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**Inductively coupled plasma mass
spectrometry applications for heavy metals
analysis of environmental samples**

PhD thesis summary

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Contents

1. Introduction.....	3
1.1 Objectives.....	3
2. Component analysis and principles of construction and operation of ICP-MS instruments.....	4
2.1 Ion selection.....	4
2.2 Sample introduction system.....	5
2.3. Plasma and interface region	6
2.4. Ion detection.....	7
2.5 Analysis of ICP-MS instruments currently available.....	7
3. Analysis methods for environment samples	7
3.1 Qualitative methods.....	8
3.2 Quantitative methods.....	8
3.3 Semiquantitative methods	8
4. Water sample analysis by spectrometric methods.....	8
4.1 Method validation.....	8
4.2 Choosing the study area	10
4.3 Results of water analysis	11
5. Isotopic ratio determination from chondrites using ICP5QMS.....	14
5.1 DRC parameters optimization	14
5.2 Lead isotopic ratio measurements from liquid solutions	16
5.3 Isotopic ratio measurement using laser ablation.....	17
5.4 Hf/Zr ratio determination	18
5.5 Semiquantitative analysis.....	19
5.6 Rare earth elements composition from Mocs and Pleşcoi meteorites.....	20
6. Elimination of isobaric, polyatomic and non-spectral interferences.....	22
6.1 Spectral interferences	22
6.2 Isobaric interferences	22
6.3 Polyatomic interferences.....	22
6.4 Non-spectral interferences	22
7. Conclusion	24
Selected bibliography	25

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1. Introduction

Mass spectrometry can be defined as a technique for mass determination of an atom or molecule, using for this the ion movement in a magnetic or electric field. From an historic point of view, this technique was developed as a tool for atomic ion detection and developed into a powerful method for identification of unknown compounds and for structural studies in chemistry, medicine or material science. Atomic mass spectrometry keeps its important role in the whole spectrometry field today due to its high sensitivity, allowing detection of metals down to $10^{-12} - 10^{-15}$ g/ml (pico or femtograms per liter) and the possibility of isotopic determination and multielemental analysis for a single sample. Its applications covers a broad spectrum, ranging from water pollutants, semiconductor impurities or pharmacokinetics analysis for tracing compounds in chemotherapy of various cancer disease.

Ions in a spectrometer can originate from atoms, molecules or molecular fragments. The electric charge of these species allows them to discriminate by using electric and/or magnetic fields. The discrimination and detection is done by one criterion: m/z ratio (mass m and ion charge z), thus the information received is related to their mass, essentially.

1.1 Objectives

The paper aims at achieving 8 points, 2 is theoretical and the other 6 are part of practical research.

Theoretical research proposed include ► a documentary study of the principles of construction and operation of components and models on the market of inductively coupled plasma mass spectrometers and ► define and characterize the main methods of analysis that can be associated with ICP-MS techniques.

The proposed experimental research include ► the study of factors that produce spectral and non-spectral interferences and implementation of processes to avoid and / or eliminate them for obtaining better analytical results, ► the development and validation of a new method of analysis of water samples and its implementation in an environmental analysis laboratory, ► developing a method for optimizing the ICP-MS instrument for determining the isotopic ratio from chondritic material, ► the development of two new methods for measuring the isotopic ratio of lead in meteorites, ► comparative semiquantitative analysis Mocs and Plescoi meteorites ► determination Zr/Hf ratio and rare earth elements concentration of the two studied meteorites.

2. Component analysis and principles of construction and operation of ICP-MS instruments

If the sample introduction system, plasma generation of ion detection is fairly similar to all inductively coupled plasma mass spectrometers that are in use today, the fundamental difference between them is the way they select (or discriminate) ions. Spectrometer classification is done following these criteria, which further dictate the performance and possible use of the instruments.

2.1 Ion selection

Sector field mass spectrometers. Sector field mass spectrometers are, from a historical point of view, the first types of instruments that were used as mass spectrometers even in the beginning of the last century for atomic and molecular mass determination. These types of instruments supplied important data that were used for fundamental scientific discoveries like isotopes or measurements of mass/charge ratio of the electron.

Quadrupole. Quadrupole mass analyzer is the most used solution today for identification and quantification of atomic or molecular species in ICP or chromatography systems. Four identical, cylindrical or hyperbolic metallic rods in a

parallel, symmetric placement (with a margin for error of only 10 μm) makes a quadrupole. A pair of rods is situated in XZ plane and the other one in YZ plane and the ion beam that came from the ionic lenses is following the symmetry axis of the system, Z. The hyperbolic shape of the rods instead of the cylindrical one generates an electric field with a shape better suited for ion transmission.

Time of flight mass spectrometers don't use magnetic or electric field for ion discrimination but, as it's may be obvious from their name, the ion beam is accelerated at a constant kinetic energy and the ions will have different energies, according to their mass/charge ratio. Ions will separate into groups of ions having the same mass and each group will have a different speed towards the detector, thus the time needed for an ion to reach the detector is determined mainly by the m/z ratio. One big advantage of the Time of Flight mass spectrometers is that it can record up to 30000 mass spectra every second, the whole mass spectrum being recorded in less than 50 μs , a low value compared to other techniques. This is very useful when dealing with fast multielemental analysis for signals originating from sample introduction system where speed is essentials (electrothermal vaporization, laser ablation) or even in isotopic ratio measurements.

Ion trap spectrometer. This spectrometer is somehow similar to the quadrupole system, but in this case, instead of the four metallic rods a toroidal ring is used. Alternative current is applied to it which oscillates to a frequency where ions are resonating and are trapped and stabilized in the core of this system. Ions which we may want to determine are not trapped and they are carried towards the detector and converted into electrical current, as it happens with other spectrometer types detectors.

2.2 Sample introduction system

Inductively coupled plasma mass spectrometry uses by default liquid samples that are, after the sample preparation phase (filtered, digested in acid, diluted) are pulverized into aerosols and guided into plasma. This first leg of sample's journey to detector is a very important one, having an important effect on the final signal quality. More samples translates into a higher signal, a better statistics and overall better results.

For liquid sample introduction, a nebulization is used for converting the sample into small aerosols that are pumped into plasma. For this, there are two heavy used alternatives. The first is a nebulization using a Meinhardt type concentric nebulizer and a cyclonic chamber. An argon flux meets the liquid that is passing through a capillary tube (which is transported via a pneumatic pump) and aerosols are formed. Before reaching the plasma they pass a circular room where the whole aerosols are spin in an argon flux, thus having the bigger ones hitting the chamber's wall and going to waste. The lighter ones are sucked into the plasma, by using a pressure gradient system. The second approach use an oscillating membrane, up to ultrasonic frequencies, which transforms the liquid jet reaching its surface into more aerosols (when compared to the first method), increasing method's sensibility.

2.3. Plasma and interface region

For analytical purposes, the plasma is obtained by inert gas ionization (Ar, he, N₂), oxidative (air, O₂) or reducing gas (H₂, CH₄) but also in chemically reactive environments (CCl₄/Cl₂, CHCl₃/Cl₂, NH₃) by gas interaction with an electric field. For plasma generation, a torch is used, coupled with a power source by a coupling system (an electrode or a coil) by which the electric field is coupled to the support gas for the plasma, passing through the torch. Usually, the torch is a simple quartz tube or a series of concentric quartz tubes, custom made for specific applications.

Plasma – mass spectrometer interface is a region of the instrument where ions generated in the plasma are transported into the quadrupole. This section of the ICP-MS coupling is a key area concerning results quality since a lot of parameters are involved and ions suffer here extreme conditions. The interface region must provide two important purposes: extracting a high numbers of ions from the plasma and focusing the ions in a beam with a high spatial integrity and constant electrical parameters that are supposed to hold for the whole plasma – detector road.

2.4. Ion detection

Selected ions from the detector must be counted for knowing the concentration of the sample. The detector is the last component in the ion's trajectory through the mass spectrometer. When they reach detector's surface, the ions generate an electric current which is further amplified and analyzed by a signal processing module. The ions reaching the detector is proportional with the atoms that enters the plasma, thus the values of the electric current generated by the ion flux is used for computing the final concentration of the sample.

Detectors used in mass spectrometry usually have two modes: pulse and analog. In pulse mode, only a limited number of ions can be handled ($2 \cdot 10^6$ ions/second). The signal is, in this case, obtained from each individual ion reaching the detector, having a highly sensitive detection method. On the other hand, if the signal is too powerful, the detector may use the analog mode, in which the ion flux creates a continuum current. Not the number of each ions but the intensity of this continuum current will tell us about sample's concentration in this case, a mode better suited for high concentration range.

2.5 Analysis of ICP-MS instruments currently available

The market for ICP-MS spectrometers is divided between two major competitors: SCIEX Perkin Elmer and Agilent Technologies. The rest of the manufacturers are sharing a small percent of the market with cheaper, lower-quality instruments or with highly expensive ones, created for specific areas: Varian, Shimadzu, Thermo Scientific and NU Instruments.

3. Analysis methods for environment samples

No matter the manufacturer or the type of the instrument, analysis methods usually splits in two, based on the following criteria: sample's type and the purpose of the analysis: concentration measurements and isotopic ratio measurements. For the first category, we have further three subcategories: qualitative, quantitative and semiquantitative.

3.1 Qualitative methods

Qualitative methods highlight the presence or the absence of a certain analyte in a sample, but cannot offer precise information about its concentration, if this is present. The simplest method consists in scanning an interval and not just a single mass and in this way a false positive signal generated by interferences can be avoided. Having information about more stable isotopes of the same element and knowing their natural abundance, one can easily check if the spectral fingerprint is for the respective element or it's created by interference, if the signal exists at all.

3.2 Quantitative methods

For more rigorous analysis, the relation between the signal generated by the detector and ion concentration for the element that one wishes to identify is needed. Usually, this relation is linear over a few orders of magnitude. By using standard solutions with known concentration, that is stable in time, more points can be obtained for the concentration – signal graph where a calibration curve is drawn, used to identify unknown concentration based on detector response.

3.3 Semiquantitative methods

In the particular case of Elan model of SCIEX Perkin-Elmer, the software offers the possibility to use a semiquantitative method called TotalQuant. It can be used for totally unknown samples to have approximate values for its composition. For more precise analysis, quantitative analysis is preferred, but there are a few key domains in which TotalQuant is very helpful, for instance fingerprinting, where precision is not as important as a high number of analytes.

4. Water sample analysis by spectrometric methods

4.1 Method validation

Within this thesis, a spectrometer method for water sample analysis was developed and validated. The method was validated for As, Cd, Co Ni and Pb only. Due to different level of concentrations and special pre-treatment of the samples caused by the fact that they are present in different standard solution, Sr and Ti were determined

by a similar method, but that one wasn't validated in this study. In table 4.1 there are listed the multielement standard solutions used for calibration curve.

Table 4.1. *Standards used for calibration curve*

Element / conc.	Standard 1 (ppb)	Standard 2 (ppb)	Standard 3 (ppb)	Standard 4 (ppb)	Standard 5 (ppb)	Standard 6 (ppb)
Cr	10	20	40	60	80	100
Co	10	20	40	60	80	100
Ni	10	20	40	60	80	100
As	10	20	40	60	80	100
Cd	10	20	40	60	80	100
Pb	10	20	40	60	80	100

For determining the homogeneity of dispersions, 6 measurements were done on the lowest and on the highest concentration. For each element, signal standard deviation and Fischer function was compared with PG factor (ratio of squared standard deviations). If $F < PG$ then the dispersions are not significantly different and the calibration curve is correct.

Method accuracy was checked by analyzing a certified reference material. Certified reference materials (CRM) are accepted if they provide values that can be traced and in this case the reference value is the certified one. Checking the accuracy by using certified reference materials, standard deviation is determined and the average and compared with value of the certified material. The ideal certified reference material has a natural matrix, certified and similar with the sample's matrix.

Table 4.2 *Comparison of values measured by ICP-MS with certified values of NIST 1643e*

µg/L	Certified values	Measured values
As	60.45 ± 0.72	61.2 ± 3.1
Cd	5.568 ± 0.073	5.4 ± 0.3
Co	27.06 ± 0.32	27.4 ± 1.4
Cr	20.40 ± 0.24	19.3 ± 1.0
Ni	62.41 ± 0.69	61.7 ± 3.1
Pb	19.63 ± 0.21	21.1 ± 1.1
Sr	323.1 ± 3.6	319 ± 16

Usually, precision is determined for specific circumstances which, in practice, can differ from one case to another. The most used items of fidelity are repeatability and reproducibility. Repeatability (the lowest precision one can expect) offers a view on the variability type when a method is used by a single user on a single instrument, on a short term. The method was validated using international standard ISO 17294 as starting point and it's currently implemented in Environment Laboratory in INCDO-INOE 2000, Research Institute for Analytical Instrumentation, method accredited by Romanian Accreditation Association from Romani (RENAR).

4.2 Choosing the study area

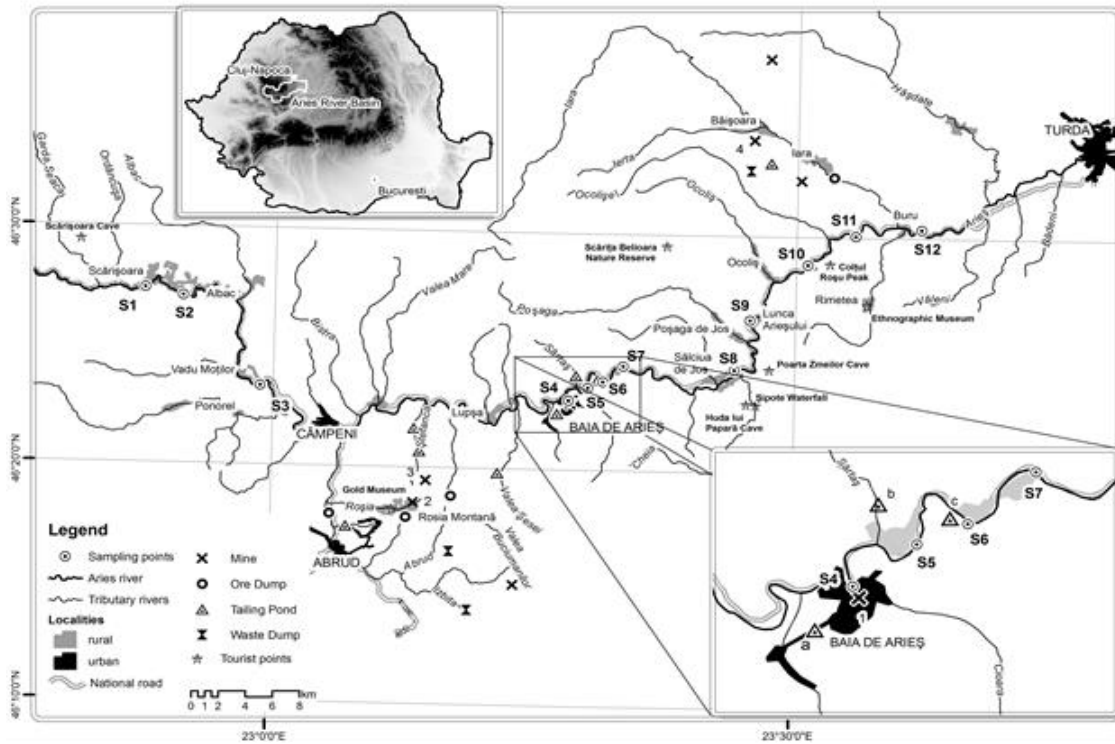


Fig. 4.1 Sampling points location and mining tailing ponds

After the method was validated, it was applied for real samples studies. Water samples were collected between March 2009 and February 2010 and include 12 points on the river and on its tributaries (Abrud, Muscani, Sesei). Some points are outside anthropogenic influence (upstream Câmpeni, S1-S3, downstream Baia de Arieș S4-S6). S7-S12 points are downstream Baia de Arieș , where a few tailing ponds are located near the river.

Soluble metals and anions were determined from filtered water (using 0.45 mm filter) according to CE Directive 2008/105/EC. Samples (100 ml) were mineralized on sandbox with 5 ml ultrapure nitric acid 65% (Merck). ICP-OES was used for determination of Ca, Cu, Zn, Mn, Mg, Na, K and Fe, using Optima 5300DV instrument and data obtained were used for statistical correlations. As, Cd, Co, Cr, Ni, Pb and Sr were analyzed using inductively couple plasma mass spectrometry with an Elan DRC II instrument (SCIEX Perkin Elmer) by using the validated method described above.

4.3 Results of water analysis

Table 4.3 lists the correlation matrix based on results obtained for Arieş hydrographic basin by applying the developed method for origin determination of elements measured by using ICP-AES instrument.

Table 4.3 Correlation matrix for elements determined by ICP-OES

	pH	EC	Cu	Zn	Na	Mg	K	Ca	Mn	Fe	Cl ⁻	NO ₃ ⁻
pH	1	-0.037	0.307	0.377	0.004	0.230	0.093	0.125	0.294	0.199	0.028	-0.186
EC		1	0.156	0.048	0.537	0.605	0.635	0.691	0.333	0.161	0.106	-0.130
Cu			1	0.438	0.410	0.278	0.105	0.189	0.357	0.502	0.301	0.231
Zn				1	0.123	0.274	0.190	0.173	0.363	0.429	0.092	0.305
Na					1	0.641	0.521	0.621	0.282	0.379	0.674	0.152
Mg						1	0.831	0.869	0.453	0.323	0.190	0.062
K							1	0.852	0.481	0.243	-0.031	-0.121
Ca								1	0.505	0.249	0.188	-0.014
Mn									1	0.515	0.086	0.009
Fe										1	0.252	0.201
Cl ⁻											1	0.458
NO ₃ ⁻												1

The values are not correlated for information regarding natural or anthropic origin of the studied elements. In some cases we have values greater than normal which puts the water beyond class I quality, but generally speaking, the average is beyond class V (Cd, Cr, Ni and Pb). Arsenic have an uniform behavior and does not go beyond class I not even with an extreme value and Co is in the same situation. For Ti and Sr there are no regulated values. For arsenic determination, oxygen was used for the

Dynamic Reaction Cell, thus avoiding the interference caused by Cl by forming ArCl species and overlapping mass 75, the only stable isotope for arsenic. For avoiding the false signal at mass 75, the Dynamic Reaction Cell was pressurized with oxygen thus allowing AsO to form and moving the measured mass from 75 to 91, where there are no interference.

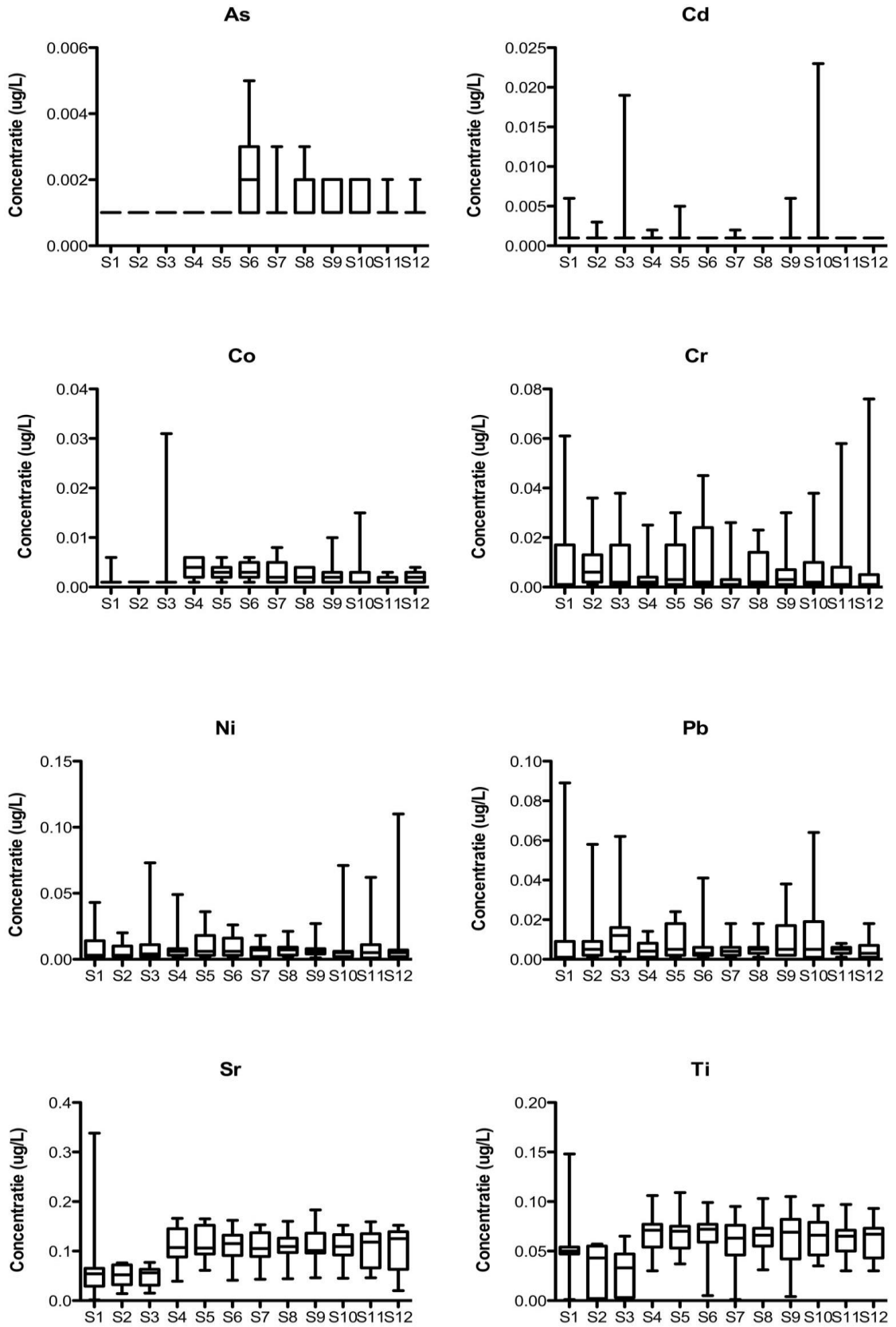


Fig 4.2 Graphic visualization of the result: average concentrations are on Ox axis (for the entire time interval) and on Ox their respective localization.

5. Isotopic ratio determination from chondrites using ICP5QMS

5.1 DRC parameters optimization

Two parameters were optimized: number of sweeps and RPq parameter (derived from the q parameter in the Mathieu equations). All the optimization were done using a NIST standard reference material, NIST SRM 981, which is an homogenous wire of lead with know and certified isotopic composition. A fragment from this wire was dissolved in ultrapure nitric acid and a solution of 20 µg/L Pb was prepared. This concentration was chosen that it would not saturate the detector, but still providing a strong signal while in pulse mode. Sweep is the number of times the quadrupole reads each mass, consecutively. 100, 200, 400, 600 and 800 are the values chosen for test and 5 measurements were done and then the results were averaged. The results were graphically displayed (sweep times versus relative standard deviation) in fig. 6.1

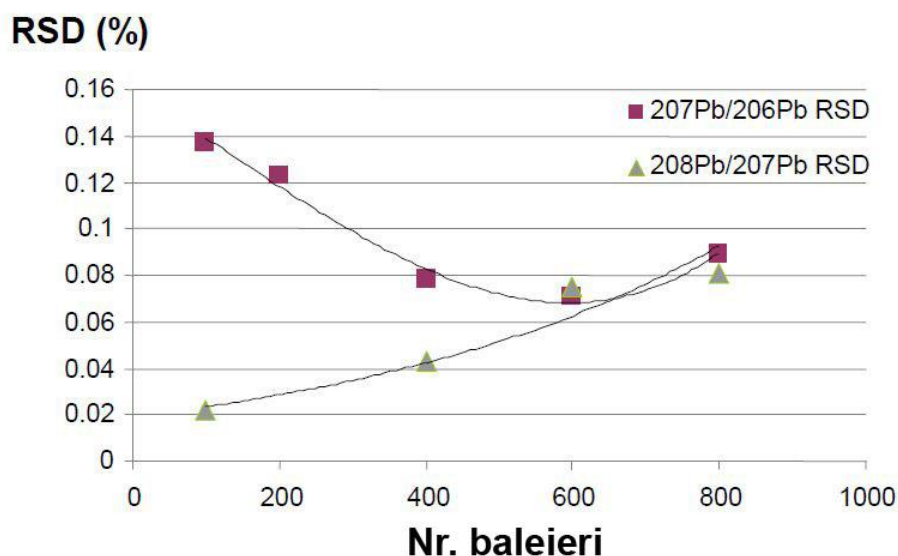


Fig. 5.1 Optimization of quadrupole sweeps

The value of 400 sweeps / reading was chosen as the optimum one, offering a satisfactory value for relative standard deviation for both $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$. For RPq parameter, even if lower values offers better precision, the optimum accuracy for both sets or isotopic ratio is obtained by a RPq value of 0.45.

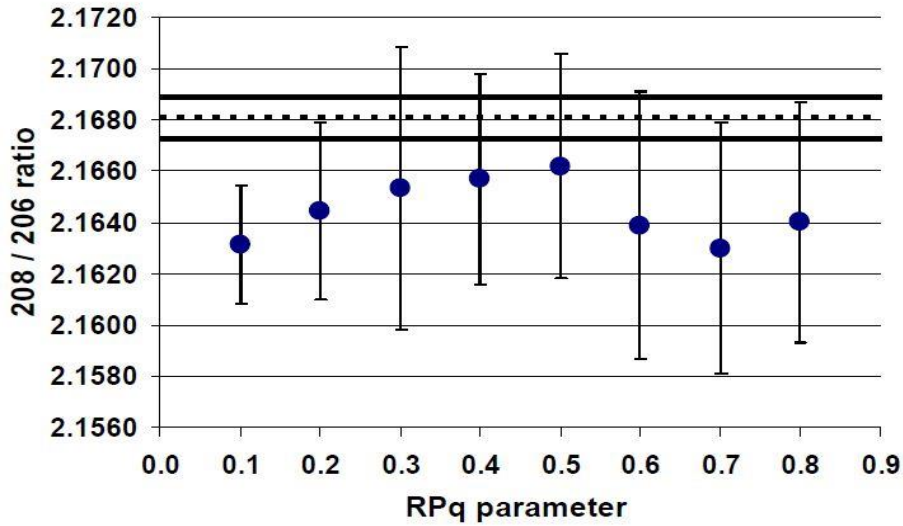


Fig. 5.2 $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic ratio, function of RPq

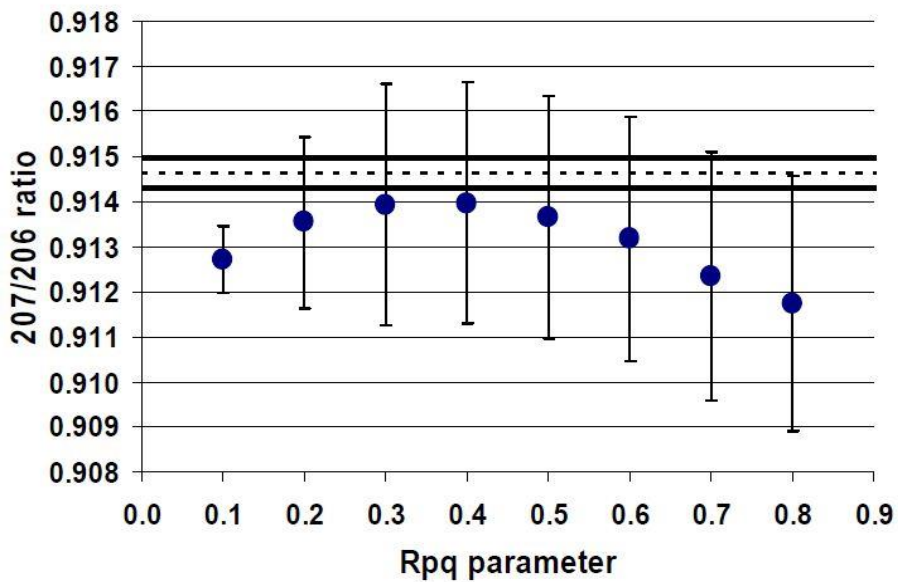


Fig. 5.3 $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic ratio, function of Rpq

Choosing the time spent by the quadrupole on each mass was done considering the isotopic abundance, thus compensating for lower abundance isotopes delivering fewer ions on the detector. 30ms was chosen for ^{208}Pb – the most abundant lead isotope and 60 ms for ^{206}Pb and ^{207}Pb .

Peak hoping was used for reading the samples, which is the most usual approach in this situation: the signal is acquired using a single channel, at the corresponding atomic mass for the selected ion. Another way of acquiring the data would be by

using multichannel mode by assigning 20 channels for every mass, but this procedure is not used for routine measurements. For maximum sensibility setting on peak-hoping approach, in the morning of every measurement day, a calibration of the mass scale was performed, assuring that the reading is not shifted and that the signal acquisition is done right on the tip of the peak.

Tabel 5.1. *Instrument parameter*

Parameter	Value
Plasma	
Power (W)	1300
Argon flux for plasma (l/min)	12.00
Auxilliary argon flux (l/min)	1.20
Nebulizer flux	0.92
Cones	Platinum
Quadrupol	
Quadrupol Offest (V)	0.00
Offset DRC (V)	-8.00
Reading mode	p.h.
Integration time (ms)	30 / 60
Readings	variabil
Ionic lenses (V)	10

5.2 Lead isotopic ratio measurements from liquid solutions

Meteoritical samples were provided by Mineralogic Museum of Babeş Bolyai University, Cluj-Napoca. They were washed with ultrapure water and dried in argon atmosphere before removing the crust (thus avoiding any contamination with lead during handling or atmospheric passage). The samples were mechanically

First step consisted on adding 10 ml nitric acid and evaporating till 2 ml. In second phase, 5 ml hydrofluoric acid was added and 1.5 percholic acid, evaporating again until 2 ml. Then the sample is heated in step three, while adding another 5 ml of nitric acid , 1 ml chlorhidric acid and ultrapure water. The fourth and final step required adding 5 ml nitric acid, 6.5 hydrofluoric acid and 1 ml sulfuric acid, evaporating until 2 ml when ultrapure water was added up to 25 ml.

^{204}Pb was excluded from this study due to its low abundance, which would have created a significant source of error in determination due to the fact that quantitative analysis revealed 1.047 mg/kg mercury content in Mocs meteorite. Mathematical correction can't be applied since the exact mercury isotopic ratio for our samples are not know so ^{204}Hg would severely interfere with ^{204}Pb .

Table 5.2. *Isotopic ratio measurements (solution)*

		$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
NIST 981	<i>Measured</i>	0.9142 ± 0.012	2.1683 ± 0.0023
	<i>Certified</i>	0.9146 ± 0.0003	2.1681 ± 0.0008
Mocs		0.8656 ± 0.0084	2.1011 ± 0.0036
Pleşcoi		0.8610 ± 0.0092	2.1329 ± 0.0041

Quantitative analysis revealed 0.23 ± 0.03 mg/kg Pb in Mocs and 0.04 ± 0.03 mg/kg Pb in Pleşcoi meteorite. The difference between isotopic ratio values of terrestrial lead and meteoritical lead is not surprising since the source of the lead deposits is different and its evolution in time is also distinctive for the two types of samples.

Although SCIEX Perkin-Elmer DRC II isotope is not specifically designed for isotopic ratio measurements, after sever optimization of some parameters, the instrument can provide satisfactory results for isotopic composition of various samples.

5.3 Isotopic ratio measurement using laser ablation

The above described method is a destructive one, fragments of samples being dissolved in acid solutions. In some cases, when dealing with unique and rare samples, like meteorites, this is not always the best approach for analysis and laser ablation method can be consider as an alternative.

Due to the lack of matrix-matching reference materials, it's impossible a rigorous method validation for laser ablation system. The most used certified reference material in the field is NIST 610, a piece of glass that have certified only the concentration values, not the isotopes ratio. However, the NIST 610 material is homogenous, so there is data available of it isotopic ratio for lead. This is not data

certified by the manufacturer, but the values can be used for testing and evaluating our own method.

Within this thesis, isotopic ratio for Pb was determined for Mocs and Pleşcoi meteorite samples, by using a laser ablation system coupled with an ICP-MS (LA-ICP-MS). Values for the determined ratios are listed in the following table.

Tabel 5.4 *Isotopic ratio for Mocs and Pleşcoi meteorites using laser ablation and ICP-QMS (LA-ICP-QMS).*

	$^{207}\text{Pb}/^{206}\text{Pb}$	SD	RSD	$^{208}\text{Pb}/^{206}\text{Pb}$	SD	RSD
Mocs	0.8564	0.0135	1.58	2.1092	0.0432	2.05
Pleşcoi	0.8576	0.0140	1.63	2.1349	0.0561	2.63

5.4 Hf/Zr ratio determination

Zirconium and hafnium are incompatible and refractory elements. They have the same valence (4+) and approximately the same ionic radius. Both have similar geochemical behavior and that is why their ratio can help solve a few geochemical phenomena that happened in the first stages of our solar system forming. Being refractory elements (meaning that they have high melting point temperature), Hf and Zr were among the first elements to condensate from planetary nebula that eventually formed our solar system. Their condensation temperature varies by 60K: 1764 K for Zr (ZrO_2) and 1703 K for Hf (HfO_2).

Studies performed on various types of chondrites and achondrites meteorites found out that a value of 34.3 ± 0.2 for Zr/Hf ratio could be considered an average for our solar system, thus all the meteorites originating here should have similar values. The study was recently performed again by another team, considering a broader spectrum of meteorites (29 chondrites and 5 achondrites) using the same technique as the previous study: LA-ICP-MS. This time, the results varied in a larger interval, the ratio being between 28 and 38 and the new average value for our solar system was considered to be 34.1 ± 0.3 with variations depending on the meteorite class.

For Mocs and Pleşcoi meteorites, liquid samples reading was selected as measurement technique, thus assuring sample's homogeneity and offering a stronger

signal for ICP-MS detector. The method is somehow similar with the one used for Pb isotopic ratio measurement with the exception that this time only ^{90}Hf and ^{180}Zr were determined, using an integration time sufficient enough for both isotopes. The detector was used in pulse mode, for better sensitivity, saturation wasn't a problem since the concentration for both Zr and Hf being low enough to avoid this.

For Mocs samples, the Zr/Hf was 35.2 ± 0.8 and for Pleşcoi 35.4 ± 0.8 . The values are not significantly different, which is not a surprise since both meteorites are from the same class (chondrites) and type (L5-6). The values are close to other meteorites (Allende - CV3 or Richardton - H5).

5.5 Semiquantitative analysis

Semiquantitative analysis is a very important tool for fast measurement of the entire mass spectrum, especially for a sample with an unknown composition. Detection limit and precision are inferior when compared to quantitative methods, but a semiquantitative offers a good view on elemental composition of any sample without needing calibration for each separate component.

Tabel 6.3 *Semiquantitative results for Mocs and Pleşcoi*

(mg/kg)	Mocs	Pleşcoi
Li	1.2	1.1
Sc	6.0	5.6
Ti	368	342
V	25	21
Cr	460	408
Mn	1559	1428
Co	326	333
Ni	6519	5851
Cu	57	52
Zn	38	38
Ga	3.6	3.0
Ge	6.9	7.2
Rb	2.1	1.8
Sr	5.2	3.5
Y	1.2	1.6
Zr	4.3	4.7
Nb	0.3	0.3
Mo	0.7	0.8
Ag	<0.2	<0.2

Cd	<0.2	<0.2
Sb	<0.2	<0.2
Ba	1.7	2.6
La	<0.2	0.2
Ce	0.4	0.5
Nd	0.3	0.4
Sm	<0.2	<0.2
Eu	<0.2	<0.2
Gd	0.2	0.2
Tb	<0.2	<0.2
Dy	0.2	0.3
Ho	<0.2	<0.2
Er	<0.2	0.2
Yb	<0.2	0.2
Hf	<0.2	<0.2
W	<0.2	<0.2
Re	<0.2	<0.2
Ir	0.3	0.3
Pt	0.5	0.5
Au	<0.2	<0.2
Hg	0.9	<0.2
Pb	1.0	1.0
LD=0.2		

Detection limit is 0.2 mg/kg and can be improved by using a quantitative method. Presence of iridium in both Mocs and Pleşcoi can be highlighted as a mark of meteoritic material. Significant difference can be observed only in the case of Ba and Sr. Measurement uncertainty differs upon sample matrix and element and cannot be precisely determined using semiquantitative method, varying between 5% and 25% (for elements with very low or very high concentration).

5.6 Rare earth elements composition from Mocs and Pleşcoi meteorites

For a more precise analysis of rare earth elements from Mocs and Pleşcoi, a quantitative method was used. Information offered by semiquantitative analysis hinted low concentration for all rare earth elements and that is why the use of an ultrasonic nebulizer was chosen as the appropriate way of measuring REE concentration. Aerosols particles are up to 10-20 times more numerous than cyclonic nebulization, enhancing the detector signal accordingly. For example, the daily performance check solution consisted in 1 µg/L In which translated into a signal

between 30000 and 50000 cps (depending on various parameters). Using an ultrasonic nebulizer and the same solution, the signal was near a value of 800000 cps which directly improves method sensibility. In this case, the blank solution plays an even greater role: a high background level, canceling the advantage of the ultrasonic nebulizer. Results of rare earth elements determination is listed in table 6.4. This time, the detection limit was 0.003 mg/kg, significantly better value than for the semiquantitative method and uncertainty was 8%. A multielement solution manufactured by Perkin Elmer (Standard II) was used for calibration purposes.

Table 5.4 lists the obtained results on rare earth element composition for Mocs and Pleşcoi meteorites. The determination was done within an 8% uncertainty and a detection limit of 0.003 mg/kg.

Tabel 5.4 *Rare earth elements concentration for Mocs and Pleşcoi (LD=0.003, incertitudine: 8%)*

(mg/kg)	Mocs	Pleşcoi
Ce	0.606	0.512
Dy	0.429	0.460
Er	0.283	0.308
Eu	0.118	0.061
Gd	0.367	0.375
Ho	0.090	0.097
La	0.470	0.470
Lu	0.044	0.040
Nd	0.532	0.567
Pr	0.086	0.085
Sm	0.256	0.216
Sc	6.293	3.509
Tb	0.054	0.055
Tm	0.032	0.034
Y	1.860	1.689
Yb	0.283	0.308

Again, the concentrations for the two samples are not varying significantly, which is no surprise. The only differences can be spotted for Sc and Eu. The ultrasonic nebulization can be successfully applied for concentration to low for cyclonic nebulization. In fact, the concentration level must be carefully monitored because the high signal intensity could easily render the detector saturated.

6. Elimination of isobaric, polyatomic and non-spectral interferences

Interferences are generated by relatively low resolution of the quadrupole used in inductively coupled mass spectrometer and it negatively affects the quality of the measurements, no matter of the instrument or method. Their effect can be completely eliminated or reduced, depending on their origin. Removal of interferences gets complicated if the sample matrix is complex.

6.1 Spectral interferences

Spectral interferences can be generated by different elements that have isotopes with the same mass as the element that is determined or by polyatomic species with mass overlapping the one where we search for a specific component.

6.2 Isobaric interferences

This type of interference can be overcome by simple mathematical corrections, because the natural abundance of isotopes is known and it remains constant over time, from one measurement to another. Luckily for the use, all modern instruments have these corrections implemented in the software, automatically, for each isotope.

6.3 Polyatomic interferences

When polyatomic species are mistakenly considered by the quadrupole to have the same mass as the measured ion or if that ion reacts and forms a stable compound of another mass, it is said that a polyatomic interference occurs. An important class of polyatomic interferences are the oxides. A surplus of oxygen in the plasma could react with species like ^1H , ^{16}O or $^{16}\text{O}^1\text{H}$ that could shift the real mass of the analyte by 1, 16 or respectively 17 atomic masses away, thus being eliminated by the mass filter. This usually happens in the colder region of the plasma.

6.4 Non-spectral interferences

Matrix sample composition can play an important role in the signal quality of a sample (matrix effects). A variation in the matrix viscosity can influence aerosols

generations in the cyclonic chamber during nebulization and can affect the final result or alter the calibration curve. Also, a higher acid concentration in the sample could lead to negative effects on the ionization process in the plasma. An element with a higher concentration could deteriorate the signal of the desired analyte we want to determine and this effect increases with concentration, due to electrostatic scattering between unwanted ions at the interface region. These are only a few examples of non-spectral interference sources

7. Conclusion

A method for analyzing heavy metals from water samples was validated and it's currently applied in an environment laboratory, accredited by Romanian National Accreditation Body RENAR (Environment Laboratory of INCDO-INOE2000 ICIA Cluj-Napoca). The method can be further extended to contain other elements as well. Also, a study of the Arieş hydrographic basin was performed.

Isotopic ratio measurement was performed using inductively coupled plasma, quadrupole mass spectrometry for two meteorites, an old Mocs and a brand new Pleşcoi chondrite, after carefully optimizing the SCIEX Perkin Elmer Elan DRC II instrument. The study was done on lead, but it also can be extended on other elements if needed.

A comprehensive study from an elemental composition point of view was performed on the new Pleşcoi meteorite and the results were compared with Mocs chondrite, probably the most known and studied Romanian meteorite available. Both meteorites are in the same class, a fact confirmed also by our analyses on their composition and lead isotopic ratio measurements. Hf/Zr ratio was also determined, together with data about rare earth element composition for both Mocs and Pleşcoi, using different analytical methods that offered high data volume or respectively high sensibility and precision.

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