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OPTIMIZATION OF OPERATING PARAMETER OF A QUADRUPOLE INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER USED IN THE DETERMINATION OF LEAD ISOTOPIC RATIO

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ABSTRACT. Due to small (but random) plasma variations while the quadrupole scans multiple masses, the single detector of a commercially available ICP-MS instrument will sequentially receive data that is affected by the non constant plasma power. Present study focuses on DRC's RPq parameter and quadrupole's sweeps optimization, for a quadrupole based ICP-MS instrument. The proposed method is used for lead isotopic ratio in vegetables, soils, concentrated mining ores and leaded gasoline, offering a RSD between 0.12% and 0.91%. Measured isotopic ratio for ^{207}Pb / ^{206}Pb varied from 0.829 (mining ore) to 0.890 (leaded gasoline) respectively 2.048 (mining ore) to 2.155 (leaded gasoline) for ^{208}Pb / ^{206}Pb.

Keywords: *mass spectrometry, isotopic ratio, instrument optimization*

INTRODUCTION

Lead, as a heavy metal, it is known to be a toxic pollutant and total world production has increased continuously beginning from Roman Empire to present days [1]. The natural level of lead present in the atmosphere today is 1-2 levels of magnitude greater than the natural sources [2]. Lead is present in nature in 4 stable isotopes among which only ^{204}Pb (1.4%) is primordial lead, thus being distributed almost homogeneous in Earth's crust, all the other three are final stages of heavier nuclei decay processes, with their distribution varying accordingly with the uranium and thorium deposits nearby. ^{238}U is responsible for ^{206}Pb isotope (24.1%), ^{235}U for ^{207}Pb (22.1) and ^{232}Th finally decays in ^{208}Pb (52.4%). [3]

Isotopic ratio from one sample does not change, not matter the chemical or conventional physical phenomena suffered, thus one can trace the origin for a specific sample.

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Historically, thermo-ionization mass spectrometry was the technique mainly used for isotopic ratio. A major drawback of TIMS is the lengthy process of sample preparation and reading time so that when ICP-MS start emerging on the market, new alternatives appeared. Multi-collector ICP-MS counter-balance the plasma fluctuation by adding multiple detectors and in this way doing simultaneous mass detection, as opposed to single-collector ICP-MS where the detector sequentially reads the ion coming from the mass filter, on which little plasma fluctuation have a unwanted effect [4]. In this paper we tried to minimize those effects by carefully optimizing two parameters (sweeps and Rpq) and using a single detector, commercially available ICP-MS instrument for precise isotope ratio determination. The proposed method offers cost effective and fast lead isotopic ratio measurements with minimal sample preparation with good accuracy, using a standard quadrupole ICP-MS instrument.

RESULTS AND DISCUSSION

Instrument was carefully optimized daily, using a solution of 1 ppb In, Mg, Ce, Th, U and 10 ppb Ba. Oxides and double ionization levels were monitored and kept under 3% during all analysis. Also a mass tuning was performed periodically. Lens voltages were optimized specifically for optimum passage of Pb ions.

Isotope ^{204}Pb was excluded from all measurements due to its low natural abundance that causes errors on all other ratios involving this isotopes and increases analysis time needed to read it. Furthermore, ^{204}Pb can be affected by interference caused by ^{204}Hg [8] and the focus of this study was to provide a method with DRC used in rf-only mode, without any pressurized gas (which could remove the unwanted interference).

For all optimization measurements, a solution prepared from NIST 981 standard reference material (SRM) was used. The standard is shipped in wire form and it was cut, weighted and used to prepare a concentrated stock solution from which, by multiple dilutions, we've created a 20 ppb solution, used daily for all measurements. This concentration was chosen to avoid any pulse pile-up phenomenon that can occur if lead concentration is to high in the ion beam [9].

Sweeps are number of times during one reading when the specified mass range is scanned from the lowest to the highest mass. Higher value for sweeps translates into better statistics and lower RSD, but if the sweeps value got to high, then plasma variation over longer time period affects the results and overcome the statistical positive factor. NIST 981 SRM solution prepared in-lab as described above and 100, 200, 400, 600 and 800 sweeps values were chosen and the prepared solution was read 5 times. An isotopic ratio average was calculated from the obtained results and calibration was performed at the start of each batch of 5 samples. Calibration was performed after each batch and software's correction coefficients were used each time. Averages and RSDs for sweep optimization are plotted on Figure 1.

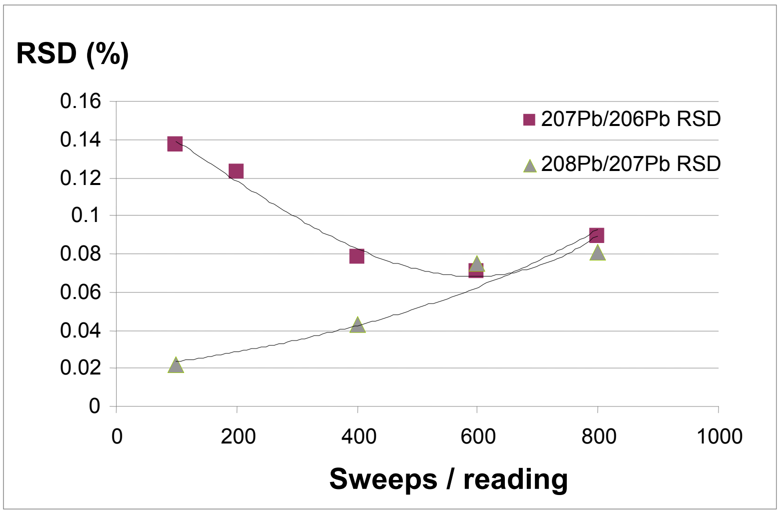

Figure 1. Sweeps /reading vs. obtained RSD

400 sweeps is an intermediary value that offers satisfactory RSD for both ^{207}Pb / ^{206}Pb and ^{208}Pb / ^{207}Pb ratio. While it is not the optimum value for both ratios, it's a good compromise between the two of them, offering satisfactory results while having a decent analysis time.

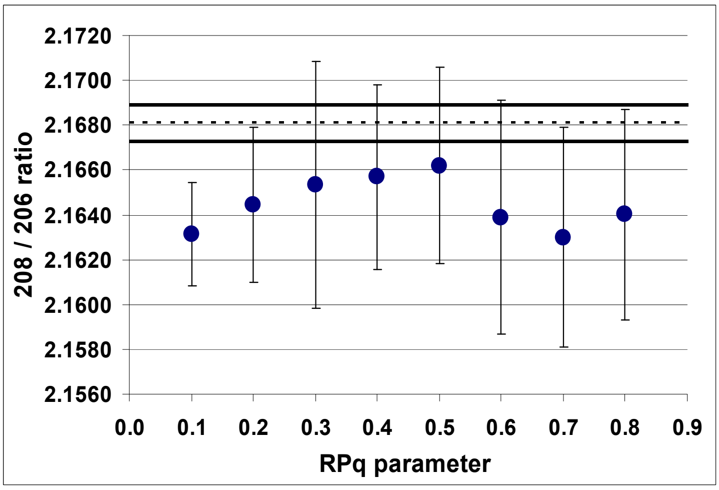

Figure 2a. RPq optimization of ^{208}Pb / ^{206}Pb ratio. The dotted line represents the NIST 981 certified value together with standard deviation (thick continuous lines)

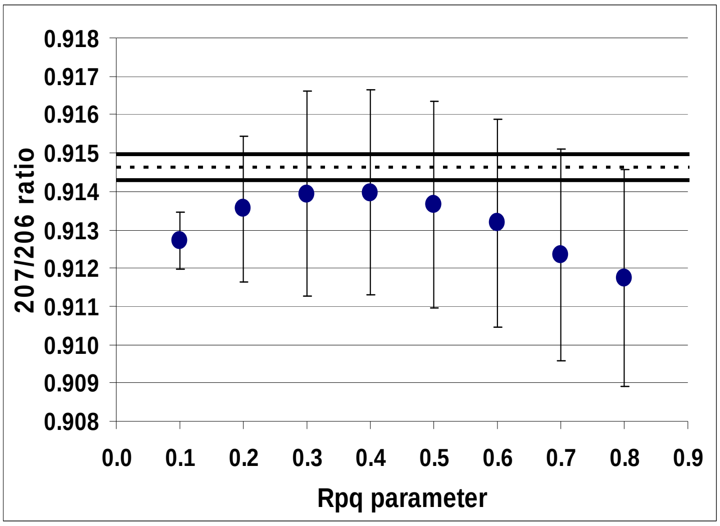

Figure 2b. RPq optimization of $^{207}Pb/^{206}Pb$ ratio. The dotted line represents the NIST 981 certified value together with standard deviation (thick continuous line)

RPq parameter optimization was done in a similar manner. After five readings, an average was considered, and then a calibration was performed and reading of the sample with the next RPq value (values were chosen from 0.1 to 0.8, with an increasing step of 0.1).

While a lower RSD value gives better precision, best accuracy for both ratios is obtained when using a Rpq value of 0.45 (compared to NIST 981 standard reference material's certified value). The certified NIST samples have better RSD values (0.036% - 0.063%), due to different techniques used, than the values obtained in this study (0.12% - 0.91%). However, those values of RSD are better enough to differentiate between mining ore samples, vegetables and leaded gasoline respectively, which fits the purpose of this study. Results of the study are listed in Table 1.

Table 1. Results range for lead isotopic ratio for mining ore, vegetables, soil and leaded gasoline samples

Sample type	$^{207}Pb/^{206}Pb$ ratio	$^{208}Pb/^{206}Pb$ ratio
Mining ore	0.829 – 0.866	2.048 – 2.100
Vegetables	0.846 – 0.849	2.095 – 2.100
Soil	0.834 – 0.842	2.110 – 2.126
Leaded gasoline	0.890	2.155

EXPERIMENTAL SECTION

For all the measurements, a SCIEX Elan DRC II (Toronto, Canada) ICP-MS was used. This model is a quadrupole based mass spectrometer, with only one detector, that does not offer the advantages of multicollector ICP-MS instruments. It is also equipped with a Dynamic Reaction Cell which consists on an enclosed second quadrupole placed after the interface part and before the main quadrupole. The quadrupole's chamber can be pressurized with a reaction (He) or reaction (NH_3, CH_4, O_2) gas for eliminating various interferences. However, only the rf-only capability of the DRC quadrupole was used (no gas), since no interferences are expected to form at the masses we are watching (206, 207, 208).

Dwell time was chosen 30 ms for ^{208}Pb and 60 ms for ^{206}Pb and ^{207}Pb. According to isotope distribution, this settings is optimum for analysis time and signal quality. Other ICP-MS settings are listed in Table 2.

Table 2. ICP-MS running parameters

Parameter	Value
Plasma	
Power / W	1300
Plasma gas flow / l min^{-1}	12.00
Auxiliary gas flow / l min^{-1}	1.20
Nebuliser gas flow / l min^{-1}	0.92
Sample/Skimmer cone	Platinum
Quadrupole	
Quadruple rod offset (QRO) / V	0.00
Cell rod offset (CRO)/V	- 8.00
Cell path voltage (CPV)/V	- 20.00
Measurement mode	Peak hopping
Dwell time / ms	30 / 60
Integration time / ms	Varying
Reading per replicate	1
Replicate measurements	5
DRC	
Reaction Gas	None
Lens voltage / V	10.00

Vegetables (VG) and were collected from resident's gardens and were washed with ultrapure water then oven-dried at 80-90°C for 30 minutes and at 65°C for 12-24h. Samples were ground and 5g of every sample were digested with concentrated HNO_3 and $HClO_4$. Gasoline (Pb-GS) was extracted with concentrated HCl at reflux conditions and then the acid layer was separated. Soils (SO) were collected from the same gardens as vegetables and were prepared according to ISO 11466:1995. Mining ores (MO) were digested in microwave oven (O-I Analytical), in a three steps program with total running time of 24 minutes, using a mixture of HNO_3, HCl, H_2O and HF and the obtained solution was diluted several times until the concentration was in range of 20 – 80 ppb of Pb.

CONCLUSIONS

This paper has shown that quadrupole ICP-MS can be used for isotopic ratio measurements, being capable of discrimate samples from various origins. For achieving this, RPq and sweeps number optimization for Pb were performed, along with standard daily procedures. The ease of sample preparation, analysis time and relatively small running costs points to quadrupole-based ICP-MS as a serious alternative to more historically used isotope ratio measurements techniques. Although the RSD values of multicollector ICP-MS are superior [17], the quadrupole offers a much more cost-effective approach. Our optimized method was successfully applied on vegetable, soil, concentrated mining ore and leaded gasoline samples from Western Romania.

REFERENCES

1. J. O. Nigrau, A history of global metal pollution, *Science*, **1996**, 272, 223
2. M. Komarek, V. Chrastny, V. Ettler, P. Tlustos, *Environment International*, **2007**, 33, 677
3. I. Planner, Modern Isotope Ratio Mass Spectrometry, John Wiley and sons, Wiley, **1997**, Appendix I
4. Y. Yip, J. Lam, W. Tong, *Trends in Analytical Chemistry*, **2008**, 27, 460
5. S. Tanner, V. Baranov, *Atomic Spectroscopy*, **1999**, 20, 45
6. D. Bandura, V. Baranov, S. Tanner, *Journal of Analytical Atomic Spectrometry*, **2000**, 15, 921
7. S. Tanner, V. Baranov, *Journal of American Society for Mass Spectrometry*, **1999**, 19, 1083
8. T. May, R. Wiedmeyer, *Atomic Spectroscopy*, **1998**, 16, 150
9. F. Monna, J. Loizeau, A. Thomas, C. Guenguen, Y. Favarger, *Spectrochimica Acta Part B*, **1998**, 53, 1317
10. I. Renberg, M-L. Brannvall, R. Binder, O. Emteryd, *Ambio*, **2000**, 29, 150

11. A. Dolgopova, D.J. Weiss, R. Seltmann, B. Kober, T.F.D. Mason, B. Coles, C.J. Stanley, *Applied Geochemistry*, **2006**, 21, 563
12. M. Barbaste, L. Halicz, A. Galy, B. Medina, H. Emteborg, F. Adams, R. Lobinski, *Talanta*, **2001**, 54, 307
13. M. Mihaljevic, V. Ettler, O. Sebek, L. Strnad, V. Chrastny, *Journal of Geochemical Exploration*, **2006**, 88, 130
14. E. Margui, Iglesias, I. Queralt, M. Hidalgo, *Science of Total Environment*, **2006**, 367, 988
15. T. Shimamura, S. Iijima, M. Iwashita, M. Hattori, Y. Takaku, *Atmospheric Environment*, **2007**, 41, 2797
16. J. Baker, D. Peate, T. Waight, C. Meyzen, *Chemical Geology*, **2004**, 21, 275
17. F. Monna, J. Lancelot, I. Croudace, A. Cundy, J. Lewis, *Environmental. Science and Technology*, **1997**, 31, 2277