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Determination of lead isotopic ratio in organic and soil materials using a quadrupole mass spectrometry method with fast inductively coupled plasma

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We investigated the lead isotopic ratio in organics and soil materials, along with leaded gasoline, one of the cause of increased lead pollution in the recent decades, using and inductively coupled plasma mass spectrometer, a relatively new method in the field of isotopic ratio measurements. Even if ICP-QMS technique is not as precise as the TIMS, it can provide short analysis time while having 0.1 - 1.5% relative standard deviation in measurement's precision, which can be considered to be sufficient for most fields. Also, we provided data about lead isotopic ratio in lead, soil and vegetable sampled from western part of Romania.

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1. Introduction

Lead is a toxic and non-essential heavy-metal and world-wide lead pollution is an important problem that we have to deal with it today. If 5000 years ago, total lead production in whole world were around 200 tones/year, during Roman Empire total world production of lead is estimated at 80 000 metric tones [1]. At the beginning of the 20 century, the global lead production increased to 1.10^6 metric tones/year [2] and this valued was four time higher in 1994 (4.10^{-6} tones/year) [3]. These increased values are due to increased industrial activities, as well as using lead as an additive for gasoline in the last decades. This caused the atmospheric level of lead in the present days being 1-2 level of magnitudes greater that natural sources [4] although in the present the lead contamination level in the environment tends to decrease, due to several laws adopted in this field by many countries [5], under UN recommendation.

Lead is present in four stable natural isotopes ^{208}Pb (52.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%) and ^{204}Pb (1.4%) [6]. From all this isotopes, ^{204}Pb is the only primordial source for lead, being distributed in constant ratio in Earth crust, the others isotopes (called radiogenic isotopes) are result of decaying processes of heavier radioactive nuclei: ^{238}U decay is responsible for ^{206}Pb isotope, ^{235}U finally decays in ^{207}Pb and ^{232}Th have ^{208}Pb isotope as a final decaying product. [7]. This means that ^{204}Pb isotopic distribution may be considered fixed, independently of source, as ^{206}Pb, ^{207}Pb and ^{208}Pb increased over time, relative to ^{204}Pb. Although other ratios are also used, normalized ratios to ^{204}Pb are the most common factor for determination of other Pb isotopes distribution variation.

Because isotope ratio in a sample does not change during natural physical or chemical processes, the ratio is used to determine the source and pathways of lead in a large variety of samples [8], as the isotopic ratio remains unaffected while lead goes trough the ecosystem. Every lead mine have a different lead isotope ratio, as this value varies accordingly to primordial uranium and thorium distribution, which was not homogeneous. Thus, American leaded gasoline differs in term of lead isotopic ratio from the European leaded gasoline, since the additive lead come from different sources. Even in Europe, leaded gasoline from eastern and western states have different lead isotopic ratio.[9]

Isotope ratio measurements were originally performed using thermal ionization mass spectrometry (TIMS). Inductively coupled mass spectrometry (ICP-MS) instruments brought ease of sample preparation, short analysis time and low sample cost, compared to TIMS, although ICP-MS fails to deliver the accuracy and precision achieved with TIMS. This is because a quadrupole is used as a mass filter for ICP-MS instruments, which performs a sequential determination of isotopes. Plasma (ion source) and detector states may vary from one isotope determination to the other, generating inaccurate ion signal. Multi-collector inductively coupled mass spectrometry (MC-ICP-MS) improves accuracy and precision [4], but the cost of MC-ICP-MS instruments is higher and they are not as widely used as ICP-MS instruments.

2. Experimental

2.1 Sample collection and treatment

Samples were collected from three areas from Baia Mare region, Western Romania: Sasar (SS), Bozanta Mare

(BZ) and Tauti Magherăus (TM) and were collected from private gardens of residents from the villages. The studied vegetable species are commonly grown and consumed in the area and were collected just before shedding to assure maximum metal accumulation. The soil samples were collected from 0-20 cm depth, using a stainless steel shovel. All samples were stored in a clean, labeled, polyethylene bags, closed tightly to avoid contamination during transportation to the laboratory.

Soil samples were air dried to constant weight, sieved through the 2 mm sieve, than ground to a fine powder in a tungsten-carbide swing mill for 3 min and sieved through 250 μm sieve, homogenized and stored in polyethylene bags until the *aqua regia* extraction.

The *aqua regia* extractable metals in soils and tailings were determined according to ISO 11466:1995. An amount of 1 g soil sample (<250 μm) was weighted, introduced into the reaction flask and maintained at room temperature for 16 h with 21 ml of 12 M HCl and 7 ml of 15.8 M HNO_3. The mixture was then heated under reflux conditions for 2 h. The solution was filtered and diluted to 100 ml with 0.5 M HNO_3.

The collected vegetable samples (carrots - *daucus carota,* potatoes - *solanum tuberosum and* onion - *allium cepa*) were washed with ultrapure water to remove superficial dust, oven-dried at 80-90 ^oC for 15-30 minutes and at 65 ^oC for 12-24 h. The dried samples were ground with a stainless steel mill to pass a 0.5 mm sieve. A portion of plant material (*ca*. 5 g) was accurately weighed into a reaction flask and digested with concentrated HNO_3 and $HClO_4$ (5:1 v/v). Blank extractions were carried out for each set of analyses.

Control samples for vegetables and soil were collected from a region far from anthropogenic pollution (road traffic or industrial plants), situated in western Romania as well, and prepared as described above.

100 ml gasoline measured at 20 ^oC into a reaction flask and extracted with 50 ml concentrated HCl at reflux conditions and than the acid layer was separated and analyzed by ICP-MS. Gasoline was purchased from the manufactures present in the studied region. A total of 12 samples were analyzed, from 3 most widely most widely vendors.

2.2 Reagents

Ultrapure water was prepared in-lab, as described below. Lead certified material (NIST 981) was obtained from National Institute for Standards and Technology (NIST), USA. (NIST 981: $^{204}Pb/^{206}Pb$ = 0.059042 ± 0.000037, $^{207}Pb/^{206}Pb$ = 0.91464 ± 0.00033, $^{208}Pb/^{206}Pb$ = 2.1681 ± 0.0008). From the wire-shaped lead material, a solution of 9.8 ppb Pb was prepared (for optimal signal in pulse detector mode range), by dissolving parts of the initial certified material in 1% HNO3 solution on a hot plate and further dilutions.

Ultrapure grade hydrochloric, nitric acid and other reagents were purchased from Merck.

Argon gas (99.996% purity) needed for plasma was supplied by Linde Gas, Cluj-Napoca, Romania.

2.3 Instrumentation

For all isotope ratio and quantitative analysis, a quadrupole based, single detector, ICP-MS system was used (Perkin Elmer SCIEX Elan, model DRC II, Toronto, Canada), equipped with a second quadrupole, placed before the ion lenses, in a so-called Dynamic Reaction Cell (DRC). This cell can be pressurized with a reaction (or collision) gas for interference removal (which was not the case in this study) and, being a quadrupole, can also act as a ion focusing system. Also, axial field technology (AFT) improves ion transmission through the cell, reducing the time an ion spends in the cell, improving analysis time. Detector dead time was set to 50 ns. For sample delivering system, a quartz, concentric Meinhardt nebulizer was used, along with a cyclonic quartz chamber. Parameters for SCIEX Elan DRC II instrument are listed in Table 1. The instrument is placed in room under a controlled temperature (21 ± 1ºC)

Plasma and ion optics parameters were optimized for best signal/noise ratio, with all parameters being in manufacturer's recommended interval. Minimum 40 000 counts per second (cps) for 1 μl^{-1} of indium (in 0.5% nitric acid solution) was targeted and achieved for every analysis, as an optimum signal/concentration ratio. Monitoring of double charged ions and oxides was monitored also and their respective level was kept under manufacturer's specification.

An 18 MΩ cm^{-1} Millipore MilliQ DI (Millipore, Watford, Hertfordshire, UK) system was also used for in-lab ultra pure water preparation.

Table 1. Parameter settings for DRC II ICP-MS

Parameter	Value
Plasma	
Power / W	1350
Plasma gas flow / l min^{-1}	12.00
Auxiliary gas flow / l min^{-1}	1.20
Nebuliser gas flow / l min^{-1}	1.05
Sample/Skimmer cone	Nickel
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	Varying
Integration time / ms	Varying
Reading per point	300
Reading per replicate	1
Replicate measurements	4
DRC	
Reaction Gas	None
Lens voltage / V	11.00

3. Results and discussion

For an optimum tuned quadrupole mass spectrometer, the only parameter that can limit the isotope ratio determination precision is the counting statistics. It is well known how to improve counting statistics, but every such method has also some drawbacks. For example, using concentrated samples will increase ion numbers and provide a better statistics, but can also damage the detector. Besides that, the majority of mass spectrometers use pulse counting for ion detection, up to a certain limit only and automatically switching to analog mode when that limit is reached, which may lead to inaccurate results. Increasing time for reading each isotope or having a higher number of repetitive measurements may be expensive in terms of sample volume consumption or time spent per analysis.

Most instruments software allows modifying the time spent by quadrupole on every m/z species (generally speaking, on every ion). The simplest approach is to assign equal time to all isotopes, but this is obviously a rather simplistic method and it is not widely used. The most common approach is assigning the dwell time value in an inverse proportionally ratio with each isotope's abundance. This will allow for least abundant isotopes to have batter statistics, but it was shown that this approach is not optimal [10]. For our measurements, we choose to use the following dwell time distribution: 47.6% (58 ms), 21.4% (25ms), 21.4% (25 ms) and 9.6% (12ms) for ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, respectively. We also kept the signal intensity under control by multiple dilution (if they were necessary), to keep the detector in pulse mode, for better precision.

A total of 33 vegetables samples and 15 soil samples were analyzed. Mean of total lead concentration in soil samples was measured using the same instrument and found to be 6.543 mg kg^{-1}, which required multi-step dilutions before adequate isotope reading could be performed (the final lead concentration being around 10 µg l^{-1}). The mean results for isotopic ratio for all analyzed samples are listed in Table 2 and comparison with other data found in literature is listed in Figure 1. Relative standard deviation for all samples is between 0.1% - 1.5%, which we found to be adequate for our purpose. A NIST 981 solution was read as a standard between every 5 samples and the instrument's software was used for calculating the correction factors needed to compensate for the mass-bias effect. Results for measured NIST SRM solution are displayed in Table 3.

Table 2. Comparison of measured and certified values for lead isotope ratios, using a 9.8µl^{-1} NIST SRM 981 solution (n=7, ±1SD).

	Measured values	**Certified values**
^{204}Pb/^{207}Pb	0.0591±0.0001	0.059042±0.000037
^{207}Pb/^{206}Pb	0.9137±0.0013	0.9146±0.00033
^{208}Pb/^{206}Pb	2.1653±0.0031	2.1681±0.0008

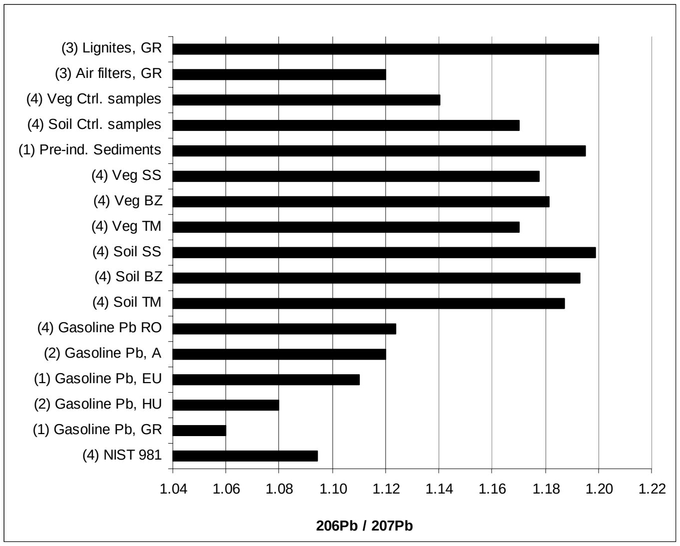

Fig 1. Comparison of ^{206}Pb/^{207}Pb ratio diagram for analytical results from 1. [11], 2. [12], 3. [13], 4. this study.

Table 3. Mean isotopic ratio (±1SD) for all samples.

	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
SS Veg.	0.063±0.001	1.178±0.002	2.473±0.014	2.100±0.010
SS Soil	0.060±0.001	1.199±0.002	2.530±0.006	2.110±0.005
BZ Veg.	0.064±0.001	1.182±0.004	2.476±0.015	2.095±0.019
BZ Soil	0.059±0.001	1.193±0.012	2.497±0.014	2.094±0.016
TM Veg.	0.063±0.001	1.170±0.012	2.492±0.016	2.130±0.010
TM Soil	0.058±0.001	1.187±0.004	2.524±0.008	2.126±0.003
Ctrl. samples	0.064±0.001	1.140±0.020	2.468±0.012	2.165±0.016
Leaded gas	0.065±0.001	1.124±0.010	2.422±0.011	2.155±0.012

4. Conclusion

Isotopic ratio of lead from vegetables, soil and leaded gasoline were investigated, using a fast method developed for and inductively coupled plasma mass spectrometer. Obtained data were compared to other data from the literature. Isotopic ratio for leaded gasoline, used in Romania and other countries from this part of the continent (Hungary, Austria, Greece) was found to be lower than the values found in vegetables and soil samples, which indicates that lead in samples did not originate from road pollution, but this do not exclude the industrial sources for lead pollution, which were not investigated in this study (as the control samples have different isotope ration than the ones from the studied villages).

The method we used proved to be reliable enough for our purposes, with relative standard deviation between 0.1% - 1.5% for both real samples and also for NIST reference material derived samples. Also, no data about isotopic ratio in leaded gasoline from Romania was found to be published before this study. [13].

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