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Isotope-ratio measurements of lead in NIST standard reference materials by multiple-collector inductively coupled plasma mass spectrometry

Abstract The capability of a second-generation Nu Instruments multiple collector inductively coupled plasma mass spectrometer (MC-ICP–MS) has been evaluated for precise and accurate isotope-ratio determinations of lead. Essentially the mass spectrometer is a double-focusing instrument of Nier–Johnson analyzer geometry equipped with a newly designed variable-dispersion ion optical device, enabling the measured ion beams to be focused into a fixed array of Faraday collectors and an ion-counting assembly. NIST SRM Pb 981, 982, and 983 isotopic standards were used. Addition of thallium to the lead standards and subsequent simultaneous measurement of the thallium and lead isotopes enabled correction for mass discrimination, by use of the exponential correction law and $^{205}Tl/^{203}Tl = 2.3875$. Six measurements of SRM Pb-982 furnished the results $^{206}Pb/^{204}Pb = 36.7326(68)$, $^{207}Pb/^{204}Pb = 17.1543(30)$, $^{208}Pb/^{204}Pb = 36.7249(69)$, $^{207}Pb/^{206}Pb = 0.46700(1)$, and $^{208}Pb/^{206}Pb = 0.99979(2)$; the NIST-certified values were 36.738(37), 17.159(25), 36.744(50), 0.46707(20), and 1.00016(36), respectively. Direct isotope lead analysis in silicates can be performed without any chemical separation. NIST SRM 610 glass was dissolved and introduced into the MC-ICP–MS by means of a micro concentric nebulizer. The ratios observed were in excellent agreement with previously reported data obtained by TIMS and laser ablation MC-ICP–MS, despite the high Ca/Pb concentration ratio (200/1) and the presence of many other elements at levels comparable with that of lead. Approximately 0.2 μg lead are sufficient for isotope analysis with ratio uncertainties between 240 and 530 ppm.

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Introduction

Thermal ionization mass spectrometry (TIMS) was considered for many years the most accurate and precise isotope-ratio measurement technique for lead. Intrinsically this technique suffers from two major disadvantages – the results are extremely sensitive to sample preparation and instrumental conditions and lead has only one non-radiogenic isotope (^{204}Pb), which prevents the use of internal normalization to correct for isotope fractionation in the thermal ionization process. Internal normalization requires two stable isotopes of the element under study, with a nature-invariant isotopic ratio and preferentially a mass difference of one or two mass units. The isotope ratio data obtained where internal normalization is applicable, as in Sr, Nd, and Hf analysis, are up to one order of magnitude better in terms of external precision than data obtained for lead. By adhering to strict reproducibility in analytical procedures and by applying external isotopic reference materials reliable lead isotope ratios were, nevertheless, obtained.

The introduction of inductively coupled plasma (ICP) ion sources in elemental analysis and, more recently, the introduction of multiple-collection ICP mass spectrometry (MC-ICP–MS) in isotope-ratio analysis [1, 2] considerably improved analytical measurement procedures by eliminating tedious sample preparation, especially for heavy metal analysis. The use of external spiking by a different element, e.g. thallium in lead analysis [3, 4], imitates the internal normalization applied in TIMS for Sr, Nd, Hf, and other elements. The ions ^{203}Tl, ^{205}Tl, ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb are monitored simultaneously. This measurement procedure enables correction for isotope fractionation in the ICP ion source and takes care of drift, further improving data precision. Consequently overall higher precision and accuracy are achieved. It has been shown that MC-ICP–MS, when combined with laser ablation sample-introduction, can be used for lead isotope ratio measurements in solid samples [5].

The objectives of this study were to demonstrate the performance of an MC-ICP–MS instrument for lead iso-

Fig. 1 Schematic diagram of the layout of the Nu Instruments Faraday cup multiple-collector array and the ion-counting detector assembly
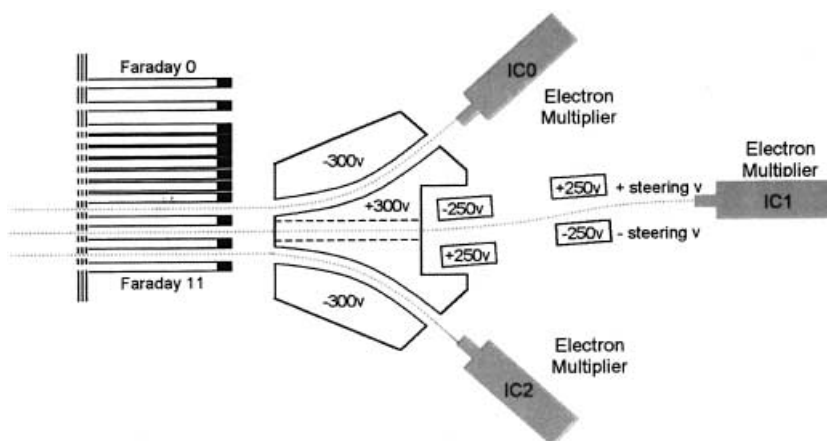
tope-ratio analysis. The precision and accuracy were determined for analysis of NIST SRM 981, 982, 983, and 610 glass; the thallium concentration effect in the thallium–lead correction method was tested; and an attempt was made to show that direct lead isotope-ratio determination is possible in real samples by sample dissolution only, i.e. without chemical separation of the lead. NIST SRM 610 glass was chosen because its lead isotope ratios are already well known.

Experimental

The mass spectrometer. The mass spectrometer was a double-focusing instrument, with Nier–Johnson geometry, manufactured commercially by Nu Instruments, UK, which has recently been installed in GSI, Jerusalem. The unique feature of this machine is the use of a fixed multiple-collector array instead the adjustable multi-collector arrangement used in the earlier generation MC-ICP–MS instruments [1, 2]. The ions are targeted into the chosen fixed collector by use of a variable-dispersion ion-optical arrangement. Figure 1 shows the schematic layout of the fixed multiple-collector array and the ion-counting detector assembly. The Nu instrument has been described in detail elsewhere [6]. Figure 2 depicts the schematic layout of the mass spectrometer. Instrumental operating conditions and signal measurement settings were as given in Table 1.

Analytical procedures. Samples of NIST SRM 981, 982, and 983 lead were prepared by dissolving the metal standard, then diluting each standard to a concentration of 500 μg L^{-1} with de-ionized water and doping with thallium (Johnson Matthey Specpure) at different concentration ratios $1 < Pb/Tl < 10$. The solutions were adjusted to 2% nitric acid with ultra pure HNO$_3$ and introduced into the plasma via a standard Meinhard nebulizer at a rate of 0.35 mL min^{-1}. NIST SRM 610 solution (containing 426 μg L^{-1} lead) was prepared by dissolving 20 mg solid in hot hydrofluoric acid, evaporating to dryness (for total removal of silica), dissolving in dilute nitric acid and adjusting to 100 and 500 μg Pb L^{-1}. No thallium was added because the sample contains 62 μg L^{-1} of this element. The solution was introduced into the plasma via an Aridus micro concentric nebulizer at a rate of 0.08 mL min^{-1}.

Seven out of twelve Faraday collectors were used in this work, in the simultaneous data collection mode of operation. Isotope [204]Pb was adjusted to the "axial" collector, [205]Tl, [206]Pb, [207]Pb, and [208]Pb to the high-1, high-2, high-3, and high-4 collectors, respectively, and [203]Tl and [202]Hg to the low-1 and low-2 collectors respectively.

Four to six samples of each standard were analyzed. The means of the results, with their $\pm 2\sigma$ uncertainty, are presented in Tables
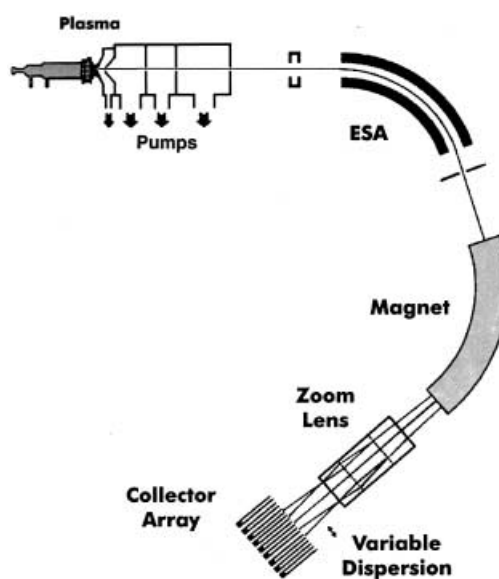

Fig. 2 Schematic diagram of the layout of the Nu Instruments multiple collector ICP mass spectrometer

Table 1 Operating conditions used for MC-ICP–MS

RF power	1300 W
Plasma gas flow rate	13 L min^{-1}
Interface cones	Nickel
Acceleration voltage	4 kV
Ion-lens setting	Optimized for maximum intensity
Instrument resolution	Approximately 300
Mass-analyser pressure	10^{-6} Pa
Detector	12 Faraday collectors and 3 ion counts
Nebulizer	Meinhard and microconcentric
Spray chamber temperature	70 °C
Desolvator temperature	160 °C
Sample flow rate	0.35 mL min^{-1} or 0.08 mL min^{-1} (MCN)
Sweep gas (argon) flow rate	3.65 L min^{-1} (optimized daily)
Typical [208]Pb sensitivity	10 V μg^{-1} L^{-1} (20 V μg^{-1} L^{-1} for MCN)
Sampling time	Three repetitions of 10×10 s

2–4. Each sample comprises of four blocks of ten integrations with 10 s duration per integration, i.e. a total of 400 s. Measurement duration was 10–11 min, including 2 min purging before measurements and the time needed for baseline and peak-centering adjustments. In analysis of SRM 981, 982, and 983, therefore, approximately 3.5–4.0 mL, or 1.7–2.0 µg Pb (for 500 µg Pb L^{-1} solutions) were consumed. The ^{208}Pb ion beam intensity was 4.5–5 V. Because of the scarcity of sample SRM 610, only three data blocks were collected during approximately 8 min. For 100 and 500 µg L^{-1} lead concentrations and 0.08 mL min^{-1} flow rate sample consumption corresponds to approximately 0.065 and 0.32 µg lead, respectively.

Results and discussion

Lead isotope-ratio determination in NIST SRM 981, 982, and 983

Table 2 summarizes our measurements of the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$, and $^{208}Pb/^{206}Pb$ isotope ratios. The values observed are in very good agreement with the TIMS values of Todt [7], who re-determined the values for NIST 981 and 982 by applying the double-spike technique with ^{202}Pb and ^{205}Pb spikes. They are also in very good agreement with the results of Belshaw et al. [6], who provided the first set of lead data using the Nu instrument. The table also contains selected literature data, mainly MC-ICP–MS results. Agreement with these data is very good except for the ratios obtained by White et al. [8] for SRM 981, in which the ^{206}Pb isotope is involved, and the ratios of Rehkamper and Mezger for SRM 982 [9]; all these ratios are slightly higher. White et al. [8] noted in their study systematic errors as a result from an "uneven background" and different collector efficiencies. The isotopic mass discrimination of the mass spectrometer (mainly of the ICP ion source) was corrected by use of the technique introduced by Longerich et al. [3] and Ketterer et al. [4] using $^{205}Tl/^{203}Tl = 2.3875$ (R_{true}), and applying the exponential correction equation

$$f = \log(R_{true}/R_{obs})/\log(m_{205}/m_{203})$$

where R_{obs} is the measured ratio, m_{205} and m_{203} are the exact atomic masses of Tl isotopes and f is the correction

Table 2 Isotope ratios for lead in NIST SRM 981, 982, and 983

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
NIST SRM 981; TIMS					
NIST 1968 [12]	16.937(10)	15.491(15)	36.721(36)	0.91464(34)	2.1681(1)
Platzner 1987 [13]	16.937(14)	–	–	0.91464(14)	2.16605(63)
Todt et al. 1996 [7]	16.9356(23)	15.4891(30)	36.7006(112)	0.914585(132)	2.16701(43)
Galer and Abouchami 1998 [14]	16.9405(15)	15.4963(16)	36.7219(44)	0.914750(35)	2.16771(10)
Thirlwall 2000 [15]	16.9409(22)	15.4956(26)	36.722(80)	0.91469(7)	2.16770(21)
NIST SRM 981; MC-ICP–MS					
Walder et al. 1993 [2]	16.937(8)	15.483(8)	36.691(15)	0.91411(21)	2.1662(2)
Hirata 1996 [16]	16.9311(90)	15.4856	36.6800(210)	0.91462(4)	2.16636(82)
Belshaw et al. 1998 [6]	16.932(7)	15.487	36.683	0.91463(6)	2.1665(2)
Rehkamper and Halliday 1998 [17]	16.9364(55)	15.4912(51)	36.6969(128)	0.91464(34)	2.16677(14)
Collerson and Palacz 1999 [18]	16.937(6)	15.491(50)	36.694(15)	0.91460(22)	2.16649(36)
White et al. 2000 [8]	16.9467(76)	15.4899(39)	36.6825(78)	0.91404	2.1646(8)
Rehkamper and Mezger 2000 [9]	16.9366(29)	15.4900(17)	36.7000(23)	0.91459(13)	2.16691(29)
This work, 2001	16.9350(22)	15.4903(26)	36.6945(72)	0.91468(2)	2.16676(8)
Uncertainty (ppm)	130	170	200	22	37
Mean, all values included	16.9365(94)	15.4885(60)	36.6897(158)	0.914750(52)	2.16633(146)
Excluding [8]	16.9350(22)				2.16657(52)
NIST SRM 982; TIMS					
NIST 1968 [12]	36.738(37)	17.159(25)	36.744(50)	0.46707(20)	1.00016(36)
Todt et al. 1996 [7]	36.7492(13)	17.1621(9)	36.7555(6)	0.467006(22)	1.00016
NIST SRM 982; MC-ICP–MS					
Walder et al. 1993 [2]	36.711(21)	17.141(9)	36.702(22)	0.46692(8)	0.99986(8)
Hirata 1996 [16]	36.712(27)	17.146	36.707(24)	0.46703(20)	0.99974(6)
Rehkamper and Mezger 2000 [9]	36.7427(30)	17.1623(8)	36.7517(39)	0.46710(4)	1.00025(13)
This work, 2001	36.7326(68)	17.1543(30)	36.7249(69)	0.46700(1)	0.99979(2)
Uncertainty (ppm)	185	175	190	21	20
NIST SRM 983					
NIST TIMS 1968 [12]	2695(145)	191.9(10.5)	36.71(2.04)	0.071201(40)	0.013619(24)
Walder et al. MC-ICP–MS 1993 [2]	2723.0(22.4)	193.8(1.6)	37.08(0.30)	0.071174(11)	0.013615(17)
This work MC-ICP–MS, 2001	2737.3(8.2)	194.91(0.55)	37.2847(94)	0.071202(2)	0.013672(2)
Uncertainty (ppm)	3000	2800	250	28	145

Table 3 Isotope ratios for NIST Lead SRM 981 and 982 (500 µg L^{-1}) and different thallium concentrations

Tl conc., µg L^{-1}	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
NIST 981					
50	16.9359(24)	15.4909(24)	36.6955(57)	0.91469(3)	2.16673(4)
100[a]	16.9366(20)	15.4910(40)	36.6959(47)	0.91465(2)	2.16663(5)
100[a]	16.9350(22)	15.4903(26)	36.6945(72)	0.91468(2)	2.16676(8)
500	16.9376(34)	15.4923(33)	36.6982(35)	0.91486(2)	2.16668(1)
Mean ± 2SD	16.9363(22)	15.4911(17)	36.6960(31)	0.91473(19)	2.16670(11)
NIST 982					
50	36.7357(40)	17.1547(25)	36.7247(45)	0.46699(1)	0.99968(9)
100[a]	36.7346(37)	17.1543(21)	36.7243(36)	0.46698(1)	0.99971(2)
100[a]	36.7326(68)	17.1543(30)	36.7249(69)	0.46700(1)	0.99979(2)
500	36.7377(17)	17.1556(13)	36.7255(24)	0.46697(1)	0.99967(1)
Mean ± 2SD	36.7352(42)	17.1548(11)	36.7249(10)	0.46699(3)	0.99971(10)

[a] Two successive measurements after 20 days

factor per atomic mass unit. In applying the 2.3875 Tl ratio value we followed the work of Belshaw et al. [6] who also used a Nu Instrument. This value is also a default in our computer software. Rehkamper and Mezger [9] discussed the Tl correction techniques applied by various groups whose data are given in Table 2. Inspecting their data, especially for SRM 982, which is an SRM of higher reliability than SRM 981, reveals that the hexapole collision cell/magnetic sector MC-ICP–MS used by them discriminates slightly against lower-mass lead isotopes. This finding is also supported by yet unpublished work by another group using a hexapole instrument [10]. Rehkamper and Mezger [9] also observed that for their instrument lead isotope-ratio results depend on the concentration of the thallium spike. In the VG Plasma 54 [2] and the Nu MC-ICP–MS [6] instruments this effect is not observed.

Effect of Tl concentration on lead isotope-ratio determination

Lead isotope-ratios were measured in NIST SRM 981 and 982 solutions with lead concentrations of 500 µg L^{-1} doped with thallium at concentrations of 50, 100, and 500 µg L^{-1}. The mean values of the ratios for 1:1 Pb:Tl SRM 981 were slightly higher relative to lower thallium concentrations but, except for the $^{207}Pb/^{206}Pb$ ratio, all were well within the quoted ± 2σ uncertainty. The $^{208}Pb/^{206}Pb$ ratio at Pb:Tl = 1:1 is indistinguishable from the values at lower Tl concentrations. No thallium concentration effect at 500 µg Tl L^{-1} concentration was observed in the SRM 982 solutions. A 100 µg Tl L^{-1} concentration (Pb:Tl = 5:1) is, furthermore, sufficient to achieve good results and was generally used in this work. All the results discussed above are summarized in Table 3. Our Pb:Tl results differ from the results of Rehkamper and Mezger [9], who used a hexapole instrument, as mentioned in above.

Lead isotope-ratio determination in NIST SRM 610 glass

After earlier work on direct lead isotope-ratio determination in SRM 610 glass by use of laser-ablation (LA–MC-ICP–MS) [5], we suggested trying direct analysis merely by dissolving the sample in hot hydrofluoric acid without further lead separation. A small sample was introduced

Fig. 3 Partial NIST SRM 610 mass spectrum. Solution introduction by means of the Aridus micro concentric nebulizer
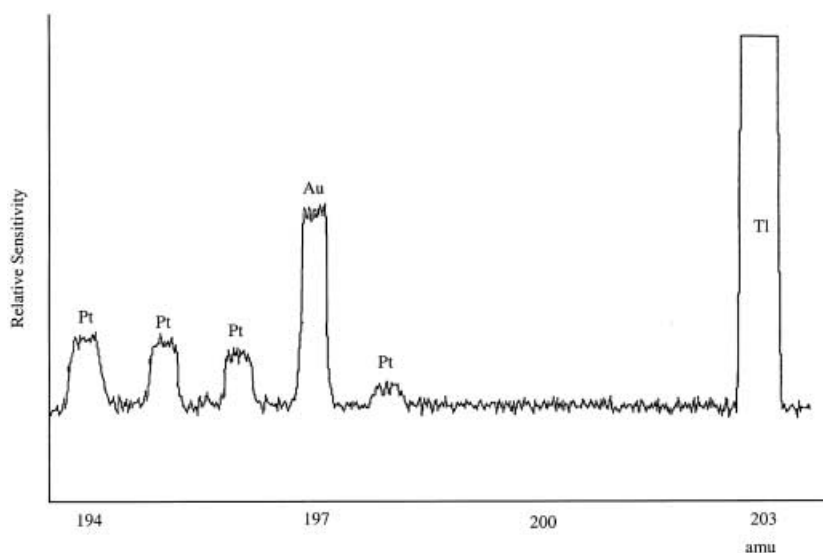
Table 4 Isotope ratios for lead in NIST SRM 610 glass

	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
Sample 1, 3 data blocks, 100 µg L^{-1}	17.052(6)	15.508(6)	36.965(15)	0.90947(1)	2.1678(2)
Sample 2, 3 data blocks, 100 µg L^{-1}	17.048(9)	15.502(9)	36.964(27)	0.90927(14)	2.1671(6)
Sample 3, 3 data blocks, 100 µg L^{-1}	17.058(7)	15.513(6)	36.977(16)	0.90938(8)	2.1677(17)
Mean, 3 samples	17.053(10)	15.508(11)	36.969(14)	0.90937(20)	2.1675(8)
Sample 2, 3 data blocks, 500 µg L^{-1}	17.046(1)	15.504(1)	36.954(4)	0.90952(4)	2.1678(1)
Sample 1, 3 data blocks, 500 µg L^{-1}	17.051(2)	15.508(2)	36.964(4)	0.90955(3)	2.1679(1)
Mean, 2 samples	17,049	15,506	36,959	0,90954	2,1679
Grand mean, 5 samples	17.051(9)	15.507(8)	36.965(16)	0.90944(22)	2.1677(6)
Uncertainty, ppm	530	520	430	240	280
Belshaw et al. TIMS 1994 [11]	17.049(12)	15.506(10)	36.989(24)	0.9095(10)	2.170(2)
Walder et al. LA-MC-ICP–MS 1993 [5]	17.051(16)	15.509(18)	36.948(38)	0.9096(8)	2.1670(18)
This work, MC-ICP–MS, 2001	17.051(9)	15.507(8)	36.965(16)	0.90944(22)	2.1675(8)

with the Meinhard nebulizer and scanned in the 200–209 mass range and revealed, besides the lead peak, thallium and ^{209}Bi peaks and a peak at m/z = 202, but no peak m/z = 201, indicating that mercury was absent from the dissolved glass. We concluded that the 202 peak is the ^{186}W^{16}O$^+$ ion. When the sample was introduced via the Aridus micro-concentric nebulizer the 202 peak disappeared, because oxide production in this type of nebulizer is significantly reduced. The relevant mass spectrum (m/z = 194–203) is shown in Fig. 3. It has been reported that the SRM 610 glass contains approximately 4 ppm mercury, which was clearly visible in the laser-ablated spectrum [5]. It is possible that the mercury was evaporated during the dissolution process. Tungsten is present as a trace element in SRM 610 glass. Table 4 summarizes the results obtained from five samples measured at two different lead concentrations. The grand mean ratio values are in remarkable agreement with the LA analysis and also with TIMS, where the sample was dissolved and the lead chemically separated [11]. In contrast with TIMS our sample preparation took 2 h only. Matrix effects from the 200 times larger calcium concentration and other elements were not observed.

Our results imply that lead isotope measurements can be performed in silicates without chemical lead separation. Whether this procedure will develop into a general technique will depend on further systematic study. Several questions, for example lead content, non-fractionated thallium presence, matrix effects, instrumental contamination, and clogging in real samples should be addressed.

Conclusions

The performance of a Nu instruments MC-ICP–MS was tested for lead isotope-ratio determinations. The ratios obtained were compared to those reported for NIST SRM 981, 982, 983, and 610 glass. External precision was high for all the results, which were in very good agreement with previously reported data. It has also been shown that the instrument does not suffer from uncontrollable discrim-

ination and relative concentration, i.e. matrix effects, at least not for the examples and conditions studied. Consequently "direct" lead isotope analysis of a solid sample could be performed merely by dissolving it, without the need for chemical separation of the lead.

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