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silvia@geofisica.unam.mx

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Rodríguez-Salazar, M. T.; Morton Bermea, O.; Hernández-Álvarez, E.; García-Arreola, M. E.; Ortuño-Arzate, M. T.

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Development and validation of an analytical method for the determination of lead isotopic composition using ICP-QMS

M. T. Rodríguez-Salazar^{1,2}, O. Morton Bermea^{3*}, E. Hernández-Álvarez³, M. E. García-Arreola⁴, M. T. Ortuño-Arzate⁵

¹Posgrado en Ciencias de la Tierra, Universidad Nacional Autónoma de México, Mexico City, Mexico

²Facultad de Química, Universidad Nacional Autónoma de México, Mexico City, Mexico

³Instituto de Geofísica, Universidad Nacional Autónoma de México, Mexico City, Mexico

⁴Instituto de Geología, Universidad Autónoma de San Luis Potosí México, San Luis Potosí, Mexico

⁵Centro Nacional de Investigación y Capacitación Ambiental, Mexico City, Mexico

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Resumen

Este trabajo reporta un método para la determinación precisa y exacta la composición isotópica de Pb en matrices ambientales y geológicas mediante ICP-QMS. Se analizaron réplicas de tres materiales de referencia (AGV-2, SRM 2709 y JSO-1), por medio de ICP-QMS con el objeto de evaluar la calidad del procedimiento analítico. La discriminación de masas para Pb/Pb fue evaluado usando el material de referencia NIST 981, y esta corrección fue aplicada a los materiales de referencia antes mencionados, para obtener la exactitud del método analítico desarrollado. Se aplicó una estandarización interna con ²⁰⁵Tl para corregir la deriva instrumental. La composición isotópica obtenida para los materiales de referencia es comparable con los valores reportados (JSO-1 and SRM 2709) y certificados (AGV-2). Los valores de exactitud de los resultados obtenidos varían en promedio entre 0.002% para ²⁰⁷Pb/²⁰⁴Pb y 0.825% para ²⁰⁷Pb/²⁰⁶Pb. Estos resultados indican que el método ICP-QMS es confiable en términos de precisión y exactitud para la determinación de relaciones isotópicas de Pb en matrices de suelos y geológicas.

Palabras clave: ICP-QMS, composición isotópica de plomo, metodología analítica, material de referencia.

Abstract

This work reports a method for the precise and accurate determination of Pb isotope composition in soils and geological matrices by ICP-QMS. Three reference materials (AGV-2, SRM 2709 and JSO-1) were repeatedly measured, using ICP-QMS instruments in order to assess the quality of this analytical procedure. Mass discrimination was evaluated for Pb/Pb with Pb isotope reference material NIST SRM 981, and the correction applied to the above mentioned reference materials to achieve good accuracy of the analytical methodology. An internal standardization using ²⁰⁵Tl was employed to avoid instrumental drift. The measured isotope compositions of all analyzed reference material were comparable with the reported (JSO-1 and SRM 2709) and certified values (AGV-2). The accuracy results agreed in average within 0.002% for ²⁰⁷Pb/²⁰⁴Pb and 0.825% for ²⁰⁷Pb/²⁰⁶Pb. These data corroborate that ICP-QMS results to be reliable in terms of accuracy and precision, for the determination of the Pb isotopic compositions in soils and geological matrices.

Key words: ICP-QMS, lead isotope composition, analytical methodology, reference material.

Introduction

Lead has four naturally-occurring isotopes: ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb. ²⁰⁴Pb is not radiogenic. The isotopic composition of Pb is commonly expressed as the ratios ²⁰⁶Pb/²⁰⁷Pb or ²⁰⁸Pb/²⁰⁶Pb. ²⁰⁶Pb/²⁰⁷Pb may be determined precisely analytically and the abundances of these isotopes are relatively important. The less abundant ²⁰⁴Pb is often used as a reference in geochronological studies because it is stable and its abundance is constant.

Another practical application of Pb isotope ratios is tracing sources of lead in the environment. The isotopic compositions characteristic of different types of Pb-containing minerals are affected by the interaction of a number of processes, including radioactive decay of U and Th to Pb, the relative proportion of U–Th–Pb in the system, and mixing of Pb from different sources. Thus the isotopic relations are distinctive of different natural sources of Pb. When the contamination is due to a single process, the pollutant will have the isotopic signature of

its source (Wong & Li 2004; Komárek *et al.* 2008; Cheng & Hu 2010).

Thermal ionization mass spectrometry (TIMS) is still regarded as the definitive methodology for lead isotope measurements. However, the relatively high cost of instrumentation and the time consuming chemical pretreatment of the sample prior to analysis limited the routine use of TIMS techniques in environmental studies where a large number of samples are analyzed. In the last ten years the utility of ICP-QMS in Pb isotopic studies has been explored and the development of sensitive and highly precise analytical techniques based on ICP-QMS has allowed the determination of isotopic relations of Pb in environmental and geologic materials with excellent results (Farmer, *et al.* 1996; Moor *et al.*, 1996; Monna *et al.*, 1997; Shotykh *et al.*, 1998; Lima *et al.*, 2005).

The main advantages of this technique include fast sample preparation, lower sample analysis cost as compared with TIMS, and instrument robustness (Townsend *et al.*, 1998; Vanhaecke *et al.*, 1998; Al-Ammar and Barnes, 2001; Marguá *et al.*, 2007). The accessibility of ICP-QMS techniques has led to a higher number of Pb isotopic studies in recent years (Weiss *et al.*, 2000; Mukal *et al.*, 2001; Gallon *et al.*, 2006; Marguá *et al.*, 2007). However, this technique has been found to be of limited precision and accuracy owing to the design and operation of quadrupole mass analyser (Townsend *et al.*, 1998; Vanhaecke *et al.*, 1998; Marguá *et al.*, 2007).

The instrumental mass bias phenomenon affects the accuracy and precision of ICP-QMS analysis (Vanhaecke *et al.*, 1998; Al Ammar and Barnes, 2001). This phenomenon occurs when an instrument does not have the same sensitivity for different masses due to differences in the ion transmission. A suitable mass bias correction aims to improve accuracy and precision of the measurements. This correction involves:

- 1) Determination of dead time of the ion counting detection systems,
- 2) Mass bias evaluation using the Pb/Pb ratio of SRM 981 solution.
- 3) Application of the mass bias factor obtained for the reference material and/or experimental data for real samples.

Detector dead time is the time required for the detection and electronic handling of an ion pulse. The choice of the optimum dead time value is based on measuring the isotope ratio at different Pb concentrations. The data were re-integrated using different dead time

values and the normalized ratio (experimental data/certified data) was plotted versus the dead time for each of the different concentration solutions. The optimum dead time was determined to be the point at which the different concentration lines intercepted, i.e., the dead time for which the normalized isotope ratio has value more about to 1 and this parameter is independent of Pb concentration.

An internal standardization is employed to correct for instrumental drift. Thallium and bismuth are used as internal standards allowing longer acquisition periods for isotope ratio measurement of Pb as analyte (Quétel *et al.*, 1997; Adgate *et al.*, 1998; Barton *et al.*, 2000; Ettler *et al.*, 2004; Marguá *et al.*, 2007). Lead isotopic composition of an environmental reference material for inter-laboratory comparison tests using ICP-QMS have been published by Aung *et al.* (2004). Tanimizu and Ishikawa (2006) reported Pb isotope ratios of rock reference samples from the Geological Survey of Japan using MC-ICP-MS.

The purpose of this study is to provide a rapid and precise analytical method to determine lead Pb isotopic composition using ICP-QMS in environmental and geologic matrices in a routine way. The method was validated via analysis of reference materials: AGV-2 (USGS), SRM 2709 San Joaquin Soil (NIST) and JSO-1 (Geological Survey of Japan). Furthermore, the results also add new data to the set of basic values of lead isotopic compositions, which will be helpful for further research in the field of environmental monitoring and assessment.

Experiment

The isotopic measurements were performed with two Model X, Series 2 ICP-QMS spectrometers by Thermo Electron Corporation. One instrument was located at the Geological Institute of the Universidad Autónoma de San Luis Potosí, Mexico (UASLP) and the other at Centro Nacional de Investigación y Capacitación Ambiental (CENICA), Mexico City, Mexico. The measurement conditions are summarized in Table 1.

Both instruments used Ni cones, Meinhard nebulizers and cooling camera. The instrument settings were optimized for maximum sensibility and minimum signal fluctuation with a multi-elemental tuning solution. The optimal dead time was selected for both instruments as 35 ns. Fig. 1 shows the dead time determination for $^{208}\text{Pb}/^{206}\text{Pb}$.

The optimal instrumental dead time was adjusted for all analyzed isotope ratios using Pb solutions of different concentrations (5, 10, 20, 50 and 100 ppb), prepared from a Pb stock solution of NIST SRM 981 by dissolving about 1 g of Pb metal wire in 20 ml HNO_3 15% transferred

into a 1 l flask and brought to volume with MilliQwater (Townsend *et al.*, 1998). In order to determine isotope ratios accurately, the mass bias factor was evaluated using the Pb/Pb ratio of the SRM 981 solution.

Table1

Operation conditions of both ICP-QMS instruments used in this study.

	UASLP	CENICA
RF power	1412	1404
Gas flow rates		
Cool	13	12.4
Aux	0.71	0.73
Nebulizer	0.86	0.89
Ion lenses		
Extract lens	-102.0	-102.0
Detector parameters		
Dead time	35 ns	35 ns
Analog	1770	1750
Pulse	2814	2800

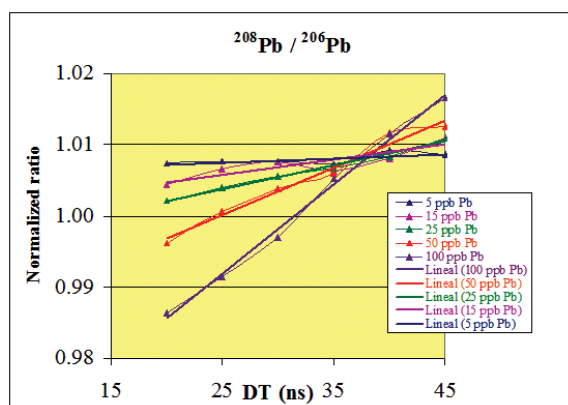


Fig. 1. Optimal Dead time calculation for $^{208}\text{Pb}/^{206}\text{Pb}$ at different detector times (ns), using 5 solutions of different Pb concentration. The normalized ratio (experimental data/certified data) is plotted versus the dead time for each of the different concentration solutions. This results were obtained using the UASLP instrument.

Standard solutions and reference material for mass spectrometry were prepared with purified water obtained from a 18 M Ω -grade Millipore system. Ten replicate measurements were performed for all isotopic masses (^{205}Tl , ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb).

The experimental procedure was evaluated for three standard reference materials: AGV-2 (USGS), SRM 2709 San Joaquin Soil (NIST) and JSO-1 (Geological Survey of Japan). The same digestion procedure was applied to all reference materials. About 500 mg of reference material were digested using a mixture of acids (10 ml HNO_3 concentrated + 3 ml HF concentrated + 5 ml H_2O_2 (30%)) in a CEM microwave, MARS XPress digestion system. After the digestion, a minimal residue was obtained from the AGV-2 reference material compared to the digested soils reference material. After cooling, sample digests were filtered through a Whatman 42 filter, transferred into a 100 ml flask and brought to volume with MilliQwater.

The raw mass data were processed for subtraction of blank and corrected for the internal standard ratio signal (^{205}Tl) and for mass bias. The impact of ^{204}Hg on the measurement of ^{204}Pb was evaluated and found to be essentially negligible, because of the low total Hg concentration in the analyzed samples.

Results and Discussion

Lead isotope ratios obtained for all analyzed reference materials are summarized in Table 2. The precision of the isotopic ratio measurement, was calculated in terms of relative standard deviation (%RSD) of two replicates. The RSD was better than 1.3% for all obtained values ($^{206}\text{Pb}/^{204}\text{Pb}$ in AGV-2 at CENICA). Reference material NIST 2709 measured at UASLP shows the best precision (0.06 % RSD for $^{208}\text{Pb}/^{206}\text{Pb}$). Accuracy was assessed in terms of % difference between reported and experimental results. The results obtained with both ICP-QMS instruments show good agreement with the reported values. Results at UASLP differed from the standard values by 0.002% to 0.625% at UASLP and by 0.009% to 0.825% at CENICA. The peak accuracy in terms of $^{207}\text{Pb}/^{204}\text{Pb}$ ratios was obtained for the AGV-2 standard at UASLP (0.002%), and in terms of $^{208}\text{Pb}/^{206}\text{Pb}$ ratios for the NIST 2709 standard at CENICA (0.009%). There is no indication of a trend that might suggest a higher accuracy for any specific isotopic ratio. There is no observable dependence of the quality of the results on the analyzed matrix.

Conclusions

The experimental results reported in this paper suggest that good precision and accuracy may be achieved by using ICP-QMS to determine lead isotope ratios provided that the experimental procedure is carefully designed and appropriate corrections for blank, instrumental drift, dead time, interference, and mass bias are used. The technique may be used in routine analysis of soils and geological samples for environmental monitoring and evaluation.

Table 2

ICP-QMS measurements of Pb isotope ratios as compared with published values

Reported(*) or certified(**) value		X series (Thermo Electron Corporation)					
		UASLP			CENICA		
		Experimental Values	Accuracy (% error)	Precision (% RSD)	Experimental Values	Accuracy (% error)	Precision (% RSD)
		JSO-1*					
²⁰⁸ Pb/ ²⁰⁶ Pb	2.112 ± 0.002	2.108 ± 0.002	- 0.173	0.12	2.123 ± 0.002	0.507	0.08
²⁰⁷ Pb/ ²⁰⁶ Pb	0.865 ± 0.001	0.861 ± 0.001	-0.421	0.10	0.863 ± 0.004	-0.184	0.42
		NIST 2709*					
²⁰⁸ Pb/ ²⁰⁶ Pb	2.043 ± 0.003	2.046 ± 0.001	0.144	0.06	2.043 ± 0.002	-0.009	0.09
²⁰⁷ Pb/ ²⁰⁶ Pb	0.821 ± 0.002	0.822 ± 0.001	0.154	0.12	0.814 ± 0.002	-0.825	0.19
		AGV-2**					
²⁰⁸ Pb/ ²⁰⁴ Pb	38.511 ± 0.020	38.503 ± 0.028	-0.022	0.07	38.423 ± 0.140	-0.229	0.37
²⁰⁷ Pb/ ²⁰⁴ Pb	15.609 ± 0.006	15.609 ± 0.021	0.002	0.13	15.501 ± 0.046	-0.690	0.29
²⁰⁶ Pb/ ²⁰⁴ Pb	18.864 ± 0.007	18.746 ± 0.025	-0.625	0.13	18.891 ± 0.246	0.142	1.30

Precision values ranged between 0.06% and 1.3% RDS, and accuracy varied between errors of 0.002% to 0.825%. No dependence on isotopic ratios or on the type of matrix was detected. The methodology is reliable and well suited to the kind of facilities available in most Mexican laboratories. ICP-QMS is a competitive, promising technique of lead isotope ratio analysis, because of its low cost, easy sample preparation and widely available compared with other mass spectrometric techniques.

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M. T. Rodríguez-Salazar^{1, 2}, O. Morton Bermea^{3*}, E. Hernández-Álvarez³, M. E. García-Arreola⁴, M. T. Ortuño-Arzate⁵

¹Posgrado en Ciencias de la Tierra, Universidad Nacional Autónoma de México, Ciudad Universitaria, Del. Coyoacán, 04510, Mexico City, Mexico

²Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Del. Coyoacán, 04510, Mexico City, Mexico

³Instituto de Geofísica, Universidad Nacional Autónoma de México, Ciudad Universitaria, Del. Coyoacán, 04510, Mexico City, Mexico

⁴Instituto de Geología, Universidad Autónoma de San Luis Potosí México, San Luis Potosí, Mexico

⁵Centro Nacional de Investigación y Capacitación Ambiental, Mexico City, Mexico

*Corresponding author: omorton@geofisica.unam.mx