



# **Plumbo-Isotopy: The Measurement of Lead Isotopes by Multi-Collector Inductively Coupled Mass Spectrometry**

By W. Ian Ridley

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# Plumbo-Isotopy: The Measurement of Lead Isotopes by Multi-Collector Inductively Coupled Mass Spectrometry

By W. Ian Ridley

## Introduction

This open-file report describes the analytical protocol for measurement of lead (Pb) isotope compositions using the Nu Plasma HR multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) facility in Building 20, Denver Federal Center, Denver, Colo. The facility is supported by The Mineral Resources Program, Geologic Discipline. Data quality is assessed by multiple analyses of the National Institute of Standards and Technology (NIST) lead standard SRM 981, which is routinely run as part of an analytical session and can be compared with the values obtained by double and triple spike thermal ionization mass spectrometry (TIMS). The data for SRM 981 reported here covers the period between April 2004 and May 2005, so analytical variability over a period of a year can be judged.

## Background

Lead has four long-lived isotopes -  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ . Their abundances in nature vary because  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$  are radiogenic daughter end products of decay chains that begin with  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$ , respectively;  $^{204}\text{Pb}$  is not radiogenic. Consequently the  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios vary widely in nature. Pb isotopes have been used extensively in age dating because three independent ages can be obtained in the U-Th-Pb system. Also, a number of natural high- and low-temperature processes fractionate the U/Th ratio so that variations in the relative abundances of the daughter isotopes of U and Th, relative to  $^{204}\text{Pb}$  and to each other, can provide useful information regarding sources of lead. Publications by Doe (1970) and Dicken (1995) provide further information on lead isotope systematics.

## Measurement of Lead Isotopes

Precise and accurate measurement of lead isotopes requires a three-step process for analysis of solid samples: (1) reaction of the material with strong acid, which provides a residue that is soluble in dilute acid; (2) concentration of lead to eliminate matrix constituents; and (3) mass spectrometry measurement of isotope abundances. For analysis of aqueous samples, step 1 is eliminated. The details of step 1 depend upon the type of material to be analyzed. For silicates, an  $\text{HF}/\text{HClO}_4 \pm \text{HNO}_3$  mixture ( $\sim 0.01$  mL HF + 0.002 mL  $\text{HClO}_4$  per mg. sample) normally is used to eliminate silica, which otherwise is highly insoluble. If the sample is likely to contain refractory phases, for example, zircon, then the dissolution step may require microwave digestion. Carbonate samples are dissolved in concentrated HCl, whereas metals and sulfides may require an aqua regia digestion. Various methods have been employed for step 2, with ion exchange being a popular and relatively easy method. Biorad AG1 X8 resin has been used extensively over the last 30 years, employing modifications of the HBr method of Chen and Wasserburg (1983). More recently,

Horwitz and others (1994) and Gale (1996) have described methods for lead separation using Eichrom™ Pb resin and Sr resin that have the advantage of reduced bed volumes, lower blank levels, and more efficient lead recovery. Step 3 involves measurement of lead isotopic composition based on spatial separation of masses. Two techniques currently are employed. Thermal ionization mass spectrometry (TIMS) has a long history for lead isotope analysis, with either a double or triple spike method being employed for the most accurate and precise data. An overview of the technique can be found in Dickin (1995). MC-ICP-MS is used increasingly for lead isotope analysis (Rehkämper and Metger, 2000; Woodhead, 2002; Collerson and others, 2002; Thirlwell, 2002). Second generation MC-ICP-MS instruments now approach the precision (< 100ppm) achieved with double/triple spike thermal ionization mass spectrometry (TIMS) data. In addition, MC-ICP-MS has the advantage over TIMS of simpler ion exchange chemistry and speed of analysis.

## MC-ICP-MS Basics

A useful tutorial on the basic principles behind ICP-MS can be found in Thomas (2001). An inductively coupled argon plasma (ICP) is used as a highly efficient source of single-charged positive ions. The detection of individual masses (m) is based on the m/z ratio, where z is the charge on each ion. Because the predominant ions extracted from an argon plasma are single-charged, their detection equates to individual isotope measurement. The ions then pass through an ion optical system. The principles behind ion optics, as used in MC-ICP-MS, are analogous to the use of light optics to provide a virtual representation of an image with minimal aberrations. In MC-ICP-MS, however, the image is an ion image rather a photon image. The ion beam is focused through a narrow slit and the ion image of this slit is used to focus specific ion masses into an array of detectors.

Between the ion optical system and the detection system is a double-focusing mass spectrometer that provides mass separation. The basic principles of mass separation in isotope measurements are based on the kinetic energy equation,  $e = \frac{1}{2}mv^2$ . Thus, monoenergetic ions travel with velocities that are proportional to their mass. However, ions generated in an argon plasma have a range of kinetic energies. In the Nu Plasma HR system the ions initially are transported through an electrostatic analyzer (ESA), which acts as an energy filter. The purpose of the ESA is to present a monoenergetic ion beam to the magnetic sector component of the mass spectrometer. The magnetic sector is a curved flight tube held within a uniform magnetic field. With this geometric arrangement, the relation between mass and velocity, as defined above, results in spatial separation of ions because ions of different mass follow different curved trajectories through the flight tube. The separation of ions exiting from the flight tube is called “mass dispersion” and is a function of instrument design. Thus, the spectrometer is said to be “double-focusing” because the ion beam is focused in energy and mass components.

Mass dispersion quantifies the physical separation, usually measured in millimeters, between adjacent masses, based on:

$$D/X = M/\Delta M \quad [1]$$

where, D = instrument dispersion (500 for the Nu Plasma HR),

X = physical separation between adjacent isotopes (mm), and

M,  $\Delta M$  = adjacent masses.

The normal case of interest is where  $\Delta M = 1$ , because this determines the separation between adjacent collectors of a multiple collector array. Because  $D$  is fixed, equation (1) indicates that as the mass decreases, the separation between adjacent masses increases. Second-generation MC-ICP-MS instruments have a maximum ion separation of ~18 percent, which allows measurement of the mass range from  ${}^6\text{Li}$  to  ${}^{238}\text{U}$ .

The array of 12 Faraday detectors (given assignments H6, H5..... AX..... L1, L2, etc. in the Nu Plasma HR) and ion counters (normally assigned ICO1, ICO2, ICO3) allows for counting of multiple ion beams. Second generation MC-ICP-MS instruments are capable of employing nine of the available 12 Faraday detectors. Taking advantage of the ion beam dispersion, individual isotopes may be detected by using either a movable detector array or a static detector array. In the latter case, the ion beam dispersion is further enhanced by an electrostatic optical system (described as “zoom optics”) to reposition individual ion beam into separate detectors. The Nu Plasma HR employs the second configuration with individual detectors being ~ 2.5 mm apart.

## **Instrumental Mass Bias: General Considerations**

Errors in mass spectrometry result from changes in individual ion mass intensities that lead to inaccurate measurement of isotope ratios. These changes are due to instrumental mass bias (also known as mass discrimination) and are distinguished from other sources of mass bias that are none instrumental. The latter usually are associated with isotope fractionation during sample preparation. It is assumed that appropriate steps have been taken to eliminate none instrumental sources of mass bias. In the case of lead, these effects are negligible.

It is well established that instrumental mass bias is a function of the measured masses ( $m_1$ ,  $m_2$ ,  $m_3$ , and so forth). Mass bias in MC-ICP-MS results in isotopic ratio measurements that are heavier than the true ratio by up to ~1.5 percent and consequently require a correction (Albarède and Beard, 2004). Mass bias also is observed in TIMS, but the effect is much less, usually < 0.2 percent. The sources of mass bias in TIMS and MC-ICP-MS are different fundamentally. In TIMS, ions are produced by heating a sample deposited on a metal filament, and this process results in isotope measurements that are initially preferentially light and become progressively heavier. Thus, the mass bias has a major component of kinetic fractionation. In MC-ICP-MS, ions are produced from an argon plasma, and mass bias is a result of ion interactions occurring principally behind the skimmer cone and within the ion optic system, referred to as “space charge effects”. In this case, the mass bias results from none representative sampling of the ion beam generated within the argon plasma. This type of mass bias has a small kinetic component and a large equilibrium fractionation component.

Mass bias in TIMS has been corrected successfully by using a variety of empirically derived mass bias laws, of which the exponential or kinetic law (Russell and others, 1978) has been most commonly applied. The application of a mass bias law requires a correction based on measurement of an isotope ratio ( $r$ ) whose value is known ( $R$ ). The exponential and power laws have been applied to MC-ICP-MS data. However, because the causes of mass bias are different in TIMS and MC-ICP-MS, it is apparent that the laws used in TIMS cannot completely account for mass bias effects in MC-ICP-MS.

## **Instrumental Mass Bias: General Application to MC-ICP-MS**

In mass spectrometry, the mass bias laws frequently are applied in a form whereby a fractionation factor  $f = f(m_x, m_y, R_B, r_B)$  is calculated and then applied to all other ratios measured during a single run. Empirically, from studies of standards of known isotopic composition, precise MC-ICP-MS data can be produced using the following correction for an isotope pair of element  $e$ :

$$R_A/r_A = [m_1/m_2]^f \quad [2]$$

where:  $R_A$  = true value of unknown ratio  $^1e/{}^2e$ ,

$r_A$  = measured value of ratio  $^1e/{}^2e$ ,

$f = \ln [R_B/r_B] / \ln [m_x/m_y]$  and has a value close to -2,

$R_B$  = known value of ratio  $^xe/{}^ye$ , and

$r_B$  = measured ratio  $^xe/{}^ye$ .

For some isotope systems, there is a natural isotope pair that is invariant in nature ( $R_B$ ) and can be used to calculate  $f$  during an analytical run. For instance, in the Sr isotope system, the true value of  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $R_A$ ) in a sample can be calculated by applying a mass bias correction to the measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio ( $r_A$ ) through the simultaneously measuring  $^{86}\text{Sr}/^{88}\text{Sr}$  ( $r_B$ ) that has an invariant value of 0.1194 ( $R_B$ ). Similarly, in measuring Nd isotope ratios, a mass bias correction can be made by applying  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ . However, as discussed below, this straightforward application cannot be used for lead isotopes.

## Instrumental Mass Bias: Application to Lead Isotopes

$^{204}\text{Pb}$  is the only stable long lived isotope of lead without a radiogenic precursor. Consequently, it is not possible to define an isotope pair within the lead isotope system that has a time-independent value. In TIMS analyses, this problem is overcome by using a lead double or triple spike method, which involves an exacting column chemistry. Lead spike methods can also be applied to MC-ICP-MS, however, a simpler method is to spike the purified lead with a thallium (Tl) solution (Longerich and others, 1987) of known isotopic composition. Commonly, NIST SRM 997 with  $^{205}\text{Tl}/^{203}\text{Tl} = 2.3871 \pm 0.0011$  is used for this purpose. The rationale behind this method (Al-Ammar and Barnes, 2001) is that the mass number of thallium is close to lead, thus the measured value of  $^{205}\text{Tl}/^{203}\text{Tl}$  can be used to calculate a value of  $f$  to correct the measured lead isotopes, that is to say,  $f_{\text{Tl}} = f_{\text{Pb}}$ . The correction scheme would be applied as follows, assuming for the sake of illustration, the application of the exponential law:

$$f = \ln[2.3871 / ({}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{meas}})] / \ln[204.9744 / 202.9723] \quad [3]$$

$${}^{204}\text{Pb}/{}^{206}\text{Pb}_{\text{corr}} = [{}^{204}\text{Pb}/{}^{206}\text{Pb}_{\text{meas}} * (203.9730 / 205.9444)] ^ f \quad [4]$$

$${}^{204}\text{Pb}/{}^{207}\text{Pb}_{\text{corr}} = [{}^{204}\text{Pb}/{}^{207}\text{Pb}_{\text{meas}} * (203.9730 / 206.9759)] ^ f \quad [5]$$

$${}^{204}\text{Pb}/{}^{208}\text{Pb}_{\text{corr}} = [{}^{204}\text{Pb}/{}^{208}\text{Pb}_{\text{meas}} * (203.9730 / 207.9766)] ^ f \quad [6]$$

A number of studies have shown that the assumption  $f_{Tl} = f_{Pb}$  is not strictly valid for MC-ICP-MS measurements (Hirata, 1996; Rehkämper and Halliday, 1998; Belshaw and others, 1998; White and others, 2000; Rehkämper and Mezger 2000); the magnitude of  $f$  is correlated inversely with analyte mass. The degree to which  $f_{Tl} \neq f_{Pb}$  is determined by individual instruments, instrument design, and daily operating conditions. Here, we examine two schemes to evaluate the relation between  $f_{Tl}$  and  $f_{Pb}$ .

(1) The exponential law with regard to lead can be expressed as follows, taking  $^{208}\text{Pb}/^{204}\text{Pb}$  as an example:

$$[^{208}\text{Pb}/^{204}\text{Pb}]_{\text{corr}} = [^{208}\text{Pb}/^{204}\text{Pb}]_{\text{meas}} * [m_{208}/m_{204}]^{f_{Pb}} \quad [7]$$

Similarly, the exponential law for thallium of known isotopic composition can be expressed as:

$$[^{205}\text{Tl}/^{203}\text{Tl}]_{\text{true}} = [^{205}\text{Tl}/^{203}\text{Tl}]_{\text{meas}} * [m_{205}/m_{203}]^{f_{Tl}} \quad [8]$$

Taking the natural logarithm of equations (7) and (8), dividing, and rearranging gives:

$$\ln[^{205}\text{Tl}/^{203}\text{Tl}]_{\text{meas}} = \ln[^{205}\text{Tl}/^{203}\text{Tl}]_{\text{true}} + [f_{Tl}/f_{Pb}] [\ln(m_{205}/m_{203}) / (m_{208}/m_{204})] * [\ln(^{208}\text{Pb}/^{204}\text{Pb})_{\text{meas}} - \ln(^{208}\text{Pb}/^{204}\text{Pb})_{\text{corr}}] \quad [9]$$

A plot of  $\ln[^{205}\text{Tl}/^{203}\text{Tl}]_{\text{meas}}$  against  $\ln[^{208}\text{Pb}/^{204}\text{Pb}]_{\text{meas}}$  defines a straight line with slope (S), given by:

$$S = [f_{Tl}/f_{Pb}] [\ln(m_{205}/m_{203}) / (m_{208}/m_{204})] \quad [10]$$

The case where  $f_{Pb} = f_{Tl}$  defines a slope of 0.50497. Deviations from this value define the value  $x$  in  $f_{Pb} = x f_{Tl}$ . The value of  $x$  is first determined from repeat analysis of a lead isotope standard and then used to correct raw sample ratios of  $^{208}\text{Pb}/^{204}\text{Pb}$ . Similar expressions can be written for  $^{207}\text{Pb}/^{204}\text{Pb}$ , etc. In principle, this is an excellent method of adjusting the  $f$  value. In practice, the utility is determined by mass bias stability because a sufficient linear spread of  $[^{205}\text{Tl}/^{203}\text{Tl}]_{\text{meas}}$  relative to  $[^{208}\text{Pb}/^{204}\text{Pb}]_{\text{meas}}$  is required to accurately define the slope S.

(2) Equation [8] can be re-written:

$$f_{Tl} = \ln[(^{205}\text{Tl}/^{203}\text{Tl}_{\text{standard}}) / (^{205}\text{Tl}/^{203}\text{Tl})_{\text{meas}}] / \ln [m_{205}/m_{203}] \quad [11]$$

The value of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{standard}}$  can be adjusted ( $^{205}\text{Tl}/^{203}\text{Tl}_{\text{adjusted}}$ ) to give a value for  $f_{Tl}$  that provides the most accurate value for  $^{208}\text{Pb}/^{204}\text{Pb}$  in a lead isotope standard. In principle, each isotope pair would have a slightly different value for  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{adjusted}}$ . In practice, a single value for  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{adjusted}}$  can be determined for a standard by a least squares fit of individual values of  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{adjusted}}$  to  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ , and  $^{207}\text{Pb}/^{206}\text{Pb}$ , and this single value used to correct sample data. This procedure would appear to have a circular logic, but the purpose is simply to determine an empirical factor that can be used to adjust isotope ratios for samples where the true ratios are unknown (Rehkämper and Halliday, 1998, Belshaw and others, 1998). In other words, this scheme recognizes the limitations of strict application of mass bias laws to MC-ICP-MS data and adds a degree of flexibility based on statistical manipulation of standard isotope data. Unlike procedure (1), this scheme assumes that mass bias is stable over the period of several hours and does not require that a standard be measured several times during an analytical session.

## Lead Isotope Measurements

Each 25 µg/L lead solution is spiked with 10 µg/L of thallium. The solution is aspirated at approximately 100µL/min through a desolvation nebulizer (Nu Instruments DSN100). Each Faraday detector has a maximum range of 10V, although for one detector pair this can be extended to 20V. Using the Nu Plasma HR, a 25 µg/l solution of lead produces ~3V of signal for  $^{208}\text{Pb}$  in low resolution mode. The detector setup is as follows:

H4	H3	H2	H1	AX	L1	L2
$^{208}\text{Pb}$	$^{207}\text{Pb}$	$^{206}\text{Pb}$	$^{205}\text{Tl}$	$^{204}\text{Pb}$	$^{203}\text{Tl}$	$^{202}\text{Hg}$

[Note: Hg contamination of Ar gas has been reported, although contamination has not been detected in the liquid Ar used in our laboratory. As a further precaution we use a Hg trap in the Ar gas line.  $^{202}\text{Hg}$  is measured to correct for potential  $^{204}\text{Hg}$  isobaric interference on  $^{204}\text{Pb}$ ].

Data are collected in three blocks involving 15 measurements per block, and 10 seconds of signal integration per measurement. Each block is preceded by a 30 second on peak background measurement that is achieved by deflecting the ion beam at the ESA. Thus, the duration of each lead isotope measurement is approximately 10 minutes. The standard deviation ( $\sigma$ ) from the mean is calculated after each measurement and all measurements outside of  $2\sigma$  are rejected. The internal standard error also is calculated. For each block of data, and for the total data set, the mean value and standard error are reported.

## Results for SRM 981

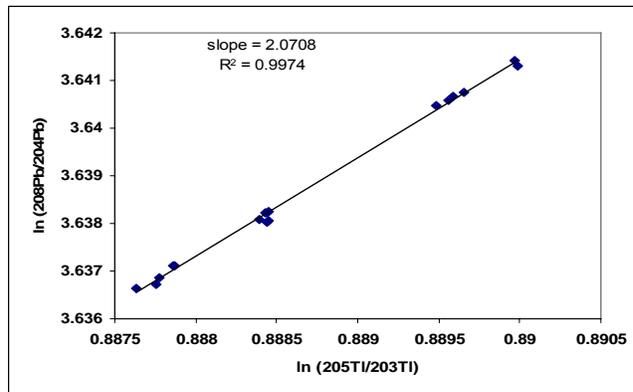
The lead isotopic composition of NIST SRM 981 has been determined over several analytical sessions from April 2004 through May 2005. The variations in mass bias for three analytical sessions, each 2 days, are shown in table 1. The increase in mass bias variation from 2004 to 2005 is partly a function of the cleanliness of the sample and skimmer cones, because mass bias can be induced by contamination from the surface of the cones.

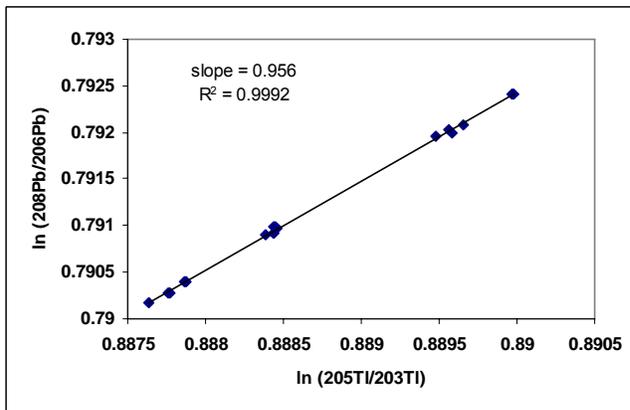
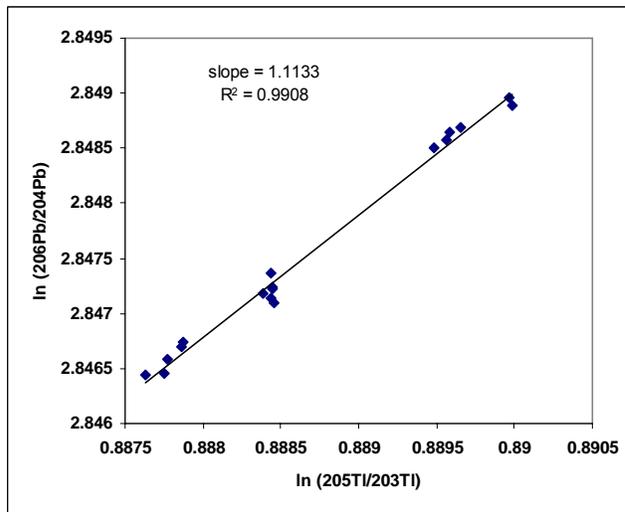
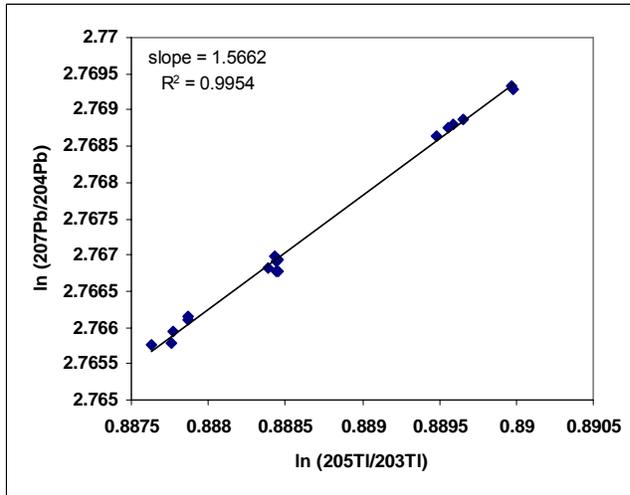
**Table 1.** 1 $\sigma$  deviations of mass bias, in ppm, in three analytical sessions

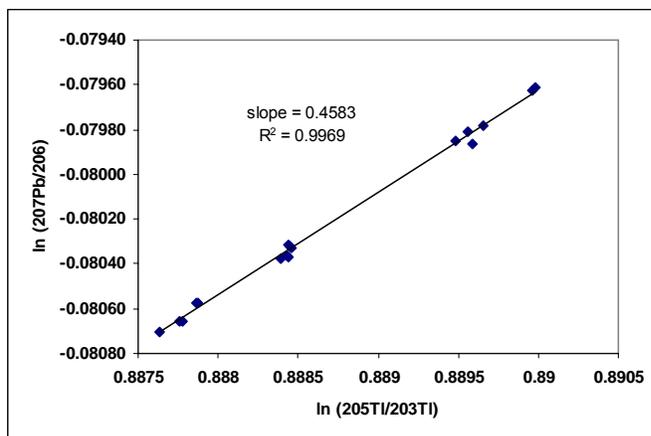
	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{205}\text{Tl}/^{203}\text{Tl}$
April 2004	92	93	94	38	27	23
May 2004	221	183	135	97	56	97
June 2005	394	291	180	207	112	215

To test scheme (1), uncorrected ratios of  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ , and  $^{207}\text{Pb}/^{206}\text{Pb}$  are plotted against uncorrected  $^{205}\text{Tl}/^{203}\text{Tl}$  in Figure 1 for the 1 year time period.

**Figure 1.** Uncorrected lead isotope ratios versus uncorrected  $^{205}\text{Tl}/^{203}\text{Tl}$  for data collected in three analytical sessions over 1 year. The slope for each dataset is determined by a linear least squares fit.







The data define linear spreads. The slope of individual linear regression lines (see equation [10] and discussion thereof) is shown in table 2. The spread of analytical data over a 1 year period varies from 1700 ppm ( $^{208}\text{Pb}/^{204}\text{Pb}$ ) to 400 ppm ( $^{207}\text{Pb}/^{206}\text{Pb}$ ).

**Table 2.** Slopes of data for lead isotope ratios versus  $^{205}\text{Tl}/^{203}\text{Tl}$  for three analytical sessions over a period of 1 year. See text for details.

	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
Slope ( $f_{pb} = f_{Tl}$ )	1.9803	1.4889	0.9848	0.9855	0.4941
Slope ( $f_{pb} = x f_{Tl}$ )	2.0708	1.5662	1.1133	0.9561	0.4583
x	1.0456	1.0519	1.1119	0.9700	0.9275
$x_1$	1.0391	1.0425	1.1053	0.9721	0.9251
$x_2$	1.0944	1.1664	1.2713	0.9959	1.1404
$x_3$	1.0449	1.0432	1.0881	0.9848	0.9888

The value of x in table 2 relates the measured slopes to theoretical slopes. The values  $x_1$ ,  $x_2$ ,  $x_3$  are calculated from data for each of the analytical sessions covering a time span of 2 days. The values of x can then be used to adjust the measured  $f_{Tl}$  values to correct the measured lead isotope sample data.

The measured slopes for all isotopes deviate significantly from the theoretical values for  $f_{pb} = f_{Tl}$  as noted by other authors; in the case of  $^{206}\text{Pb}/^{204}\text{Pb}$  by >10 percent. Adjusting the  $f_{Tl}$  value by the various values for x does not produce precise and accurate data for SRM 981. The data slopes for individual analytical sessions ( $x_1$ ,  $x_2$ ,  $x_3$ ) are significantly different from the overall slope (table 2). Correcting the  $f_{Tl}$  values for individual sessions by the values for  $x_1$ ,  $x_2$ , and  $x_3$  also produces isotope ratio values for SRM 981 that are of unacceptable quality. This problem is principally the result of the very limited variation in mass bias during individual analytical sessions, so that the linear slopes cannot be defined with sufficient accuracy to be useful. Thus, the relative stability of mass bias in the Nu Plasma HR instrument precludes the accurate measurement of a correction factor using the raw analytical data.

To test scheme (2) the raw ratios for  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ , and  $^{207}\text{Pb}/^{206}\text{Pb}$  were corrected using normalization values for  $^{205}\text{Tl}/^{203}\text{Tl}$  that varied from 2.3870 to 2.3885. The corrected ratios for each of the three analytical sessions then were compared to the

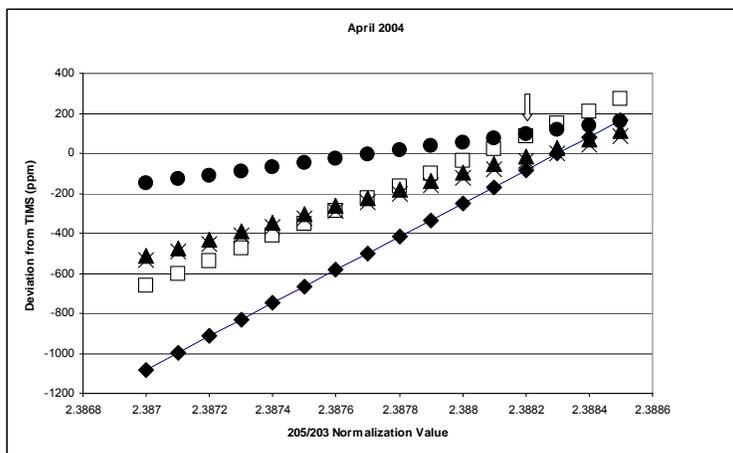
TIMS values from Todt and others (1996), differences are reported in parts per million (ppm). Results are shown in Figure 2. The TIMS values are from Todt and others (1996) as follows:  $^{208}\text{Pb}/^{204}\text{Pb} = 36.7006$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.4891$ ,  $^{206}\text{Pb}/^{204}\text{Pb} = 16.9356$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.16701$ ,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.914585$ . The arrow indicates the dataset that has the smallest standard deviation from the TIMS values. The datasets that have the smallest standard deviation from the TIMS values are corrected with  $^{205}\text{Tl}/^{203}\text{Tl}$  ratios of 2.3882 (April 2004, June 2004) and 2.3881 (March 2005) and are shown in table 3.

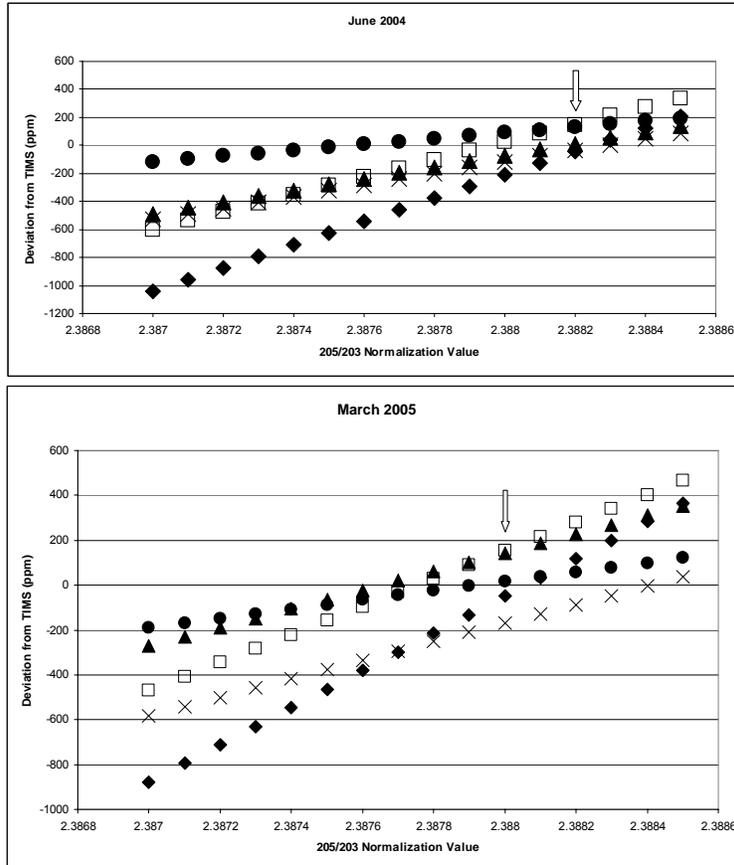
**Table 3.** Recalculated isotope ratios for SRM 981. Values in parenthesis are parts per million differences from the TIMS values of Todt and others (1996). The  $^{205}\text{Tl}/^{203}\text{Tl}$  ratios are optimal values based on a least squares fit.

	$^{205}\text{Tl}/^{203}\text{Tl}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
April 2004	2.3882	36.6975(84)	15.4904(83)	16.9354(12)	2.1669(51)	0.914674(97)
June 2004	2.3882	36.6990(44)	15.4914(148)	16.9358(12)	2.1669(51)	0.914706(132)
March 2005	2.3881	36.7018(46)	15.4924(213)	16.9387(6)	2.16673(129)	0.914619(37)
TIMS		36.7006	15.4891	16.9356	2.16701	0.914585

The small variation in the optimal values for  $^{205}\text{Tl}/^{203}\text{Tl}$  between each analytical session indicates that this empirical scheme for correcting raw lead isotope data is robust in accounting for mass bias. The small differences reflect also the relative stability of mass bias over a period of a year.

**Figure 2.** Graphical representation of deviations of SRM 981 lead isotope data TIMS data as a function of variable  $^{205}\text{Tl}/^{203}\text{Tl}$ .  $^{208}\text{Pb}/^{204}\text{Pb}$ -filled diamonds;  $^{207}\text{Pb}/^{204}\text{Pb}$ -open squares;  $^{206}\text{Pb}/^{204}\text{Pb}$ -filled triangles;  $^{208}\text{Pb}/^{206}\text{Pb}$ -crosses,  $^{207}\text{Pb}/^{206}\text{Pb}$ -filled circles.





## Discussion

Mass bias effects are more severe in MC-ICP-MS than in TIMS and are not completely corrected by mass bias laws that have been applied to TIMS analysis. This observation is consistent with the premise that mass bias in MC-ICP-MS is due principally to ion interactions within the ion optic system, but also includes contributions from the plasma and the desolvation nebulizer system. Thus, a specific physical law is unlikely to embrace all of these mass bias sources. Consequently, empiricism provides the best approach to correct raw ratio data. In effect, this approach makes no assumptions regarding an applicable mass bias law but uses an empiric fractionation factor that is statistically derived from an examination of all the lead isotope.

The second generation Nu Plasma HR instrument shows only small variations in mass bias over individual analytical sessions and even over a period of a year. This severely limits the application of mass bias correction schemes that rely on precise calculation of the linear relations between raw ratios of  $^{205}\text{Tl}/^{203}\text{Tl}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$ . However, advantage can be taken of the limited range of mass bias as a function of time by another correction scheme that involves optimizing the value of  $^{205}\text{Tl}/^{203}\text{Tl}$  used as the normalization ratio. The optimization involves a least squares fit that minimizes the differences between calculated values of  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ , and  $^{207}\text{Pb}/^{206}\text{Pb}$  and TIMS values for SRM 981. Application of this scheme to data collected over a period of a year indicates minimal variation in the optimal value of  $^{205}\text{Tl}/^{203}\text{Tl}$  ( $2.38815 \pm 0.00005$ ). This scheme produces data for SRM 981 that generally are within 100 ppm of TIMS values.

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## References Cited

- Al Ammar, A.S., and Barnes, R.M., 2001, Improving isotope ratio precision in inductively coupled plasma quadrupole mass spectrometry by common analyte internal standardization: *Journal of Analytical Atomic Spectrometry*, v. 16, p. 327-332.
- Albarède, F., and Beard, B., 2004, Analytical methods for non-traditional isotopes: *In Geochemistry of Non-Traditional Stable Isotopes, Reviews in Mineralogy and Geochemistry (Mineralogical Society of America)*, v. 55, p. 113- 152.
- Belshaw, N.S., Freedman, P.A., O’Nions, R.K., Frank, M., and Guo, Y., 1998, A new variable dispersion double-focusing plasma mass spectrometer with performance illustrated for lead isotopes: *International Journal of Mass Spectrometry*, v. 181, p. 51- 58.
- Chen, J.H., and Wasserburg, G.J., 1983, The isotopic composition of silver and lead in two iron meteorites: Cape York and Grant: *Geochimica Cosmochimica Acta*, v. 47, p. 1725-1737.
- Collerson, K.D., Kamber, B.S., and Schoenberg, R., 2002, Application of accurate, high-precision Pb isotope ratio measurements by multi-collector ICP-MS. *Chemical Geology*, v. 188, p. 65-83.
- Dicken, A.P., 1995, *Radiogenic Isotope Geology*. Cambridge University Press, 490 p.
- Doe, B.R., 1970, *Lead Isotopes*. Springer Verlag, 137 p.
- Gale, N.H., 1996, A new method for extracting and purifying lead from difficult matrices for isotopic analysis: *Analytica Chimica Acta*, v. 332, p. 15-21.
- Horwitz, E.P., Dietz, M.L., Rhoads, S., Fellinto, C., Gale, N.H., and Houghton, J., 1994, A lead-selective extraction chromatographic resin and its application to the isolation of lead from geological samples: *Analytica Chimica Acta*, v. 292, p. 263-273.
- Kamenov, G.D., Mueller, P.A., and Perfit, M.R., 2004, Optimization of mixed Pb-Tl solutions for high precision isotopic analyses by MC-ICP-MS: *Journal of Analytical Atomic Spectrometry*, v. 19, p. 1262- 1267.
- Longerich, H.P., Fryer, B.J., and Strong, D.F., 1987, Determination of lead isotope ratios by inductively coupled plasma-mass spectrometry: *Spectrochimica Acta Part B*, v. 42, p. 39- 48.
- Rehkämper, M., and Halliday, A.M., 1998, Accuracy and long-term reproducibility of lead isotope measurements by MC-ICP-MS using an external method for correction of mass discrimination: *International Journal of Mass Spectrometry*, v. 181, p. 123-133.

- Rehkämper, M., and Mezger, K., 2000, Investigation of matrix effects for Pb isotope ratio measurements by multiple collector ICP-MS: verification and application of optimized analytical protocols: *Journal of Analytical Atomic Spectrometry*, v. 15, p. 1451- 1460.
- Russell, W. A., Papanastassiou, D.A., and Tombrello, T.A., 1978, Ca isotope fractionation on the Earth and other solar system materials: *Geochimica. Cosmochimica. Acta*, v. 42, p. 1078-1090.
- Thirlwell, M.F., 2002, Multicollector ICP-MS analysis of Pb isotopes using a  $^{207}\text{Pb}$ - $^{204}\text{Pb}$  double spike demonstrates up to 400ppm/amu systematic errors in Tl-normalization: *Chemical Geology*, v. 184, p. 255-279.
- Thomas, R., 2001, A beginner's guide to ICP-MS: Spectroscopy, v. 16-18.
- Todt, W., Cliff, R.A., Hanser, A., and Hoffman, A.W., 1996, Evaluation of a  $^{202}\text{Pb}$  –  $^{205}\text{Pb}$  double spike for high-precision lead isotope analysis: *In Earth Processes: Reading the Isotopic Code, Geophysical Monograph 95* (American Geophysical Union), p. 429-437.
- Wombacher F., and Rehkämper, M., 2003, Investigation of the mass discrimination of multiple collector ICP-MS using neodymium isotopes and the generalized power law: *Journal of Analytical Atomic Spectrometry*, v. 18, p. 1371-1375.
- Woodhead, J., 2002, A simple method for obtaining highly accurate Pb isotope data by MC-ICP-MS: *Journal of Analytical Atomic Spectrometry*, v. 17, p. 1381-1385.