approach measurements of the standard are used to correct for all instrument effects during the measurement of the unknown, including collector gains and mass bias.

Samples of unknown and NBS-981 Pb standard dissolved in 2% HNO_3 were introduced into the mass spectrometer using a Cetac MCN-6000 microconcentric nebuliser. Standards and samples were run in various sequences in order to assess the precision, accuracy and repeatability of measurement when operating the instrument using Tl doping and "standard–sample" bracketing. A typical analysis with ^{208}Pb 5 × 10^{-11} A had a duration of ~20 min with the ion beam varying by less than 10% over the analysis period. Particular care was taken to check and minimise memory in the Cetac nebuliser. Using careful acid and alcohol cleaning this could be reduced to negligible proportions. A careful examination of the background in the Pb mass region failed to reveal any resolvable contribution from Hg isotopes.

3.3. Instrument setup

The spectrometer was operated in static collection mode with the respective isotopes of Pb (204, 206,

207, 208) and Tl (203, 205) positioned in Faraday collectors by adjusting the magnetic field and zoom lens voltages. Ion beams were centred in all the collectors to better than 5% of half-height peak width whereas beam drift during a 15 min analysis was observed to be <2% of half-height peak width. The relative peak flats of the collectors have been measured using the plasma source by repeated scanning of the beams across the collector slits while measuring ratios, and are seen to be better than 50 ppm over 30% of the half-height peak width. The relative gains of the Faraday collectors are stable to < ±20 ppm over a period exceeding 5 weeks, using the calibration technique with ^{107}Ag and ^{109}Ag described above.

3.4. Data acquisition

The system was operated under computer control with samples, standards, and washes being selected automatically using a Cetac Auto sampler (ASX-100). Sample runs were preceded by an acid wash using 2% HNO_3 for 10–20 min in order to minimise any Pb memory from the sample introduction system. Data was acquired in blocks of 20 ratios with 10 s integration times. Background measurements of 20 s duration precede each block and were usually averaged over the complete analysis. An average run comprised four data blocks representing ~800 s of signal integration.

4. Results

4.1. Comparison with ion counting statistics

For NBS-981 and a ^{208}Pb ion beam of ~4 × 10^{-11} A, the typical standard errors over 200 s of measurement are shown for Pb and Tl isotope ratios in Table 1. The standard errors for the $^{208/206}$Pb, $^{207/206}$Pb, and $^{206/204}$Pb ratios are typically 12, 15, and 60 ppm, respectively, which is approximately a factor of two worse than the theoretical ion statistical errors of 5, 7, and 30 ppm (Table 1).

Table 1

Comparison of measurement precisions with theoretical ion statistical errors for Pb isotope analyses on the plasma multiple collector mass spectrometer

Ratio	σ_m[a] (ppm)	Approx. signal	~ISE[b] (ppm)
208/206	12	$208 \sim 4 \times 10^{-11}$A	5
207/206	15	$207 \sim 2 \times 10^{-11}$A	7
206/204	60	$204 \sim 1 \times 10^{-12}$A	30
205/203	12	$205 \sim 4 \times 10^{-11}$A	5

[a] One standard error on measurements from a typical analysis lasting ~200 s.

[b] Ion statistical error calculated for signal levels observed in a typical analysis.

4.2. Tl-doped analyses

The measured ^{205}Tl/^{203}Tl ratio in the Nu Plasma instrument is usually ~2.43, which differs from the accepted value of 2.387 ± .001 by approximately 1.8%, corresponding to a mass bias of ~0.9% per atomic mass unit. This appears to be typical for plasma source instruments. The bias factor may be derived from a "fractionation law" either linear, power, or exponential. The discrimination in this instrument appears to be described well by using an exponential relationship of the form

$$Rt/Rm = (m_1/m_2)^f$$

where Rm, Rt are the measured and true ratios, m_1, m_2 are the masses of interest, and f is the correction factor per atomic mass unit. The correction also depends upon the value chosen for Rt, in this case the true ^{205}Tl/^{203}Tl ratio, and it should be noted that the uncertainty in the accepted value is significantly greater than the precision of measurements reported here.

The $^{208/206}$Pb, $^{207/206}$Pb, $^{206/204}$Pb ratios obtained using the Tl-doping technique as described above are shown in Fig. 2. The results for ~80 analyses are displayed as a histogram in each case. The overall statistics for the data sets at 2σ are 100, 70, and 400 ppm for $^{208/206}$Pb, $^{207/206}$Pb, and $^{206/204}$Pb ratios, respectively. This repetition is competetive with careful TIMS measurements. The values measured for $^{208/206}$Pb, $^{207/206}$Pb, and $^{206/204}$Pb are 2.1665, 0.91463,
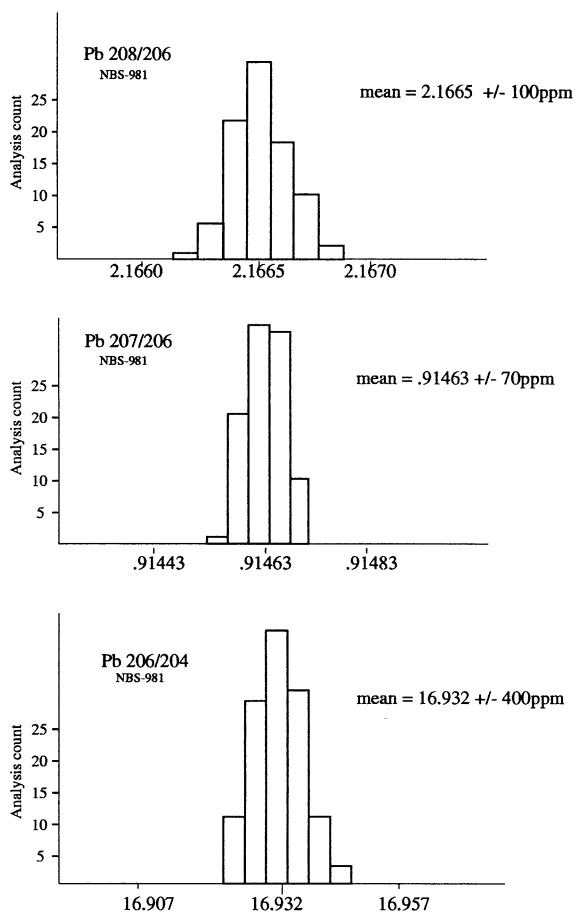

Fig. 2. Results of a series of Pb isotope ratio measurements of NBS-981 using a Tl-doping technique with correction for mass discrimination based upon the difference between the measured and accepted $^{203/205}$Tl ratio. The data were acquired over a period of 4 weeks. The mean $^{208/206}$Pb, $^{207/206}$Pb, and $^{206/204}$Pb ratios are given against the histograms together with two standard deviations.

and 16.932 using a value of 2.3875 for the $^{205/203}$Tl correction, which is in good agreement with measurements made by Hirata [11] using a Fisons Instruments Plasma-54. His published values for $^{208/206}$Pb, $^{207/206}$Pb, and $^{206/204}$Pb of 2.1664, 0.91462, and 16.931 use a power law combined with a modified external $^{205/203}$Tl correction. In both cases the measured values are slightly different from those of Todt et al. [8] with $^{208/206}$Pb, $^{207/206}$Pb, and $^{206/204}$Pb values of 2.1670, 0.91458, and 16.936, respectively. At this stage it is not known whether these small differences
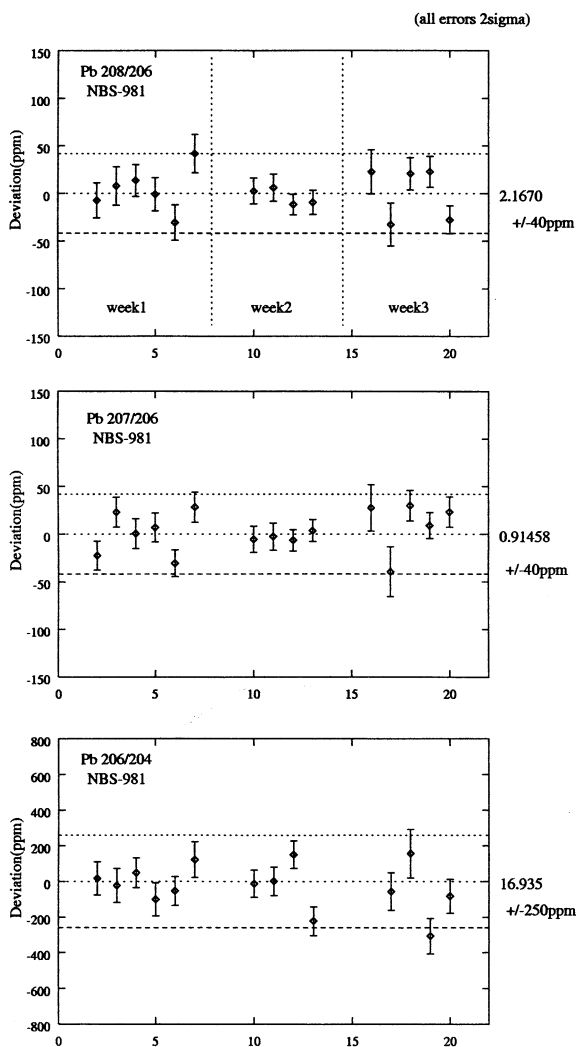
(all errors 2sigma)

Fig. 3. An assessment of the repetition of Pb isotope ratio measurements in NBS-981 using the standard–sample–standard technique. The "standard" was used to determine correction factors including discrimination and Faraday gains relative to the Todt et al. [8] reference values for NBS-981. These were applied by interpolation to the samples. The repetition of these measurements are shown with 2σ errors as ppm deviation from the Todt et al. [8] values. The repetition is competetive with the best double-spike Pb isotope ratio measurements by TIMS.

the mass bias correction alters the calculated Pb ratios and is therefore somewhat arbitrary. These effects are currently the subject of further investigation.

4.3. Sample-standard procedure

Fig. 3 displays measurements of NBS-981 taken over a period of several weeks during extended runs of ~4 h each. The data are displayed as deviations from the Todt et al. [8] values and alternate measurements are used to correct for mass bias and amplifier gain variation. This corresponds to running an unknown sample with normalisation to measurements of the reference standard (NBS-981). This procedure is slower but appears to offer higher precision of Pb isotope analysis achievable with the current configuration. Each point in the plot represents ~15 min of data bracketed by the measurement of the standard and displayed as the ppm deviation from expected value with error bars indicating the internal precision of the individual analyses ($2\sigma_m$). Because the measurements were taken during extended instrument runs over a period of several weeks the horizontal axis may be viewed as time. The errors observed in repeated measurements of NBS-981 bracketed by standard samples are displayed as deviations from the reference value. $^{208/206}$Pb, $^{207/206}$Pb, and $^{206/204}$Pb show deviations of 40, 40, and 250 ppm, respectively, using this approach. These values are higher by a factor of 2–3 than the internal precisions recorded in each case that are 16, 16, and 85 ppm, respectively. Although poorer than the internal statistics, these confidence estimates are superior to those derived so far using Tl doping. The reasons for this are in part the absence of the propagated errors associated with Tl normalisation, but there may be other sources of error in the Tl-doping method yet to be understood. The results are certainly competetive with ^{202}Pb–^{205}Pb double-spike [8–10] methods using TIMS and should become the method of choice.

4.4. TIMS/PSMS comparison

In order to compare the relative precisions and accuracy of Pb isotope ratio measurement by multiple

represent real differences in the measured materials, result from contamination, or are an artifact of uncharacterised instrumental contributions and fractionation effects.

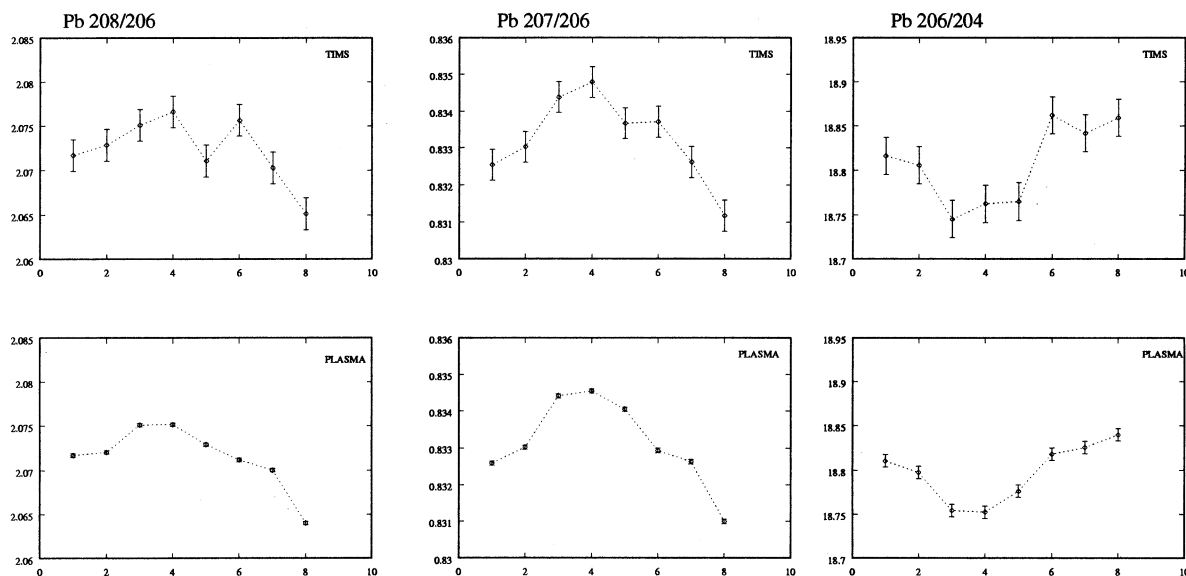Adjustment of the $^{205/203}$Tl value used to determine

Fig. 4. Comparison of conventional TIMS and PSMS Pb isotope ratios in a depth profile of a ferromanganese crust. The PSMS Pb isotope ratios were calculated using the Tl-doping method. (All errors are 2σ external.)

collector plasma PSMS and TIMS on geological materials a series of samples taken from a ferromanganese crust have been analysed. For both the TIMS and PSMS measurements samples were dissolved in 6M HCl and Pb extracted and purified using HBr anion exchange chromatography following previously reported techniques [12]. The samples were analysed for Pb isotopes by the conventional TIMS methods and by PSMS using the Tl-doping technique described above. Sample sizes were typically ~ 1 mg

and solution aliquots in 2% HNO_3 used for PSMS were doped 1:1 with Tl. The sample solutions were 1 ml with ≤ 0.5 ppm Pb.

The PSMS results are typically 10 times more precise than TIMS values, as shown for $^{208/206}Pb$ ratios in Table 2. The Pb isotope profiles for $^{206/204}Pb$, $^{207/206}Pb$, and $^{208/206}Pb$ are compared in Fig. 4. In all cases the PSMS results are substantially more precise than the conventional TIMS analyses.

Table 2
A comparison of $^{208/206}Pb$ measurements from ferromanganese crust measured by TIMS and PSMS. Sample numbers represent position in a depth profile

Sample	TIMS $(\pm 2\sigma)^{a}$	PSMS $(\pm 2\sigma_m)^{a}$
1	2.0717 (18)	2.0717 (2)
2	2.0728 (")	2.0720 (")
3	2.0751 (")	2.0750 (")
4	2.0766 (")	2.0750 (")
5	2.0710 (")	2.0729 (")
6	2.0757 (")	2.0712 (")
7	2.0703 (")	2.0700 (")
8	2.0651 (")	2.0640 (")

[a] Displayed errors are 2σ external derived from repeated measurements of SRM NBS-981.

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