
Plutonium, protactinium, uranium and thorium isotopes determination in environmental samples by SF ICP-MS

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Abstract. Alpha spectrometry is the most commonly used analytical tool for the determination of Pu, Am, Pa, U and Th long live radionuclides. Thermal ionization mass spectrometry (TIMS) and acceleration mass spectrometry (AMS) are also still considered as primary methods for the determination of their isotope ratios. Spectrometers with plasma ion sources now offer another efficient alternative method with the development of sector field inductively coupled plasma mass spectrometry (SF ICP-MS). This paper summarizes the development work performed and results obtained using this technique for the analysis of such radionuclides.

Isotopic ratios and ultra trace levels of man made radionuclides like ²³⁹, ²⁴⁰, ²⁴¹ plutonium but also naturally occurring species like ²³¹ protactinium, ²³⁴, ²³⁵, ²³⁸ uranium and ²³⁰, ²³² thorium were determined in different field samples and reference materials using a micro concentric nebulizer as an introduction system for the mass spectrometer. Prior to the mass spectrometric measurements these elements were isolated from major elements by different selective precipitations. In further steps, they were purified by anion exchange. Results of isotope ratios including plutonium ones are also discussed.

1. INTRODUCTION

Over the last decades there was an important increase in public concern regarding environmental issues, consequently studies about radioactive contamination of the environment have become a major subject for many scientific researches. Due to their high biological toxicity and their long half-lives, alpha emitters, both naturally occurring (U, Th, Pa) as well as from anthropogenic sources (Pu, Am), are of primary interest for such studies. The determination of these radionuclides is usually performed by alpha spectrometry, which requires complex chemical separation procedures prior to time-consuming measurement routines. ²⁴¹Am can also be measured by direct gamma spectrometry but in most environmental matrices its concentration is too low to permit direct measurement [1]. ²⁴¹Pu, the pure beta emitting nuclide of Pu, is usually performed by liquid scintillation [2].

In the early eighties, inductively coupled plasma mass spectrometers were available and ten years later, the development of spectrometers equipped with sector field as mass filters could offer another tool for the determination of sub pg.kg⁻¹ range of long-lived radionuclides in environmental samples [3, 4, 5].

Naturally occurring radionuclides of U and Th- series are often retained to study processes in the ocean because of their well-known sources [6]. In particular, the difference in particle reactivity of two radionuclides, ²³¹Pa (T_{1/2} = 32500 y) and ²³⁰Th (T_{1/2} = 75400 y), offers a powerful proxy in the sediment to determine the age of sediment layers and to find out whether the rain rate of particles to the seafloor and the oceanic circulation have changed with the changes from glacial to interglacial climate [7, 8]. For such investigations, the activity ratio of ²³⁰Th/²³¹Pa must be determined with a precision better than 1.5 %. Until recently ²³¹Pa was still measured by alpha spectrometry (by counting its daughter ²²⁷Th), which requires large amounts of samples (1-2 g) to obtain a precision of only 5-10 %.

In this paper, analytical procedures, developed in our laboratory prior to Pu, Am, U, Th, Pa determination in different environmental matrices by ICP-MS, are widely described. Accuracy of obtained results are discussed; particular attention is given to Pu isotope ratios.

2. EXPERIMENTAL SECTION

2.1 Instrumentation

The SF ICP-MS is an axiom single collector (VG Elemental, Winsford, Cheshire, UK). This mass spectrometer is equipped with a double-focusing magnetic sector mass analyzer of forward geometry. For sample introduction, a PFA microconcentric nebulizer allowing the uptake of $50 \mu\text{L}\cdot\text{min}^{-1}$ of sample was used. The mass spectrometer is installed in a class M 4.5 clean room.

All ICP-MS data were acquired by E-scanning in low resolution mode ($m/\Delta m = 400$). Sequential measurements at the different masses of interest were carried out in the peak-jumping mode. Isotope ratio bias is determined using the uranium reference material U-030 and this correction is applied to all isotope ratio measurements for systematic errors arising from mass discrimination. It was assumed that mass bias is the same for plutonium and uranium, thorium and protactinium. At low count rates, the signal loss due to detector dead time is not significant; consequently no dead time correction was necessary.

The different isotope concentrations were calculated by means of the isotope dilution mass spectrometry standard equation [9, 10, 11].

2.2 Chemical preparation

2.2.1 Pu analytical procedure

1 to 100 g of ash samples were added a known amount of the ^{242}Pu spike solution. The samples were previously ached at 500°C to decompose the organic matter. The ash samples were leached in HNO_3/HCl for at least eight hours. This leaching was repeated twice, a third leaching was performed again with 8 M HNO_3 . All the filtrates were combined and the leach solution was evaporated to dryness. After addition of a solution of saturated oxalic acid, Ca oxalate was precipitated at pH 1.5 by adding ammonia to extract Pu and Am. The Ca oxalate was ached to obtain Ca carbonate that was later dissolved into a few milliliters of concentrated HNO_3 . All actinides were concentrated by coprecipitation with ferric hydroxide at pH 8.5. The precipitate was dissolved, and then a second Ca oxalate coprecipitation was carried out. This Calcium oxalate was dissolved and loaded onto a 4 mL bed height anion column in order to separate plutonium and americium.

In order to further purify Pu from remaining U and Fe traces, the sample was loaded again onto another anionic micro column (2 mL bed height) [12]. The sample was finally gently evaporated to dryness and dissolved in 1 to 3 mL of 2 % m/m HNO_3 before ICP-MS measurement. It is important to have a final plutonium fraction as free as possible of uranium to avoid peak overlap on ^{239}Pu due to uranium hydride specie ($^{238}\text{U}^1\text{H}^+$) [4, 13].

2.2.2 U, Th, Pa analytical procedure

The chemical protocol for the purification of U and Th long live radionuclides from marine sediments is adapted from the protocol developed by Fleisher and Anderson [14]. 300 mg of dried sediment were spiked with a known amount of ^{236}U (ca. 2 ng), ^{233}Pa (ca. 5 pg) and ^{229}Th (ca. 30 pg) spikes. A few ml of concentrated HCl were added to eliminate carbonates. When the solution was dried to a semi-solid mixture, 10 ml of HClO_4 and a few ml of concentrated HNO_3 were added. When HClO_4 was fuming, the beakers were covered with a Teflon lid so that the perchloric acid refluxed during about one half hour. Then a few ml of concentrated HF were added to the hot solution. This cycle, refluxing - followed by HF addition, was repeated 3 times, until a complete dissolution of the sediment. The refluxing step

allows the spike-sample equilibration and a complete mineralization of the organic matter without the formation of fluoride complexes. The mineralization was achieved by washing several times the beaker walls with concentrated HNO₃. After complete dissolution and evaporation to nearly dryness, the sample was dissolved in HCl. An aliquot, corresponding to nearly 0.3 mg of sediment, was used for direct measurements of ²³⁸U and ²³²Th, after addition of ²³⁶U (*ca.* 2 ng) and ²²⁹Th (*ca.* 30 pg) without any further purification.

The following purification steps of ²³¹Pa, ²³⁰Th and ²³⁴U were performed on the remaining solution. By adding NH₄OH to pH 7-8, Th, U and Pa were co-precipitated with iron hydroxide. The precipitates were cleaned by successive dissolutions and reprecipitations, and then dissolved with concentrated HCl in order to obtain an 8M HCl solution. Th and U were separated from Pa by anion exchange. Under 8 M HCl condition, Th passes through the column, whereas U and Pa are adsorbed. Pa was then eluted with conc. HCl – 0.13 N HF. To further purify Pa, the Pa elutes were dried and passed through a silica gel resin, fixation and desorption of Pa were followed by gamma counting. The final Pa solutions were evaporated in a Teflon beaker, dissolved again into a 1 % HNO₃-HF mixture. U and Th fractions were combined for a further purification through a HNO₃ anion column. The U and Th were eluted in a Teflon beaker, evaporated and dissolved into a 1 % HNO₃-conc HF mixture.

All final fractions were filtered through 0.2 µm filters to eliminate potential remaining particles before any SF ICP-MS measurement. For each analysis batch, an overall procedural blank was also carried out.

3. RESULTS

3.1 Pu concentration and isotope ratios in environmental samples

Examples of Pu concentration and ²⁴⁰Pu/²³⁹Pu isotope ratios determined in different reference materials and field samples are given in table 1.

The experimental values achieved for the reference materials in our laboratory are in good agreement with the IAEA 95 % confidence limits.

For field samples collected in different French nuclear sites, the values obtained by ICP-MS were compared to the values obtained by alpha spectrometry. Both series of values show good agreement.

As far as the ²⁴⁰Pu/²³⁹Pu ratios are concerned, very few values can be found in the literature because most of related studies are carried out by alpha spectrometry. The ratio determined in our laboratory for the IAEA-134 cockle flesh (0.219 ± 0.006 and 0.207 ± 0.002) was compared to the value published by Lee et al (0.212 ± 0.008) [15]. Both values were found to be in good agreement.

All the isotope ratios determined in the field samples collected in France are higher than the global fallout ²⁴⁰Pu/²³⁹Pu ratio (0.176 ± 0.014) [16, 17].

3.2 ²³¹Pa/²³⁰Th activity ratios in marine sediments of Cederawasi Bay (Indonesian Archipelago)

Naturally-occurring radionuclides are often used to study processes in the ocean because of their well-known sources. Activity ratios of two radionuclides, ²³¹Pa and ²³⁰Th, have been extensively used to study boundary scavenging. Indeed the basin-wide distribution of ²³¹Pa seems to be controlled by removal at ocean margins, whereas ²³⁰Th input to the sediment is mainly linked to the local flux of particles. This difference is caused by differences in reactivity between these two elements. As the production rate ratio of ²³¹Pa to ²³⁰Th in the water column is constant, 0.093, the departure of this value is a key to estimate scavenging intensity. Nevertheless, a major limitation of the use of ²³¹Pa/²³⁰Th is the low level of ²³¹Pa usually encountered in marine sediments. The recent development of SF ICP-MS offers an interesting opportunity to measure accurately and precisely this radionuclide on small samples. This motivated the present attempt to measure ²³¹Pa/²³⁰Th activity ratios at LMRE.

The accuracy and precision of the measurement of naturally occurring radionuclides like uranium was previously assessed at LMRE by participating to different interlaboratories calibration exercises [18, 19].

For this development, we used surface sediments collected along a depth transect off Cederawasi Bay (Wepama cruise, May 2001). ^{231}Pa activity measured in each transect is expressed in disintegration per minute per gram of sample ($\text{dpm}\cdot\text{g}^{-1}$) in table 2. Two different sub-samples of the transect were analyzed separately, one by alpha spectrometry (italic characters) and the other one by SF ICP-MS. ICP-MS (bold characters).

Although sample sizes were smaller for ICP-MS than for alpha spectrometry, all ^{231}Pa and Th results show relative good agreement. Agreement could be further improved with longer ICP-MS acquisition times and complete cross calibration of the faraday cup and electron multiplier versus the masses. As a matter of fact, the Axiom SC spectrometer allows the detection of most abundant ions on the faraday cup and minor isotopes on the electron multiplier.

The treatment of a few hundred milligrams of sediment for SF ICP-MS allows a much more easier chemical preparation and lower procedural blanks as less reagents are necessary.

In this first attempt only the 1 and 7 cm layers sub-samples were analyzed, additional samples should be treated in order to set up a complete oceanographic study.

4. CONCLUSION

In addition to the accurate and precise activity of plutonium isotopes (^{239}Pu , ^{240}Pu , ^{241}Pu) in environmental samples, SF ICP-MS measurements allow to give further information by determining also the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio. This information can also help in identifying the source of the Pu introduction in the environment.

Data determined in this experiment show that ^{231}Pa and ^{230}Th in marine sediments can be precisely and accurately measured by SF ICP-MS. In this particular application field, the next step of this work will be to analyze more samples by SF ICP-MS in order to draw a complete conclusion concerning the oceanographic study itself.

Table 1. $^{239+240}\text{Pu}$ and ^{241}Pu activity in environmental samples obtained by SF ICP-M, expanded uncertainty $k=2$. * Expected values are IAEA 95 % confidence levels for reference materials, or values previously determined by alpha spectrometry for the field samples.

Sample ID	Sample size (kg)	^{239}Pu ($\text{mBq}\cdot\text{kg}^{-1}$)	^{240}Pu ($\text{mBq}\cdot\text{kg}^{-1}$)	$^{239+240}\text{Pu}$ ($\text{mBq}\cdot\text{kg}^{-1}$)	$^{239+240}\text{Pu}$ Expected value * ($\text{mBq}\cdot\text{kg}^{-1}$)	$(^{240}\text{Pu}/^{239}\text{Pu})$ (atom ratio)	^{241}Pu ($\text{Bq}\cdot\text{kg}^{-1}$)	^{241}Pu expected value * ($\text{Bq}\cdot\text{kg}^{-1}$)
Reference materials								
IAEA 134	0.004	7862 ± 426	6325 ± 472	14187 ± 636	13800-16200	0.219 ± 0.120		
IAEA 134	0.004	8882 ± 288	6768 ± 220	15650 ± 362	13800-16200	0.207 ± 0.004		
IAEA soil 6	0.011	585 ± 22	419 ± 20	1004 ± 30	962-1110	0.196 ± 0.004		
IAEA 375	0.121	129 ± 12	129 ± 14	258 ± 19	260-340	0.271 ± 0.006		
IAEA 367	0.005	16500 ± 3400	18600 ± 3800	35100 ± 5099	34400-39800	0.306 ± 0.002	166 ± 17	154-190
IAEA 367	0.003	17000 ± 2000	19100 ± 2000	36200 ± 2828	34400-39800	0.305 ± 0.004	198 ± 10	154-190
Field samples								
SOIL0031V	0.013	124 ± 4	86 ± 4	211 ± 12	219 ± 8	0.206 ± 0.020		
PRAIR0102B	0.039	12.7 ± 1.9	10.5 ± 1.5	23 ± 5	21.1 ± 2.6	0.223 ± 0.008		
FUC0102O	0.046	56.5 ± 5.5	54.8 ± 5.4	111.3 ± 15.4	119 ± 6	0.264 ± 0.010		
SED0014O	0.021	869 ± 68	729 ± 59	1597 ± 180	1476 ± 245	0.239 ± 0.005	27955 ± 3049	
SED0014M	0.100	793 ± 42	676 ± 38	1469 ± 114	1476 ± 245	0.242 ± 0.005	26307 ± 1851	

Table 2. ^{238}U , ^{232}Th , ^{230}Th , ^{231}Pa in surface marine sediment (layers 1 and 7 cm, core KTB05, 0°48.31S, 134°38.79E, Cederawasi Bay, Indonesian Archipelago): comparison of values obtained by SF-ICP-MS (bold characters, expanded uncertainty $k=2$) and by obtained by alpha spectrometry (italic characters, 2 sigma error).

Sample ID	Sample Size (g)	^{238}U (dpm.g ⁻¹)	^{232}Th (dpm.g ⁻¹)	^{230}Th (dpm.g ⁻¹)	^{231}Pa (dpm.g ⁻¹)
WEPAMA 5-1	0.3071	0.774 ± 0.031	1.29 ± 0.05	2.29 ± 0.09	0.155 ± 0.001
	1.9	<i>0.877 ± 0.046</i>	<i>1.28 ± 0.07</i>	<i>1.80 ± 0.09</i>	<i>0.13 ± 0.07</i>
WEPAMA 5-7	0.3052	0.796 ± 0.030	1.36 ± 0.05	2.36 ± 0.09	0.140 ± 0.001
	1.7	<i>0.84 ± 0.05</i>	<i>1.30 ± 0.09</i>	<i>1.80 ± 0.110</i>	<i>0.13 ± 0.07</i>

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