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# A combined method for the determination of the isotopic vector of plutonium isotopes in environmental samples

**E. Hrnecek,[1]* R. Jakopič,[2] A. Wallner,[3] P. Steier[3]**

[1] *ARC Seibersdorf Research GmbH, 2444 Seibersdorf, Austria*
[2] *Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*
[3] *Institut für Isotopenforschung und Kernphysik der Universität Wien, VERA Laboratory, Währinger Str. 17, 1090 Vienna, Austria*

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A combination of alpha-spectrometry, liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS) was used for the determination of plutonium isotopes. $^{238}$Pu and $^{239+240}$Pu were measured by alpha-spectrometry after separation of Pu by anion-exchange using $^{236}$Pu tracer as recovery monitor. After alpha-measurement, one part of the sample was dissolved for determining $^{241}$Pu by LSC. Another part was used for the measurement of the $^{240}$Pu/$^{239}$Pu atom ratio by AMS at VERA. Thus, it was possible to obtain complete information on the Pu isotopic composition of the samples. This method was applied to environmental reference samples and samples contaminated from nuclear reprocessing.

## Introduction

The measurement of plutonium isotopic composition in environmental samples can give valuable information on its sources. Isotope ratios found in environmental samples are known to vary with reactor type, nuclear fuel burn-up, source and history of discharges from reprocessing facilities[1] and, for fallout from nuclear weapons, from weapons type and yield.[2] For global weapons tests fall-out, the mean $^{240}$Pu/$^{239}$Pu and $^{241}$Pu/$^{239}$Pu mass ratios are $0.176\pm0.014$ and $0.0086\pm0.0017$, respectively,[3] although annual variations in the $^{240}$Pu/$^{239}$Pu due to the influence of different atmospheric test series can be found.[4] Weapons-grade plutonium can be characterized by the $^{240}$Pu/$^{239}$Pu ratio $<0.07$, whereas in plutonium from nuclear reactors, ratios of 0.4 and higher can be expected.[5] For weapons tests sites, plutonium isotope ratios have been shown to vary with weapon type and yield.[6–8] The determination of plutonium isotope ratios is a valuable tool for nuclear safeguards,[9] astrophysical applications[10,11] and also in nuclear forensic applications.[12]

Method for analysis of environmental plutonium is usually alpha-spectrometry after chemical separation of Pu for the determination of $^{238}$Pu and $^{239(40)}$Pu. For the determination of $^{241}$Pu, liquid scintillation counting (LSC) of the separated plutonium can be used in combination with alpha-spectrometry for the determination of the total alpha-activity.[13] A direct LSC measurement of the alpha-spectrometry sources is possible for electrodeposited sources[14] and micro-precipitated sources.[15,16]

For the determination of $^{240}$Pu/$^{239}$Pu mass spectrometry methods such as ICP-MS and AMS can be used. AMS achieves the best background suppression, which can be attributed to the destruction of molecular isobars and to the high ion energy in the spectrometer.

The question whether isotope mass spectrometry or decay counting is the better option has to be answered for every isotope independently.[17] Generally, for short lived species ($^{236}$Pu, $^{241}$Pu) decay counting will yield better results, whereas mass spectrometry is preferred for long-lived ones ($^{242}$Pu, $^{244}$Pu). However, technical details like decay spectra or interference by isobars can influence that choice. A point important to consider will be also the much larger effort involved in AMS, which requires a full-sized particle accelerator.

## Experimental

### *Materials*

Certified reference materials IAEA 135, IAEA 300, IAEA 326, IAEA 327, IAEA 375 and IAEA Soil-6 were obtained from the International Atomic Energy Agency (Vienna, Austria). The certified reference materials NIST SRM 4350b, NIST SRM 4354, and NIST SRM 4357 were obtained from the National Institute of Standards and Technology (Gaithersburg, USA). Additional samples influenced from discharges from nuclear installations were: a sediment from the tidal zone of the river Ribble, Lancashire, UK, which is influenced both by tidal borne radionuclides originating from Sellafield and by manufacture of fuel elements at Springfield upstream (Ribble Sediment) and an intertidal sediment from the Cumbrian coastline, collected in 1997 for an international characterization[18] (Cumbrian Sediment).

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* Present address: European Commission, Joint Research Centre,
Institute for Transuranium Elements,
P.O. Box 2340, 76125 Karlsruhe, Germany.
E-mail: Erich.Hrnecek@ec.europa.eu

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*Springer, Dordrecht*

### *Sample pre-treatment*

IAEA reference materials and sediment samples were dryed to a constant weight at 105 °C, NIST reference materials at 40 °C (the different drying temperatures were chosen with respect to the values given in the reference sheets). After drying the samples were ashed for 15 hours at 450 °C in an electric muffle furnace. 5–20 g of ash was taken for the analysis.

### *Separation of plutonium*

After a known amount of $^{236}$Pu tracer was added as a recovery monitor, Pu in a sample was leached with 200 ml 8M $HNO_3$ for 3 hours. After filtration (Blue ribbon filter, Whatman plc, UK), the filtrate was evaporated to dryness. The residue was dissolved in 20 ml 1M $HNO_3$. Furthermore, 100 mg $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ was added into the solution for reducing Pu to the trivalent state. Then the solution was adjusted to 8M $HNO_3$ by addition of 20 ml 65% $HNO_3$ and plutonium was oxidized to the tetravalent oxidation state by addition of 0.5 g $NaNO_2$. After boiling to destroy the excess nitrous acid, the solution was loaded on a column containing 10 g Biorad AG 1X8 resin, 100–200 mesh preconditioned with 2×25 ml 8M $HNO_3$. The column was washed with 2×15 ml 8M $HNO_3$ to remove uranium and matrix elements. The loading and washing effluent were used for the analysis of americium. To remove thorium from the column 2×25 ml 32% HCl was used. Finally, Pu(III) was eluted from the column with 50 ml 0.1M $NH_4I$–9M HCl. The Pu strip solution was evaporated to dryness and fumed several times with 5 ml 65% $HNO_3$ and 2 ml 30% $H_2O_2$.

### *Preparation of alpha-spectrometry samples*

The residue was dissolved in 20 ml 1M $HNO_3$ and 100 mg $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ were added to reduce Pu to Pu(III). Then the Pu(III) was oxidized to Pu(IV) by addition of 1 ml of 25% $NaNO_2$ solution. After addition of 100 µl of 1 mg/ml $Nd^{3+}$ solution, Pu was co-precipitated with $NdF_3$ by adding 5 ml 40% HF and leaving the solution at room temperature for 1 hour. Finally, the $NdF_3$ solution was filtered membrane filter (NC 10, Schleicher & Schuell, Germany, pore size 0.1 µm). The filter was washed with 2×2 ml 4% HF and 2×2 ml deionized water, dried and mounted for alpha-activity measurement.

### *Alpha-spectrometry*

For the alpha-spectrometry measurements, low background ion-implanted silicon detectors (Ultra-AS, Ortec) with an active area of 450 mm² were used. All samples were placed at a distance of 3 mm from the detector at $5 \cdot 10^{-3}$ mbar pressure in the measurement chamber. The counting time was between 80000 and 320000 seconds. For evaluation of the spectra, Genie 2000 2.1 software (Canberra) was used.

After the completion of alpha-spectrometry measurements, the filters were divided into two parts: one part was used for LSC measurements for $^{241}$Pu, the second part was used for AMS isotopic ratios measurements. Samples for LSC were prepared by directly dissolving a part of the membrane filter in a suitable LSC cocktail.[16] In the present work, a part of the filter was dissolved in 6 ml Filter-count cocktail (PerkinElmer Inc., USA) and 12 ml Ultima Gold LLT (PerkinElmer Inc., USA) was added for LSC measurement.

### *Liquid scintillation counting*

For LSC measurements, a Quantulus 1220 (PerkinElmer Inc., USA) low-level LS counter equipped with a pulse-shape analyzer (PSA) was used for determining the $^{241}$Pu content of the sample, together with total alpha-activity for normalization. A blank was prepared from half a membrane filter and adding 6 ml Filter count and 12 ml Ultima Gold LLT cocktail. Each sample was measured for 600 minutes using alpha-beta discrimination with PSA 90 to determine the total alpha-activity from the dissolved filter part. For evaluation of alpha-activity, a region of interest (ROI) from channel 500–800 was used. The alpha-counting efficiency for these instrument settings could be shown to be 100% within measurement uncertainty (±0.9%) by measuring a blank sample with 100 µl certified $^{242}$Pu solution (NIST SRM 4334G, National Institute for Standards and Technology, USA) added. For determination of $^{241}$Pu, samples were measured for 600 minutes using the H-3 setup of the instrument. Beta-efficiency was calibrated by measuring a blank sample with 188720 dpm $^{3}$H standard (No. 1210-121, PerkinElmer, USA) and was found to be (40.9±0.7)% in the ROI channels 30–220.

### *AMS*

Another part of the filter sample was dissolved with 2 ml 65% $HNO_3$ and 2 ml 30% $H_2O_2$. The oxidation step was repeated twice. 3 ml of a 1 mg·ml$^{-1}$ $FeCl_2$ solution was added and diluted with deionized water to 10 ml. Plutonium isotopes were quantitatively co-precipitated with $Fe(OH)_3$ by adjusting the pH to 9–10 with 25% $NH_3$. The $Fe(OH)_3$ precipitate was separated by centrifugation and then, combusted in quartz cups at 500 °C for 10 hours. The resulting iron oxides were mixed together with silver powder and pressed into aluminum sample holders suitable for the AMS measurements.

### *AMS measurements*

The VERA setup (Fig. 1) as used for actinide measurements is described in VOCKENUBER et al.[19] A cesium sputter source is used to extract negative ions. The yield of $PuO^-$ ions (on the order of $5\cdot10^{-4}$, WINKLER et al.)[11] is the largest factor in the efficiency calculation. The low-energy mass spectrometer is tuned using $^{238}U^{16}O^-$ as a pilot beam. To measure the various Pu isotopes, the mass spectrometers are scaled to $^{239}Pu^{16}O^-$ and $^{240}Pu^{16}O^-$, respectively. Negative molecular isobars are destroyed in a tandem accelerator with 3 MV terminal voltage and gas stripping. From the resultant positive ions one charge state is selected by the high-energy mass spectrometer. The stripping yields (and energies) achieved for the charge states investigated are 5% for 5+ (18 MeV), and 1% for 7+ (24 MeV), respectively. A main criterion for the choice of the charge state is the absence of ions from stable isotopes with the same mass over charge ratio, which are not distinguished by the electric and magnet fields of the mass spectrometer (so called mass/charge ambiguities). This is, e.g., the case for $^{240}Pu^{5+}$, which is accompanied by $^{144}Nd^{3+}$ (introduced during sample preparation). A time-of-flight (TOF) detector can be inserted into the beam path to obtain a velocity information of the remaining particles. This detector has a transmission of 17%, thus the efficiency can be increased significantly if the velocity information is not needed for background suppression. For the present work, $^{240}Pu/^{239}Pu$ data was obtained both with and without TOF. The results show excellent agreement, and no background with different velocity was visible in the TOF measurement. Finally, the energy is measured with an ionization chamber. For $^{240}Pu^{5+}$, a high count rate ($\sim$1000 $s^{-1}$) of $^{144}Nd^{3+}$, despite in principle resolved, overloads the detector electronics. Thus, the 7+ charge state was used for $^{240}Pu/^{239}Pu$ determination.

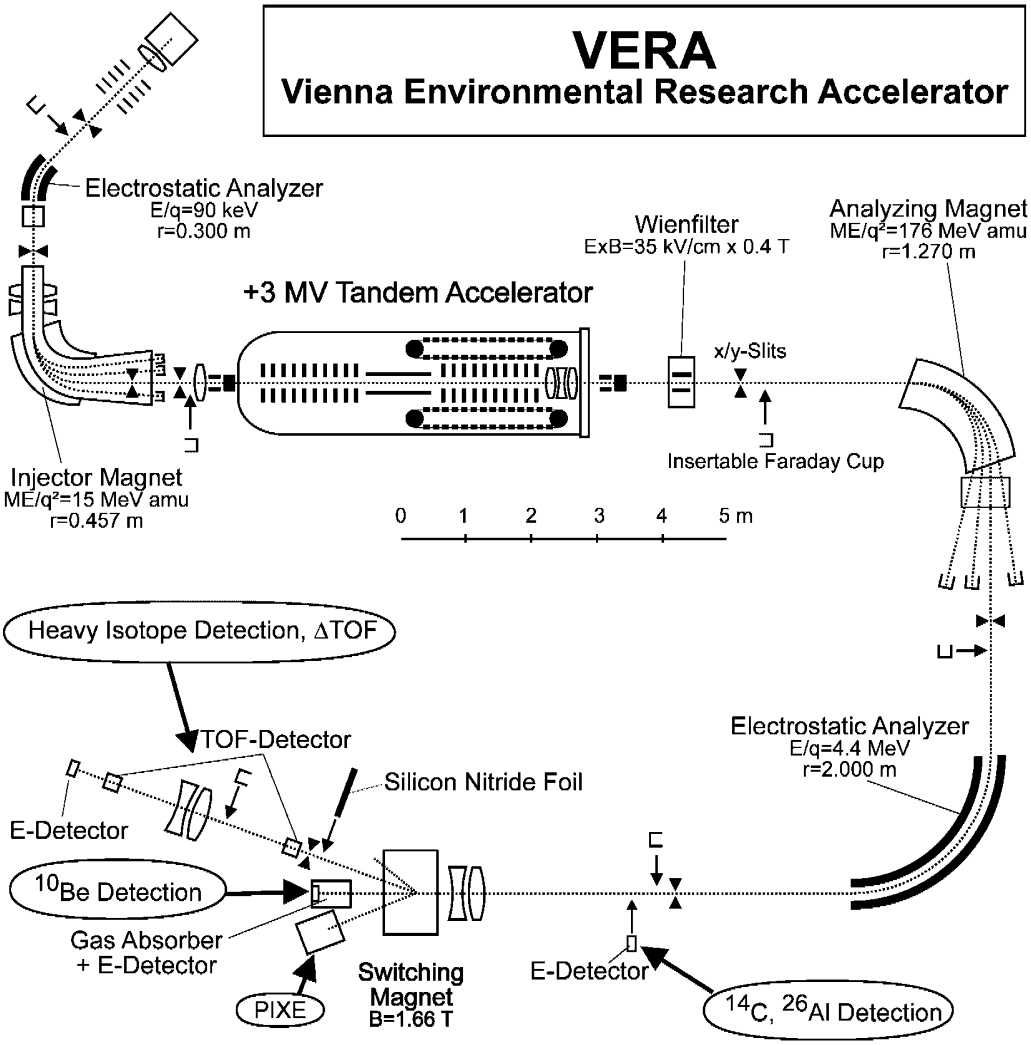

*Fig. 1.* Schematic layout of VERA. Pu is measured in the heavy ion detector

## Results and discussion

In Table 1, activity concentrations found by alpha-spectrometry and LSC are shown. Our results for the $^{238}$Pu and the $^{239(40)}$Pu specific activity are consistent with the reference values, with the exception of sample IAEA-300, which deviates by about 2σ.

For the $^{241}$Pu activity concentrations determined by LSC, only for one material (IAEA-135) an information value exists, which is in agreement with our measurement.

In Table 2, the measured isotopic ratios are given. The $^{240}$Pu/$^{239}$Pu ratios determined by AMS with and without the TOF detector agree within the measurement uncertainty, so only a combined value is shown. Only sparse data exists in the literature for comparison. Our AMS result for IAEA-135 shows good agreement with the value of 0.207±0.006 given by LEE et al.[20] The value of 0.212±0.013 found for IAEA-Soil-6, agrees within 2σ with the value of 0.191±0.005 given by MURAMATSU et al.[21]

*Table 1.* Activity concentrations (in Bq·kg$^{-1}$) dry weight

| Sample<br>(reference date) | $^{238}$Pu, Bq·kg$^{-1}$ | $^{239(40)}$Pu, Bq·kg$^{-1}$ | $^{241}$Pu, Bq·kg$^{-1}$ |
|---|---|---|---|
| IAEA-135 | 46.0 ± 1.8 | 224.5 ± 9.2 | 2740 ± 130 |
| (1 Jan. 92) | (41.6 – 45.0) | (205 – 226) | (2262 – 3990) |
| IAEA-300 | 0.200 ± 0.025 | 4.03 ± 0.16 | 14.8 ± 2.2 |
| (1 Jan. 93) | (0.14 – 0.36) | (3.44 – 3.65) | |
| IAEA-326 | 0.018 ± 0.004 | 0.55 ± 0.03 | 4.0 ± 1.0 |
| (31 Dec. 94) | (0.017 – 0.021) | (0.48 – 0.52) | |
| IAEA-327 | 0.021 ± 0.005 | 0.61 ± 0.03 | 2.2 ± 0.7 |
| (31 Dec. 94) | (0.018 – 0.022) | (0.56 – 0.60) | |
| IAEA-375 | 0.064 ± 0.010 | 0.32 ± 0.02 | 6.0 ± 1.5 |
| (31 Dec. 91) | (0.056 – 0.085) | (0.26 – 0.34) | |
| IAEA Soil-6 | 0.033 ± 0.006 | 1.05 ± 0.05 | <5.1 |
| (30 Jan. 83) | | (0.96 – 1.11) | |
| NIST 4350B | <0.02 | 0.48 ± 0.04 | n.d. |
| (9 Sept. 81) | | (0.508 ± 0.029) | |
| NIST 4350B | <0.02 | 0.56 ± 0.04 | <2.0 |
| (9 Sept. 81) | | | |
| NIST 4354 | 0.28 ± 0.04 | 4.30 ± 0.22 | 31.8 ± 3.4 |
| (14 Feb. 86) | (0.16 – 0.30) | (3.28 – 4.28) | |
| NIST 4357 | 2.18 ± 0.13 | 10.1 ± 0.5 | 120.8 ± 7.5 |
| (14 Feb. 94) | (1.96 – 2.98) | (9.3 – 13.2) | |
| Ribble Sediment | 36.7 ± 1.7 | 196.4 ± 8.7 | 1960 ± 100 |
| (1 Jan. 96) | | | |
| Cumbrian Sediment | 226 ± 10 | 1057 ± 46 | 11950 ± 570 |
| (1 Jan. 96) | | | |

$^{238}$Pu and $^{241}$Pu are decay corrected to reference date. Uncertainties are given at ±1σ. Reference and information values are given in parenthesis.

*Table 2.* Isotope ratios at measurement date (1 Nov. 2005)

| Sample | $^{238}$Pu/$^{239(40)}$Pu activity ratio | $^{241}$Pu/$^{239(40)}$Pu activity ratio | $^{240}$Pu/$^{239}$Pu atom ratio |
|---|---|---|---|
| IAEA-135 | 0.184 ± 0.004 | 6.3 ± 0.4 | 0.198 ± 0.003 |
| IAEA-300 | 0.045 ± 0.005 | 2.0 ± 0.3 | 0.142 ± 0.007 |
| IAEA-326 | 0.029 ± 0.010 | 4.3 ± 1.1 | 0.180 ± 0.007 |
| IAEA-327 | 0.031 ± 0.006 | 2.1 ± 0.7 | 0.191 ± 0.022 |
| IAEA-375 | 0.178 ± 0.030 | 9.5 ± 2.5 | 0.304 ± 0.023 |
| IAEA Soil-6 | 0.026 ± 0.006 | <1.7 | 0.212 ± 0.013 |
| NIST 4350B | <0.041 | n.d. | 0.111 ± 0.003 |
| NIST 4350B | <0.036 | <1.2 | n.d. |
| NIST 4354 | 0.056 ± 0.010 | 2.9 ± 0.3 | 0.184 ± 0.004 |
| NIST 4357 | 0.198 ± 0.010 | 6.8 ± 0.5 | 0.233 ± 0.008 |
| Ribble sediment | 0.173 ± 0.004 | 6.2 ± 0.4 | 0.195 ± 0.003 |
| Cumbrian sediment | 0.198 ± 0.002 | 7.0 ± 0.5 | 0.199 ± 0.003 |

n.d.: Not determined.

## Conclusions

Using a combination of radiometric methods and AMS, it is possible to determine the isotopic vector of an environmental sample after chemical separation from the bulk material. The general agreement of the $^{238}$Pu and the $^{239(40)}$Pu specific activity measurements with the reference values suggests a good accuracy of our method. At the present status, a normalization standard of known isotopic composition is needed for the characterization of unknown samples by AMS.

Unfortunately, little information is given for reference materials on $^{241}$Pu and $^{240}$Pu/$^{239}$Pu in literature, so a final judgment of the accuracy for these isotopes is not yet possible. The use of $^{236}$Pu as tracer for alpha-spectrometry will allow the subsequent determination of $^{242}$Pu and $^{244}$Pu in environmental samples.

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