

LEAD AND STRONTIUM ISOTOPIC RATIO METHOD DEVELOPMENT USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Abstract. Inductively coupled plasma mass spectrometry (ICP-MS) method was developed to measure lead and strontium isotopic ratio from tailings samples, but the method can be extended to any solid or liquid samples. Careful optimization of the instrument parameters and method settings (time settings, quadrupole parameters) can overcome some of the limitations of the quadrupole mass analyzer and can provide useful isotopic ratio data for environment applications. A bracketing calibration method was employed, using certified reference materials, to ensure that the results are not affected by mass bias or signal shift during measurements.

Keywords: ICP-MS, isotopic ratio, lead, strontium, mass spectrometry, quadrupole, tailings

INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) offers several advantages over other analytical techniques for environment analysis. The first commercial ICP-MS instrument was available on the market since 1983, and the number of laboratories across the world using it is constantly increasing. Not only that it offers multielement capabilities and fast analysis time, but since it uses ions to characterize samples, as opposed to photons as used in most of other techniques, ICP-MS methods can be developed to measure isotopic ratio for stable elements. Single detector quadrupole ICP-MS is not the best tool for measuring isotopic ratios due to plasma instability and sequential character of recording the signal (Liu, 2012) but careful optimization of parameters, time management (Monna et al., 1998) and other quadrupole specific elements (Tănăselia et al., 2008) can lead to useful results for applications that don't require extreme precision of results. Isotopes are a useful tool for measuring traces of various geochemical formations (Stevenson, 2016) but have applications for many other fields, from archaeology (Copeland et al., 2010) to medical sciences (Yedomon et al., 2016).

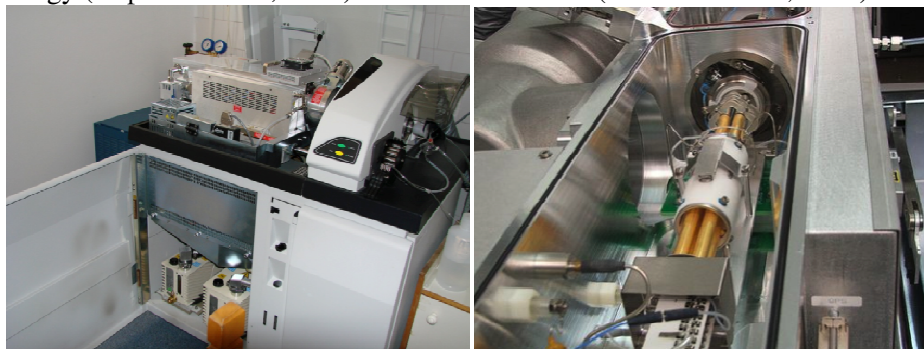


Fig. 1. Perkin-Elmer Elan DRC II inductively coupled plasma mass spectrometer (left) and its quadrupole mass filter (right)

MATERIALS AND METHODS

For measurements, an Elan DRC II inductively coupled plasma mass spectrometer (ICP-MS) was used (Perkin-Elmer, Canada), with a quadrupole used as mass analyzer. The dynamic reaction cell (DRC, a second quadrupole employed before the main one to remove or reduce isobaric and polyatomic interferences) was used in rf-only mode (vented, no gas). Due to low natural abundance (1.4%, Plantzer, 1997) and isobaric ^{204}Hg interference from mass 204, ^{204}Pb was not measured. ^{84}Rb was also discarded from this study due to its even lower abundance (0.56%). Mercury quantitative determination and mathematical correction could be employed in this case, but low abundance of ^{204}Pb would cause errors that wouldn't make this approach feasible.



Fig. 2. Sampling area, in Hunedoara mining region

Certified reference materials were used for calibration and method verification: NIST 981 for lead and NIST 987 for strontium both purchased directly from NIST. Ultrapure water (produced in the lab, using a Millipore Milli-Q instrument) was used in all sample preparation steps. Ultrapure hydrochloric acid and nitric acid were used for *aqua regia* (required for sample mineralization) and the reagents needed for sample treatment were purchased from Merck (Darmstadt, Germany).

As a case study, two sampling sites were considered, two tailing impoundments, from Vorța and Săliște (Hunedoara), as shown in Fig. 2, and from each place, two samples were prepared. The samples were dried, grinded and homogenized, then treated with *aqua regia* according to SR ISO 11466:1995. The filtrate was diluted to 100 ml with ultrapure water. Instrument was carefully optimized daily, using a solution of 1 ppb In, Mg, Ce, Th, U and 10 ppb Ba. Oxides (CeO) and double ionization (Ba^{++}) levels were monitored and kept under 3% during all measurements. Mass tuning procedure was performed periodically. Lens voltages were optimized specifically for optimum passage of Pb ions before each batch of samples.

Measurements were carried out using the detector in pulse mode, thus providing better sensitivity and better statistics for the measured signal. In the case of detector saturation, the samples were diluted accordingly, keeping the count rates per second below 10^6 , otherwise the statistics of the results would be compromised (Monna et al., 1998).

Measurements for strontium and lead were carried out separately. The instrument was calibrated and optimized independently for each batch. For calibration, NIST 987 (strontium carbonate) and NIST 981 (metallic wire) were used. After each sample measurements, a certified reference material was measured and bracketing was used for calibration, thus eliminating mass bias effect and potentially signal shifting due to cone depositions and other factors leading to signal variation in time.

RESULTS AND DISCUSSIONS

Sweeps are number of times when the specified mass range is scanned from the lowest mass to the highest mass (from 86 to 88 for Sr or from 206 to 208 for Pb). Increasing this number lead to better overall statistics, better RSD values for analysis, but also increase analysis time and for a large enough time window signal drift and mass bias can start to affect the result. DRC rejection parameter q (RPq) is a parameter derived from Mathieu's multipole equations and used in bandpass function of a dynamic reaction cell (Tanner et al., 1999). Both sweeps and RPq values were adjusted for best precision and accuracy. For lead measurements, relative standard deviation for all measured samples was below 1% and for strontium, relative standard deviation was below 2%. Each sample was read 7 times and quadrupole sweep time for lead was set to 400, while the best value for strontium was 600. RPq was set to 0.45 for both elements. Other sets of values would either drastically increase the analysis time or negatively impact the relative standard deviation of the result. Quadrupole dwell time was configured to attenuate the differences in elemental abundances and provide the detector with the optimal flux of ions, thus 20 ms for ^{208}Pb and 40 ms for the rest of measured Pb isotopes (^{206}Pb , ^{207}Pb), while for strontium 100 ms seconds was the dwell time set for ^{86}Sr and ^{87}Sr and 10 ms for the most abundant isotope, ^{88}Sr .

Table 1.

Isotopic ratio results for measured samples. Samples A and B are from Vorța, while samples C and D are from Săliște, Hunedoara mining area

	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{88}\text{Sr}/^{86}\text{Sr}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
Sample A	0.902	8.408	0.847	2.093
Sample B	0.874	8.413	0.851	2.125
Sample C	0.719	8.441	0.853	2.123
Sample D	0.723	8.507	0.852	2.112

Results for all measurements are listed in Table 1. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ show a clear distinction between the two chosen locations for sampling, while the differences of lead isotopes are not significant between the four samples. The geological background could explain these results.

CONCLUSIONS

Careful optimization of running parameters of an ICP-MS with a quadrupole as a mass separator can lead to relevant results of isotopic ratio measurements for at least lead and strontium. While the obtained precision doesn't allow results useful for dating techniques, other environmental oriented applications can be developed (source tracking, fingerprinting, authentication methods etc.). Proper certified reference materials must be provided for calibration, to avoid effects that could lead to erroneous detector response, but overall, using a quadrupole ICP-MS instrument for isotopic ratios used in environmental samples can be a cost-effective solution, instead of a much more expensive multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS).

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REFERENCES

1. Copeland S., Sponheimer M., Lee-Thorp J.A., le Roux P., de Ruiter D., Richards M.P., (2010). Strontium isotope ratios in fossil teeth from South Africa: assessing laser ablation MC-ICP-MS analysis and the extent of diagenesis, *Journal of Archaeological Science* 37:1437-1446.
2. Dewan N., Majestic B.J., Ketterer M.E., Miller-Schulze J.P., Shafer M.M., Schauer J.J., Solomon P.A., Artamonova M., Chen B.B., Imashev S.A., Carmichael G.R., (2015). Stable isotopes of lead and strontium as tracers of sources of airborne particulate matter in Kyrgyzstan, *Atmospheric Environment* 120:438-446.
3. Kolacinska K., Chajduk E., Dudek J., Samczynski Z., Lokas E., Bojanowska-Czajka A., Trojanowicz M. (2016), *Talanta*, in press.
4. Liu H.C., You C.F., Huang K.F., Chung C.H. (2012). Precise determination of triple Sr isotopes using ICP-MS, *Talanta* 88:338-344.
5. Monna F., Loizeau J., Thomas BA, Favarger PY., (1998). Pb and Sr isotope measurement by inductively coupled plasma mass spectrometer: efficient time management for precise improvement, *Spectrochimica Acta Part B: Atomic Spectroscopy* 53(9):1317-1333.
6. Plantzer IT., (1997). *Modern Isotope Ratio Mass Spectrometry*, Appendix I, John Wiley and sons, ISBN: 978-0-471-97416-1.
7. Santoni S., Huneau F., Garel E., Aquilina L., Vergnaud-Ayraud V., Labasque T., Celle-Jeanton H., (2016), Strontium isotopes as tracers of water-rocks interactions, mixing processes and residence time indicator of groundwater within the granite-carbonate coastal aquifer of Bonifacio (Corsica, France), *Science of Total Environment* 573:233-246.
8. Stevenson, E.I., Aciego S.M., Chutcharavan P., Parkinson I.J., Burton K.W., Blakowski M.A., Arendt C.A., (2016). Insights into combined radiogenic and stable strontium isotopes as tracers for weathering processes in subglacial environments, *Chemica Geology* 429:33-43.
9. Tanner S., Baranov V., (1999) A dynamic reaction cell for inductively coupled plasma mass spectrometry (ICP-DRC-MS). II. Reduction of interferences produced within the cell, *Journal of the American Society for Mass Spectrometry* 10(11):1083-1094.
10. Tănăselia C., Miclean M., Roman C., Cordoș E., David L., (2008), Optimization of operating parameters of a quadrupole inductively coupled plasma mass spectrometer used in the determination of lead and isotopic ratio, *Studia Universitatis Babeș-Bolyai, Chemia* 53(4):123-129
11. Tănăselia C., Popov S.I., Pop D., Abraham B., Roman C., Stafilov T., David L., Udrescu M., (2010). Preliminary investigation of Mocs meteorite by lead isotopic ratio using quadruple inductively coupled plasma mass spectrometry, *Studia Universitatis Babeș-Bolyai, Chemia*, 55(3):191-196

12. Yedomon B., Menudier A., Lecavelier F., Anani L., Fayomi B., Druet-Cabanca M., Moesch C., (2016). Biomonitoring of 29 trace elements in whole blood from inhabitants of Cotonou (Benin) by ICP-MS, Journal of Trace Elements in Medicine and Biology, in press.

13. Zhu Y., Hioki A., Chiba K. (2014), Measurements of strontium isotope ratio in nitric acid extract of peanut testa by ICP-Q-MS after removal of Rb by extracting with pure water, Talanta 119:596-600.