APPLICATION OF LEAD ISOTOPE RATIOS FOR POLLUTION SOURCE INVESTIGATION IN THE MARINE ENVIRONMENT

IAEA
International Atomic Energy Agency
Atoms for Peace and Development

Emilia Vassileva[a], Anna Maria Orani[a], Sergey Assonov[b]

[a] International Atomic Energy Agency, Environment Laboratories, Monaco

[b] International Atomic Energy Agency, Environment Laboratories, Seilbersdorf, Austria

E mail address: e.vasileva-veleva@iaea.org

1. Introduction

Lead is a non-essential toxic element that at high levels of human exposure causes damage to many organs of the human body. This element naturally occurs in the Earth crust, but its biogeochemical cycle has been altered by anthropogenic activities, which have introduced high amount of this element from different sources. Among inorganic contaminants, Pb is perhaps the most studied, but the determination of its total concentration only is not sufficient for a proper evaluation of contamination sources. Discrimination of anthropogenic and geogenic lead sources requires both precise and accurate isotope ratio determination as well as high versatility due to the complexity of environmental matrices, such as sediments, biota and seawater. This element has a partially radiogenic isotopic composition with 208Pb, 206Pb and 207Pb originating from the radioactive decay of 238U, 235U and 232Th respectively and 204Pb representing the only natural stable isotope. This characteristic isotopic composition represents a powerful analytical tool as it allows to trace the sources, fate and effects of possible Pb contamination. The most common way to express the Pb isotopic composition is using the ratio 206Pb/207Pb, because of the easy interference-free determination and isotopes' abundance. The determination of 204Pb by ICP-MS is quite challenging as this is also the least abundant among Pb isotopes (about 1.4%) and it is also affected by isobaric interference from 204Hg. The latter derives from both sample matrices and from plasma/sweep gas supplies and it represents a big analytical challenge, especially for marine biota samples, where the amount of Hg can be up to 100 times higher than Pb.

In this work we present the development and the application of analytical methodology for the accurate and precise determination of Pb isotope ratios by HR-ICP-MS in different marine environmental matrices (sediments, seawater and biota). Analytical procedures are involving a separation of Pb from the sample matrix and mercury, present in the sample. For seawater samples, the use of the SeaFAST automated system allowed simultaneous matrix separation and analyte pre-concentration before ICP-MS analysis. A comparison of results for lead isotope ratios obtained with MC-ICP-MS and HR ICP-MS in the same samples, in all cases, showed very good agreement. The total uncertainty associated to each result was estimated and all major contributions to the combined uncertainty of the obtained results were identified. As all such studies involve companions of different datasets, the uncertainty estimation is critical to ensure correct companions. The developed methodology was applied to different marine samples, namely sediments from Namibian coast, biota samples from French Polynesia, seawater samples from different sampling areas.

2. Samples

Sediments Namibia coast (surface and cores)

Biota: French Polynesia

Seawater:

Namibian Seawater

Irish Seawater

Arctic Seawater

Mediterranean Seawater

3. Analytical procedure

Sediments and biota samples

About 0.1 g sediment or biota sample: microwave digestion with 5ml Ultrapure HNO3 + 1.5ml H2O2 (+1ml HF for sediments)

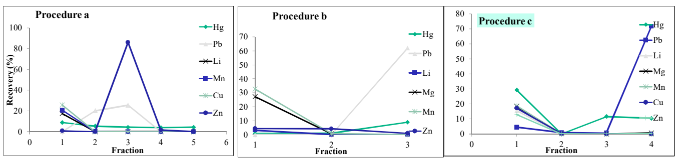
Biota: resin separation to remove high Hg content

Sediment: high dilution

Determination of Pb total content with Q ICP-MS. Isotope ratios measurement by HR SF ICP- MS. Measured isotopes: ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb

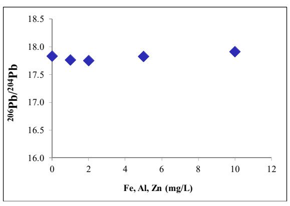
Correction of intensities for : Instrumental background, Isobaric Interferences on ^{204}Pb, Mass discrimination effect, Dead time effect, Instrumental background

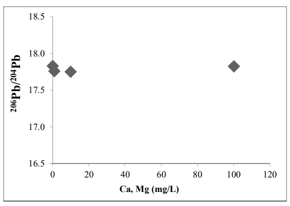
Selection of resin separation for biota samples



Procedure c, using Eichrom resin, was selected as it allowed ideal separation of Pb from interfering Hg and a relative high Pb recovery in the analysed fraction

Evaluation of remaining matrix components for biota and sediments





Seawater: matrix separations and analyte pre-concentration

Sea Fast automated system for Pb separation and Pb pre-concentration. Acidified seawater samples are loaded directly in the system without any pre-treatment. Pre-concentration factors of 50 are achievable

4. Instrumentation and Intensity Corrections

High Resolution Sector Field Inductively Coupled Plasma – Mass Spectrometer

HR-ICP-MS working parameters

Parameter	Value
Coolant gas flow	13.5 L• min^{-1}
Auxiliary gas flow	0.8 L• min^{-1}
Nebulizer gas flow	29.2 L• min^{-1}
Plasma power	1300 W
Sensitivity for 1 ng • g^{-1} ^{208}Pb	> 400000 cps
Background on mass 220	0 cps
Dead time	14 ± 2 (k=2) ns
Accusation Mode	Peak Jumping, Fast scanning
Number of sweeps	1000
Number of cycles	25
Dwell time per amu per isotope [ms]	500
Measured Isotopes	^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb
Mass resolution	300
Oxide Formation CeO^+/Ce	<2%

Correction for dead-time effects

$$I_{\_dt} = \frac{I_{raw}}{(1 - I_{raw} \cdot \tau)}$$

$$R = \frac{I_A}{I_B}$$

Correction for Mass discrimination

$$R_{corr} = rK$$

Correction on isobaric interferences

$$I_{a1}^{cor} = I_{a1}^{tot} - I_{b2} \cdot \frac{A_{b1}^{IUPAC}}{A_{b2}^{IUPAC}}$$

Correction for instrumental background

$$I_{\_bkg} = I_{raw} - I_{bkg}$$

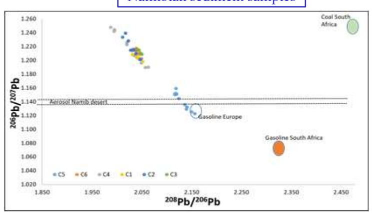
5. Uncertainty evaluation

Individual uncertainty components were combined together by applying the uncertainty propagation procedure according to the ISO/GUM guide. In practice, a dedicated software program was used, based on the numerical method of differentiation. In addition, cost-free NIST uncertainty calculation tool can be used online (https://uncertainty.nist.gov/)

The estimation of the total uncertainty associated to each measurement result was fundamental tool for sorting the main sources of measurement biases. Preliminary forecast of the uncertainty budgets was used as a strategy to ensure demonstrated traceability to a stated system of reference within less than 0.1 % expanded uncertainty (k=2).

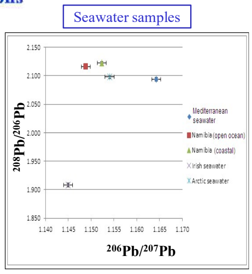
6. Applications

Namibian sediment samples

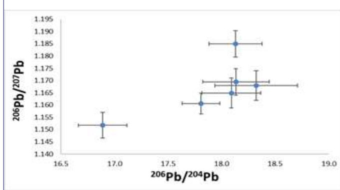


Three isotope representation of Pb Isotope ratios calculated for different sediment core samples (C1, C2, C3, C4 and C5) collected in Namibian coast. The results are plotted with some literature data showing that the core C5, collected close to a commercial harbor, has different isotopic signature, influenced by anthropogenic activities.

Seawater samples



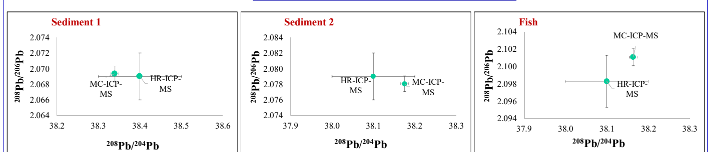
Three isotope representation of Pb Isotope ratios calculated seawater samples collected from different regions. The results were obtained by measuring fractions obtained from the automated system SeaFAST used for matrix separation and pre-concentration



Fish samples from French Polynesia

Three isotope representation of Pb Isotope ratios calculated for fish samples after resin separation achieved by applying the procedure c which uses Eichrom resin. For some of the samples the Hg content was more than 100 times higher than Pb content

Comparison with MC-ICP-MS results



8. Conclusion

A method for the determination of the Pb isotope ratio in marine samples is proposed. The analytical procedure includes matrix separation for biota samples in which the interfering Hg can reach very high concentrations.

The method proposed allows accurate Pb isotope ratio determination in challenging environmental samples such as marine sediments, biota and seawater samples with precision and reproducibility, which fits with the requirements of environmental pollution studies. These methods now open new fields of application in the studies related with the provenance of environmental pollution in marine environment.