

LEAD ISOTOPIC RATIO DETERMINATION IN CAVE SEDIMENTS USING TRIPLE-QUADRUPOLE INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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ABSTRACT. Lead isotopic ratio determination is significantly affected by the isobaric interference of mercury (^{204}Hg), thus many studies lack $^{204}\text{Pb}/^{206}\text{Pb}$ values. Removal of ^{204}Hg from sample is resource consuming, while mathematical correction can be employed if the Hg isotope ratio in the sample is known. Triple quadrupole inductively coupled plasma mass spectrometry (TQ-ICP-MS) offers a mechanism for removing the ^{204}Hg , by pressurizing the reaction cell with ammonia, that reacts with ^{204}Hg positively charged ions rendering them neutral, thus filtering them out and removing them from the ion beam. The Pb isotope ratio determination can be used as “fingerprint” to identify the sources of contamination and environmental pollution. The method developed based on this mechanism was used for Pb isotopic ratio determination in cave sediment samples. Relative standard deviation of this method was between 0.36% - 0.59%.

Keywords: ICP-MS, Pb isotopic ratio, lead, cave sediments, triple-quadrupole

INTRODUCTION

Lead (Pb) is the 36th most abundant element in the Earth's crust (16 ppm crustal abundance), occurring with four naturally occurring stable isotopes: ^{204}Pb (1.4% abundance), ^{206}Pb (24.1% abundance) ^{207}Pb (22.1 % abundance)

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and ^{208}Pb (52.4% abundance), with ^{204}Pb being the only isotope that is not radiogenic. The other three isotopes are the products of the radioactive decay of uranium (^{235}U , ^{238}U) or thorium (^{232}Th) [1]. Hence the geographically Pb abundance is correlated with former U and Th ore deposits, thus making Pb isotopic ratio determination an excellent geological tracer and an important geochronometer [2-4].

Pb isotopic measurements are used to determine the age of meteorites, Earth and other planetary bodies (Mars and Moon) [2]. Also, it can offer information on geochemical origins by “fingerprinting” minerals, lavas and pollutants as potential Pb sources and on the pathways by which Pb enters into the environment [5, 6]. Moreover, Pb isotopic studies can offer valuable information on the geogenic or anthropogenic sources of Pb in various environmental matrices (water, soil, sediments, rocks, plants etc.). Pb is considered one of the most toxic heavy elements that occurs naturally in the environment, with no known function in the human body [7]. Pb occurs in the atmosphere as fine particulate ($<1\ \mu\text{m}$) from anthropogenic sources, and it can also be found in ore deposits such as galena (PbS), anglesite (PbSO_4), cerussite (PbCO_3), or minimum (Pb_3O_4) [3]. Distribution in the environment takes place through a series of complete well-balanced chemical and physical processes such as weathering, runoff, precipitation, stream/river flow, erosion, though which Pb is transferred to atmosphere (air, dust), hydrosphere (water), lithosphere (soil and sediments) and biosphere (biota) [3, 8].

Thermal ionization mass spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) are the most used techniques to measure Pb isotopic ratios from various matrices. One of the biggest disadvantages of these techniques are the high cost and the labor-intensive sample preparation in ultraclean laboratories [9]. However, the precision of single detector ICP-MS instruments is at least one order of magnitude poorer when compared to MC-ICP-MS methods, due to inherent sequential reading that is affected by plasma variations between readings. Single detector ICP-MS offers a higher versatility and lower initial and maintenance costs, and its precision can be considered satisfactory for some applications.

If not chemically separated, the ^{204}Hg isotope (mass 203.973476 amu), will overlap ^{204}Pb isotope (mass 203.973029 amu) and separating them in a mass spectrometer requires a resolution of over 400000. That is well beyond the limits of current instruments as the ICP-MS resolution varies from 400 for a single detector, quadrupole instrument, to around 10000 for a sector field instrument, which is 40 times lower than the required value to separate ^{204}Hg from ^{204}Pb isotopes [10-12]. Thus, lead isotopic ratio studies are published incompletely, without specifying the ^{204}Pb isotope, since ^{204}Pb

analysis is often unreliable. As chemical separation is a resource consuming step in sample preparation, recent advances in ICP-MS design makes it possible to have an online chemical sample alteration that removes the ^{204}Hg , making ^{204}Pb determination possible to an acceptable precision level.

In the case of ^{204}Pb determination, a triple-quadrupole ICP-MS will filter out all the isotopes with masses different than 204 amu using the first quadrupole (Q1), leaving a mix of Pb and Hg passing through the rest of the mass spectrometer. The ion beam will enter the second quadrupole (Q2), that doesn't have a filtering role, but it guides the beam through the collision/reaction cell. The cell has the possibility to be pressurized with a collision and/or a reaction gas in case of the most ICP-MS instruments on the market. In this case, if the cell is pressurized with ammonia, it will react with $^{204}\text{Hg}^+$ ions much more often than with $^{204}\text{Pb}^+$ ions, transferring an electron to the Hg ions, rendering them neutral (due to instrument design, the ion beam in ICP-MS is usually made exclusively from negative ions). Thus, the third quadrupole (Q3) will guide only the $^{204}\text{Pb}^+$ ions to the detector, filtering out the remaining $^{204}\text{Hg}^0$ atoms [13], a process depicted in Figure 4.

The main objective of this study was to optimize the determination of Pb isotopic ratio from cave sediment samples, using triple-quadrupole ICP-MS instrument with reaction cell by pressuring with ammonia, in order create a neutral ^{204}Hg species that is filtered out from the ion beam. Cave sediment samples are considered to be significant part of caves science, offering valuable information about the caves hydrogeological and palaeoclimatological records. Take into consideration further application possibilities, cave samples were used as test samples for Pb isotopic ratio method optimization. Five different caves from Romania were selected in order to study the scattered distribution of Pb isotopic ratio from the sediment samples.

RESULTS AND DISCUSSION

The Pb concentration is displayed in Figure 1. The highest Pb content was measured in case of the sampling sites from Ferice cave ($19.4 \text{ mg/kg} \pm 4.53$). High Pb values were found also in case of the sites from Lesu cave ($12.3 \text{ mg/kg} \pm 0.84$). The lowest Pb values were registered in case of Tausoare cave ($3.9 \text{ mg/kg} \pm 1.28$).

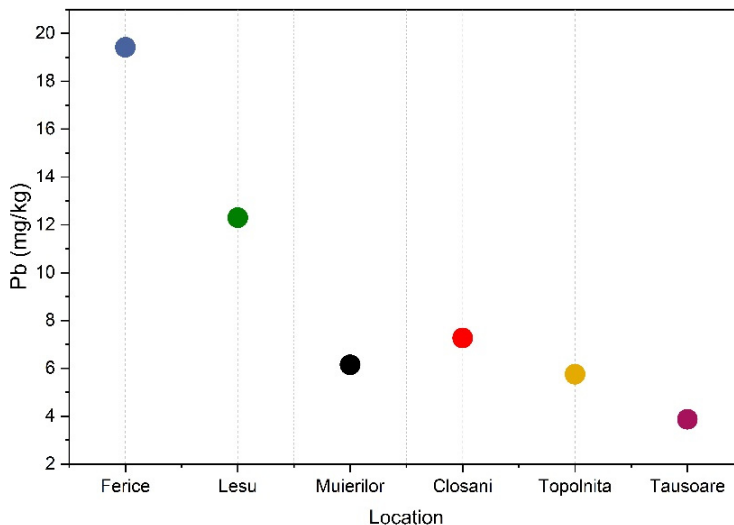


Figure 1. Pb concentration (mg/kg) in the cave sediment samples.

Table 1. Results of NIST 981 SRM reading for the Pb isotopes (n=10)

	204/206	207/206	208/206
Certified values (NIST 981 SRM)	0.059042 ±0.000037	0.91464 ±0.00033	2.1681 ±0.0008
Average measured values (this study)	0.059558 ±0.000865	0.91817 ±0.00842	2.1555 ±0.0062

A batch of 10 measurements of NIST 981 standard reference material (SRM) was performed and the results are listed in Table 1. Uncertainty was calculated as three times the standard deviation. The uncertainty for $^{204}\text{Pb}/^{206}\text{Pb}$ is not significantly different from than $^{207}\text{Pb}/^{206}\text{Pb}$, but it's higher (at least one order of magnitude) than the one reported for NIST 981 SRM, due to differences in employed techniques (Figure 2). Relative standard deviation of measurements was between 0.36% - 0.59%.

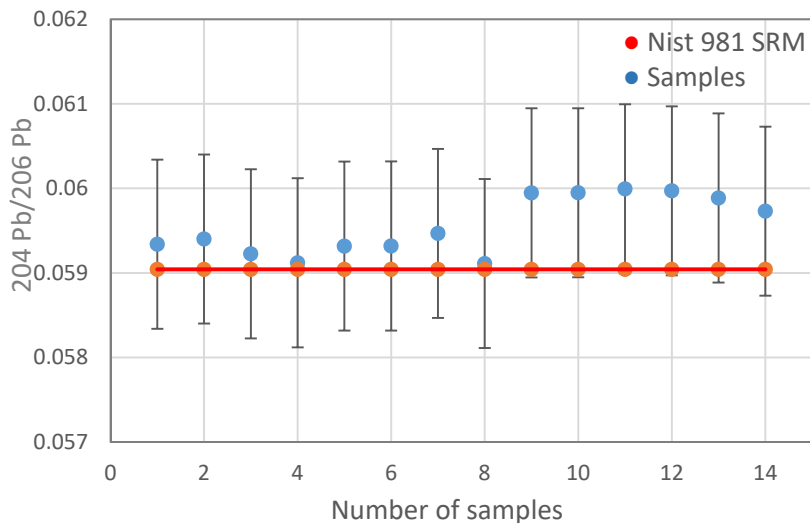


Figure 2. $^{204}\text{Pb}/^{206}\text{Pb}$ measured values (blue dots) and the NIST 981 SRM certified value (line).

The results for NIST981 measurements are displayed on Table 2 and graphically plotted on Figure 3. Pb isotope ratio data shows a clear distinction between NIST 981 SRM and the rest of the sample, as expected, due to different analytical techniques used in this study (triple-quadrupole, single-collector inductively coupled plasma mass spectrometry) and NIST laboratory (triple filament solid-sample mass spectrometry).

Table 2. Pb isotopic ratio in studied samples, including NIST 981 standard reference material for reference (5 readings/sample)

Sampling sites	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
Ferice	0.053859 ± 0.0004	0.846714 ± 0.0051	2.044527 ± 0.0099
Lesu	0.05361 ± 0.0001	0.845489 ± 0.020	2.047661 ± 0.048
Muierilor	0.052027 ± 0.0017	0.816579 ± 0.0187	1.992496 ± 0.0353
Closani	0.052456 ± 0.0001	0.807570 ± 0.020	1.971243 ± 0.035
Topolnita	0.054545 ± 0.0001	0.832732 ± 0.0008	2.006947 ± 0.0017
Tausoara	0.05491 ± 0.0002	0.83748 ± 0.0024	2.013048 ± 0.0010
NIST 981 SRM	0.059555 ± 0.001019	0.918095 ± 0.009818	2.145219 ± 0.037757

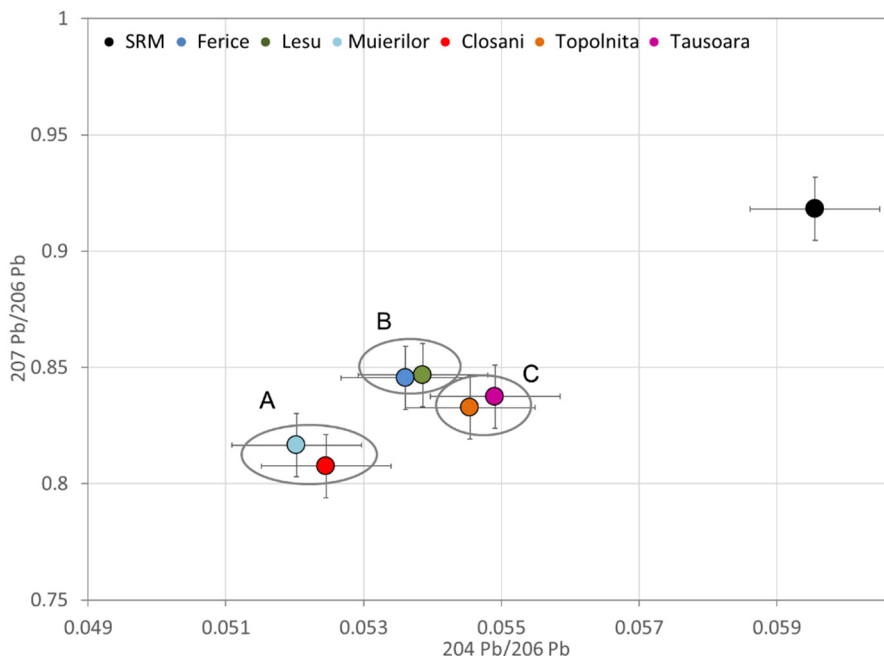


Figure 3. Sample results including NIST 981 SRM (top right): $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{204}\text{Pb}/^{206}\text{Pb}$ values. The error bars are calculated as three times standard deviations for each sample.

The samples from Muierilor and Cloșani (group A) are clearly separated from the other samples (Figure 3). Despite being sampled from different geographical locations, samples from Ferice and Leșu (group B) seems grouped together, as well Topolnița and Tausoara (group C) (Figure 3). A low separation between groups B and C is observed, but the isotopic ratio data doesn't show a clear distinction for samples within groups B and C. This can be explained by insufficient precision, due to inherent plasma variation, associated with other geological factors that may be similar between the mentioned locations.

CONCLUSIONS

A triple-quadrupole ICP-MS was successfully used to determine Pb isotopic ratio from cave sediment samples, including data on ^{204}Pb , usually left out due to ^{204}Hg interference. The ^{204}Hg was removed in the reaction cell by pressuring the cell with ammonia, a reactive gas that would initiate a

charge transfer to ^{204}Hg , creating a neutral ^{204}Hg species that is filtered out from the ion beam. While further optimizations could improve the precision, this will remain an order of magnitude lower than multi-collector ICP-MS instruments, due to design limits. However, the achieved precision using this approach is satisfactory in some cases, especially if we consider the advantages of single collector ICP-MS (versatility, low initial and tuning costs) over more expensive and less flexible multi-collector ICP-MS instruments.

EXPERIMENTAL SECTION

Instrumentation

The Pb concentration and isotopic ratio measurements were performed using a Thermo Scientific iCAP TQ ICP-MS instrument. In order to minimize the effect of plasma variations, the dwell time was set to 0.02 seconds for ^{208}Pb , 0.04 seconds for ^{206}Pb and ^{207}Pb and respectively 0.2 seconds for ^{204}Pb , to increase the number of counts for the least abundant isotope, while keeping the counts low enough for the most abundant isotope so that the detector would stay in ion counting mode and won't switch to analog (Faraday) mode. For each isotope, one channel was used for reading its counts ("peak-hopping"). The number of sweeps was set to 250. Both Q1 and Q3 quadrupoles were used in "high resolution" mode, while the collision cell gas flow was set to 0.6 ml/min. Nickel cones were used for all the measurements in this study and the instrument was configured in "High-Matrix" mode. Data acquisition and ICP-MS operation were performed using Qtegra software (v. 2.10.3324.131), provided by the manufacturer. ICP-MS operating parameters are listed in Table 3.

Table 3. Thermo Scientific iCAP TQ ICP-MS parameters

ICP-MS parameter	Value
Nebulizer gas flow (Ar)	0.90 l/min
Ammonia reaction gas for the remove of ^{204}Hg	0.6 l/min
Extraction Lens	-132.1 V
Spray chamber temperature	2.7 °C
Q1 Focus Lens	-1 V
Q1 Bias	-0.9602 V
QCell Bias	-2.01 V
Q3 Bias	-1.0002
Focus Lens	19.20 V
RAPID Lens	-377 V
Plasma power	1550 W
Cool Flow	14 l/min
Auxiliary Flow	0.8 l/min

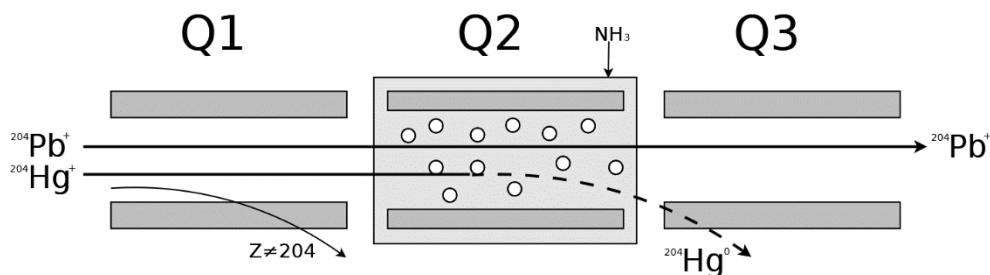


Figure 4. Removal of ^{204}Hg interference using a triple-quadrupole ICP-MS. Q1- first quadrupole, Q2- second quadrupole (inside the reaction cell pressurized with ammonia) and Q3- third quadrupole.

Description of SRM and cave sediment samples

For measuring the total Pb concentration, a calibration curve was used in the 1-100 $\mu\text{g/L}$ range and ^{208}Pb was chosen, due to its highest abundance. The standard solutions for the calibration curve were prepared by successive dilutions from Perkin-Elmer Multi-Element Calibration Standard 3. For isotopic ratio calibration and to calculate the method uncertainty for each isotopic ratio, a NIST 981 standard reference material (SRM) was used. Blank values were subtracted from each measurement. The SRM was used in a bracketing technique: the reference material was measured before and after each sample, to avoid any signal shift in isotopic determination. Ultrapure deionized water from a water purification system (Elga Veolia, UK) with HNO_3 (5%) was used for the blank samples and the Pb counts were measured and subtracted from the subsequent sample values. The deionized water was also used to prepare the calibration standard solutions and for all dilutions. The sediment samples were dried at 60-65 $^\circ\text{C}$ for 12h. The dried samples were ground and sieved in order to obtain a fine powder. Three grams of the ground samples were dissolved in a 3:1 (v/v) mixture of HCl (30%) and HNO_3 (65%) on sand bath, then transferred and diluted with ultrapure water to a final volume of 100 mL in volumetric flask. NIST 981 SRM was acquired as a solid sample (wire) and it was purchased directly from NIST. For analysis, 1 g of the solid sample was digested in HNO_3 (65%) and 1 L stock solution was prepared, the diluted for daily use (down to 50 $\mu\text{g/L}$).

The sediment samples were collected in February 2020, from five Romanian caves: Ferice, Lesu, Muierilor, Tausoare, and Topolnita sampling sites.

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