PU and NP analysis of soil and sediment samples with ICP-MS

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ABSTRACT

A method to analyse Pu and Np was optimised to achieve low detection limits and high sample throughput. Soil and sediment samples were ashed and digested with a borate fusion. After dissolving the melt in nitric acid, Pu and Np were separated on a TEVA extraction chromatography column. It was measured with a sector field ICP-MS. Detection limits in soils and sediments as low as 1 × 10^{-15} g/g for Pu and Np were achieved. The method was applied to reference materials, soil profiles from Switzerland and sediment samples from the river Yenisei (RU), where radioactive nuclides have been discharged.

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1. Introduction

Plutonium and neptunium have been introduced to the environment from several different sources, such as activities related to nuclear weapons explosions, transport accidents and accidental or authorised discharges from nuclear facilities. Disposal of high level radioactive wastes and “dirty-bomb” scenarios is further possible sources for releases of actinides to the environment. It was estimated that 2.8 t Plutonium (UNSCEAR, 2000) and 1.5 t Neptunium (Lindahl, 2003 and references therein) have been injected into the atmosphere due to nuclear weapons testing. Based on measurements of 90Sr, global fallout was estimated to have deposited to 76% on the northern hemisphere (Ayronov et al., 2005a, b) was optimised to achieve lower detection limits for Pu in environmental samples were achieved with mass spectrometric measurements. Furthermore, due to the possibility of measuring isotopic ratios, information about the origin of the Pu can be achieved. A recent review of Pu analysis with ICP-MS is given by Kim et al. (2007). In this work, the method to measure Pu and Np (Ayyonov et al., 2005a, b) optimised to achieve lower detection limits and high sample throughput. By the use of an Apex introduction system connected to an ACM desolvator, detection limits for Pu and Np as low as 0.002 Bq/kg and 0.03 mBq/kg could be achieved, respectively. The method was verified by analysing soil and sediment reference material. The developed method was applied for samples from two projects. Soil samples were taken in the frame of in situ gamma spectrometry intercomparisons from the radioactivity monitoring program in Switzerland (Estier et al., 2003). Sediment samples originated from the river Yenisei, where radionuclides from a nuclear facility have been discharged.

2. Experimental

2.1. Instrumentation and data acquisition

Mass spectrometric measurements were performed using a double-focusing sector-field ICP-MS (Element2, Finnigan MAT, Bremen, Germany). Aqueous solutions were introduced into the ICP-MS with a SC-2 autosampler, an Apex nebulising system connected to an ACM desolvator and a self-aspirating PFA-ST-nebuliser (all from Elemental Scientific Incorporation, Omaha, USA). All measurements were performed in the low resolution mode (m/Δm = 300). In this configuration the sensitivity for U was about 9 × 10^{6} s^{-1} per ng/ml U-238 compared to a sensitivity of about 1 × 10^{6} s^{-1} per ng/ml U-238 with the advanced spray chamber (Finnigan). The electronic background signal was measured on mass 220 amu and was less than 0.2 s^{-1}. Oxide rates for UO and CeO lower than 0.3% were achieved. An uptake time of 1 min was enough to get stable signals. The total acquisition time per sample was 5 min. U and Th interferencies due to hydride generation and tailing were corrected mathematically. The interference correction factors were determined with 100 ng/ml U and Th standard solutions. Typical correction factors for the masses 237, 239, 240 were 6.4 × 10^{-6}, 1.2 × 10^{-5}, 1.8 × 10^{-6} for 238U and 1.4 × 10^{-6}, 3.1 × 10^{-8}, 1.2 × 10^{-8} for 232Th. Pu isotope concentrations were calculated from the signal of the Pu tracer. Pu yields were measured with gamma spectrometry on high purity germanium gamma detectors from Canberra. Efficiency calibrations were made with a standard solution of 243Am (in radiological equilibrium with 239Np). 239Np was measured on the energies 106, 228, 277, 316 and 334 keV.

2.2. Standards and reagents

A 242Pu standard solution (Joint Research Centre, B) and a 243Am standard solution (AEA Technology, UK) were used as...
tracers. For determinations of yields and separation factors, standard solutions of U, In (Alfa Aesar) and Th (SPEX, USA) were used. The reagents used for sample preparation were deionised water from a Milli-Q system (Barnstead), 65% nitric acid p.a., subboiled on a quartz subboiling apparatus, 30% hydrochloric acid suprapur, 40% hydrofluoric acid suprapur, Ammonium iron (II) sulphate hexahydrate pro analyti (all from Merck), polyethylene glycol PEG-2000 (Fluka) and LiBO2/Li2BaO2 (80%/20%) Spectro Flux 100 B (Alpha Aesar).

2.3. Samples

The method was validated with three reference soils (IAEA-326, IAEA-327, IAEA-soil6) and four reference sediments (IAEA-135, IAEA-300, IAEA-367, IAEA-368).

Two soil profiles were taken in the southern part of Switzerland. One was taken 2003 at Coglio (Valle Maggia) and the other one 2005 at Stallone (airport Locarno). A U-shaped stainless steal device with an inner cross section of 10 × 10 cm was driven in the soil with a hammer. The profiles were sliced with a thickness of 5 cm and packed into plastic bags.

Sediment samples originated from the river Yenisei, one of the world's largest rivers, 3000 km long, flowing north into the Kara Sea. The Mining and Chemical Combine (MCC) is situated on the right bank of the Yenisei river, 60 km downstream of the city of Krasnoyarsk. The Combine has been producing weapon-grade plutonium in uranium–graphite reactors since 1958, when the first of three reactors was started up. The two direct cooling reactors were shut down in 1992. One of the reactors is still running. The spent uranium fuel is reprocessed at the radiochemical plant to separate uranium, plutonium and fission products. Traces of the discharges of artificial radionuclides from this facility can be found in water and sediments up to 2000 km downstream the MCC (Bolsunovsky et al., 2007). Sediment profiles from the river Yenisei were collected from 1999 to 2005 at different sampling positions up to 1500 km downstream from Krasnoyarsk. The profiles were taken with a cylindrical corer at positions where the water was shallow and the speed of the water flow was reduced by systems of islands. The inner diameter of the steel tube was 12 cm. The sediments were sliced immediately and packed into plastic bags. The results of the Pu and Np measurements are given for the sediment core 1801 and core 4101, taken 276 and 594 km downstream Krasnoyarsk.

2.4. Sample preparation

Samples were air dried and carefully mixed. About 50 g of a sample was ashed at a temperature of 520 °C. 30 pg of the 242Pu tracer was added to 5 g of the ashed sample and mixed with 7 g of the lithium–borate fluxing agent. For 237Np analysis, 16 Bq of the 243Am, which is in radioactive equilibrium with 239Np, was added as a tracer. Fusions were performed in 50 ml Pt/Au (95%/5%) crucibles in a muffle furnace at 1100 °C. The crucibles were left in the furnace for 15 min with periodical swirling. The hot melt was poured in a 250 ml glass beaker, containing 175 ml 4.5 M HNO3, 1 ml 0.1 M PEG was added to precipitate the silicates while dissolving the melt under stirring at 40 °C. The silicate precipitation was removed with cellulose filter papers (Schleicher & Schüll). 3 g Ammonium iron (II) sulphate hexahydrate was added to the filtrate and separated on a 2 ml TEVA Spec (Eichrom) column. The separation procedure for the separation of Pu was as follows. The TEVA column was rinsed with 10 ml 0.2% HNO3/0.2% HF/0.01 mM Fe(II) and conditioned with 10 ml 3 M HNO3/0.1 mM Fe(II). The filtrate was loaded to the column. The column was rinsed with 50 ml 6 M HCl and 100 ml 3 M HNO3/0.1 mM Fe(II). Pu was eluted with 20 ml 0.2% HNO3/0.2% HF/0.01 mM Fe(II).

3. Results and discussion

3.1. Yields, separation factors and detection limits

The fusion technique to dissolve soil samples has been proved to be a very reliable digestion method for hundreds of soil samples (UNEP, 2003). As the 242Pu and 239Np tracer are added before the fusion, isotopic equilibrium between analyte and tracer can be assumed, which was proved by measuring reference material. The dissolved Pu is in the oxidation state Pu(IV) and is retained to almost 100% on the TEVA column. Np is reduced to Np(IV) with Fe(II) before the separations. It was recognised that an improved elution of Pu from the column was achieved when Fe(II) was added to the filtrate before the separation. A reason for this could be the Pu to elute as Pu(III) instead of Pu(IV). The Pu and Np yields for the separation were in the range of 50–80%.

Separation factors for U up to 20,000 and for Th up to 2000 could be achieved. Detection limits were calculated from the interferences due to hydride generation and U-, Th-tailing. Detection limits for 239Pu, 240Pu, 241Pu and 237Np in soil and sediments were about 10−6 g/g, which corresponds to 0.002, 0.02, 0.02 and 1.8 mBq/kg, respectively.

Table 2

Analytical results for 237Np.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pu (mBq/kg)</th>
<th>Np (mBq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA-326</td>
<td>1.2 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>IAEA-327</td>
<td>1.2 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>IAEA-soil6</td>
<td>3.4 ± 1.8</td>
<td></td>
</tr>
<tr>
<td>IAEA-300</td>
<td>2.5 ± 1.3</td>
<td></td>
</tr>
<tr>
<td>IAEA-135</td>
<td>85 ± 68</td>
<td>883 ± 18</td>
</tr>
<tr>
<td>IAEA-367</td>
<td>420 ± 3.4</td>
<td>390 ± 210</td>
</tr>
<tr>
<td>IAEA-368</td>
<td>2.7 ± 0.2</td>
<td>13 ± 3</td>
</tr>
</tbody>
</table>

The IAEA reported only information values for the sediments, as only one laboratory analysed 237Np in the proficiency test. No results were reported for the soil samples.

Table 1

Analytical results for 239Pu, 240Pu and their atom ratios compared to the IAEA-reference values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>This work</th>
<th>IAEA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>239Pu (Bq/kg)</td>
<td>240Pu (Bq/kg)</td>
</tr>
<tr>
<td>IAEA-326</td>
<td>0.28 ± 0.01</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>IAEA-327</td>
<td>0.35 ± 0.02</td>
<td>0.25 ± 0.02</td>
</tr>
<tr>
<td>IAEA-soil6</td>
<td>0.64 ± 0.02</td>
<td>0.44 ± 0.02</td>
</tr>
<tr>
<td>IAEA-135</td>
<td>121 ± 4</td>
<td>90 ± 3</td>
</tr>
<tr>
<td>IAEA-300</td>
<td>2.17 ± 0.08</td>
<td>1.45 ± 0.04</td>
</tr>
</tbody>
</table>
0.008, 4 Bq/kg and 0.03 mBq/kg, respectively, depending on the U and Th concentration of the sample, separation quality, yield and the performance of the ICP-MS. $^{238}$Pu cannot be measured because of the $^{238}$U interference.

### 3.2. Reference material

In Table 1, the Pu measurements are compared with the IAEA referenced values. Only values for the sum of $^{239}$Pu and $^{240}$Pu were reported by the IAEA. The sum agreed well with the IAEA referenced values. $^{240}$Pu/$^{239}$Pu atom ratios agreed well with values found by other authors (Nygren et al., 2003; Muramatsu et al., 2001; Boulyga et al., 2003).
In Table 2, the $^{237}$Np measurements are compared with the IAEA values. The IAEA reported only information values for the sediments, as only one laboratory analysed $^{237}$Np in the proficiency test. For the analysis of the sediment samples IAEA-135, -367 and -368, $^{239}$Np was used as a tracer for the Np yield. Good agreement was only found for the sediment IAEA-135, which showed the highest $^{237}$Np concentrations. For the sediment material IAEA-367 and -368 the analysed $^{237}$Np concentrations were 9 and 5 times lower than the information values reported by the IAEA.

For the soil samples no values were reported by the IAEA. The $^{237}$Np concentrations in the soil samples IAEA-326, -327 and -soil-6 were estimated in this work from the Pu measurements. The Np yield was estimated from the measurements of other samples to be equal to 75% of the Pu yield, with an error of 50%. The reason for the lower yield of Np is that some of the Np is not in the Np(IV) valence state. For more precise measurements, the analysis would have to be repeated with $^{239}$Np as a yield tracer.
3.3. Soil samples

Figs. 1 and 2 show the Pu measurements for the two soil profiles. More than 70% of the Pu could be found in the sediment layers from 0 to 10 cm. Fig. 1 shows the expected vertical distribution of Pu, when deposited Pu is washed into the soil. The atomic ratios \( \frac{^{240}\text{Pu}}{^{239}\text{Pu}} \) in the upper most layer were 0.19 ± 0.02 for both profiles. The uncertainties of the Pu measurements increased for lower Pu concentrations.

Figs. 3 and 4 show the \( ^{237}\text{Np} \) measurements for the two soil profiles. The Np yield was measured with the \( ^{239}\text{Np} \) tracer for the profile in Fig. 4. For the profile in Fig. 3, the Np yield was assumed to be equal to 80% of the Pu yield. For more precise measurements, the analysis would have to be repeated with \( ^{239}\text{Np} \) as a yield tracer. \( ^{237}\text{Np} \) showed to be more mobile as only 40% and 50% of the \( ^{237}\text{Np} \) could be found in the sediment layers from 0 to 10 cm. The atomic ratio for \( ^{237}\text{Np}/^{239}\text{Pu} \) of the total deposited Np and Pu in Fig. 4 was 0.50 ± 0.03, which agrees well with the ratio.
0.48 ± 0.07 from the literature (Lindahl, 2003 and references therein). For the profile Stallone 2005, the total deposited Pu and Np was calculated to 70 and 0.3 Bq/m², respectively. Assuming that 75% of the Pu and Np from atmospheric atomic bomb testing had deposited evenly on the northern hemisphere, the global fallout of Pu and Np can be estimated to 10 t Pu and 4 t Np.

3.4. Sediment samples

Figs. 5–7 show the Pu and Np measurements of the sediment profile, taken 276 km downstream Krasnoyarsk. The $^{239}$Pu deposited in the sediment from Fig. 5 was calculated to 2816 Bq/m², about 94 times higher than the deposited $^{239}$Pu in the soil at Thukansk. Atomic ratios $^{240}$Pu/$^{239}$Pu < 0.07, typical for weapons
The Np yield was assumed to be 75% of the Pu yield. The atomic ratios of Pu seem to be influenced by global fallout Pu. 

grade Pu, were found for most of the layers. In some of the layers, atomic ratios 240Pu/239Pu up to 0.4 were found. For three layers, another fusion was made (Exp 2). The isotope ratios were significantly different, which could be a hint for hot particles. The Np yield was measured with the 239Np tracer. The atomic ratio of the total 237Np/239Pu was 0.12 ± 0.01.

Figs. 8–10 show the Pu and Np measurements of the sediment profile, taken 594 km downstream Krasnoyarsk. The 239Pu deposited in the sediment from Fig. 8 was calculated to 553 Bq/m², about 18 times higher than the deposited 239Pu in the soil at Thurukansk. Only for some layers with higher Pu concentrations atomic ratios 240Pu/239Pu < 0.07 were found. Most of the layers showed atomic ratios 240Pu/239Pu between 0.07 and 0.18. The atomic ratios of Pu seem to be influenced by global fallout Pu. The Np yield was assumed to be 75% of the Pu yield. The atomic ratio of the total 237Np/239Pu was estimated to 0.13.

Fig. 11 shows the total deposited 239Pu, 237Np and 137Cs per square meter for different distances from the MCC. 137Cs was deposited in the sediment from Fig. 8 was calculated to 553 Bq/m², about 18 times higher than the deposited 239Pu in the soil at Thurukansk. Only for some layers with higher Pu concentrations atomic ratios 240Pu/239Pu < 0.07 were found. Most of the layers showed atomic ratios 240Pu/239Pu between 0.07 and 0.18. The atomic ratios of Pu seem to be influenced by global fallout Pu. The Np yield was assumed to be 75% of the Pu yield. The atomic ratio of the total 237Np/239Pu was estimated to 0.13.

Fig. 11 shows the total deposited 239Pu, 237Np and 137Cs per square meter for different distances from the MCC. 137Cs was measured with gamma spectrometry at the university of applied sciences, Ravensburg–Weingarten (Spasova, 2003). An exponential fit show that the total deposited activity is decreasing by a factor of ten for a distance of 700–900 km downstream the discharge site.

4. Conclusion

With the method described, detection limits in soils and sediments as low as 1 × 10⁻¹⁵ g/g for Pu and Np were achieved. The sum of 239Pu and 240Pu in reference materials agreed well with the certified values. Furthermore, the isotope ratios agreed well with values from the literature. The 237Np results could only be compared to the results from one laboratory for three IAEA sediment samples. Good agreement was only found for the sediment sample with the highest 237Np concentrations. Pu and Np could be analysed down to 50 cm in soil profiles from Switzerland with a typical isotope ratio for global fallout Pu, whereas in the Yenisei samples, Pu with an isotopic composition of weapons grade Pu could be found. A first estimation of the migration of Pu and Np showed that the total deposited activity is decreasing by a factor of ten for a distance of 700–900 km downstream the MCC.

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References


