
Determination of Plutonium 240/239 Ratios in Lake Ontario Sediments

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A thermal ionization mass spectrometric procedure was developed for determination of 240/239 ratios in subpicogram quantities of plutonium (Pu), and was applied to Pu extracted from Lake Ontario sediment. The detection limit was ~ 4 fg of Pu and the precision of 240/239 ratio measurement was ~ 7% in the 0.07–0.42 pg range. Results of sediment analyses at various depths showed in all cases 240/239 ratios near the mean global fallout value of 0.176 ± 0.014 . The lack of variability of the ratios with depth negated the use of Pu, present in excess in the near-surface samples due to leakage from a nearby reprocessing plant, as a geochronological meter. The 240/239 ratio of the leakage Pu appeared to be very similar to that of fallout Pu. (*J Am Soc Mass Spectrom* 1991, 2, 240–244)

Elemental plutonium (Pu) has isotopes from mass 232 to 246, none of which are stable or naturally occurring. The most well known are those from mass 238 to 242, which are produced in relatively high quantities by neutron-induced transmutations during fission of uranium. The major source of Pu in the environment is stratospheric fallout from nuclear weapons testing, which began in the late 1940s [1]. Stratospheric fallout is characterized by small particles, < 1 μm , that were expelled into the stratosphere and remained in the atmosphere for at least one year. A secondary source of environmental Pu is tropospheric fallout, which refers to particles, usually of larger sizes, that did not reach stratospheric altitudes and that had atmospheric residence times ranging from days to weeks [1]. The 240/239 ratio in both types of fallout is dependent on the type of explosive, and ranges from 0.035 for explosives from the Nevada Test Site to 0.36 for the "Mike shot" at the Eniwetok atoll. Global fallout levels are dominated by large-yield Soviet tests in the early 1960s, and the global average 240/239 ratio is 0.176 ± 0.014 [2]. A third, more localized source of Pu in the environment may be leakage from nuclear-powered generating stations, reprocessing plants, or other nuclear facilities. A wide range of 240/239 ratios is expected from these sources; for example, the ratio in fuel irradiated in a thermal neutron reactor environment was reported to be 0.33 [3], whereas the ratio in reprocessing plant Pu may be much less than 0.03.

The isotopic composition of Pu in environmental materials can be used to understand the biogeochemical fate of fallout Pu or to identify different sources of Pu release. For example, Noshkin and Gatrousis [4] discovered that 240/239 ratios in sediment and biological samples from the North and South Atlantic ranged from 0.11 to 0.24. They suggested that fractionation of fallout material following deposition to the ocean may have caused this wide range of ratios. Beasley et al. [5] reported a 240/239 ratio of 0.19 for cores from Washington state shelf and attributed the slight elevation in ratio to the presence of small amounts of higher ratio fallout from tests conducted by the People's Republic of China. Buesseler and Sholkovitz [1] reported a systematic decrease in 240/239 ratios with increasing water depth, e.g., from 0.18 to 0.10 along a transect of cores between Woods Hole and Bermuda. They attributed the low ratios to the presence of some tropospheric fallout from the testing done at the Nevada Test Site in the early 1950s. Koide et al. [6] have used unique 240/239 ratios as a geochronological tool for polar ice sheets.

Joshi [7] has analyzed Lake Ontario sediment cores for combined $^{239,240}\text{Pu}$ content by α -spectrometry and has discovered inventories in excess, by 56%, of that expected from global fallout. He also reported that $^{238}\text{Pu}/^{239,240}\text{Pu}$ and $^{241}\text{Am}/^{239,240}\text{Pu}$ activity ratios were substantially different from those expected for fallout. These anomalies were attributed to discharges from the Western New York Nuclear Service Center located at West Valley on the Cattaraugus Creek, which drains into the eastern end of Lake Erie. The data show a continuous accumulation of West Valley radionuclides in Lake Ontario sediment since 1967, and are consis-

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tent with previous data that showed that nearly all of the West Valley-derived ^{137}Cs is present in Lake Ontario sediment [8].

The objective of the present study was to determine Pu 240/239 ratios as a function of depth in Lake Ontario sediment at the same location as used in the abovementioned studies. West Valley-derived Pu was expected to have a 240/239 ratio sufficiently different from fallout Pu so that it could serve as a long-term geochronometer in western Lake Ontario, since both ^{239}Pu and ^{240}Pu have long half-lives. The geochronological data would be complementary and supportive to that obtained using ^{137}Cs , which is also a fallout radionuclide [8].

Activity data from the previous study [7] indicated that ^{239}Pu levels would be in the 0.2–20 pg range per 100 g of sediment. Thermal ionization mass spectrometry was chosen for isotopic ratio measurements because of its high and equivalent sensitivity for the isotopes of Pu. However, even for this technique, attainment of sufficient sensitivity for isotopic measurements at the picogram level is a challenge that has been overcome by only a few laboratories. Lagergren and Stoffels [9] assembled a high-transmission, triple-sector mass spectrometer with a Daly-type detector that, when used with resin bead-type sample loading, had sufficient sensitivity to measure uranium isotopes at the 0.36-pg level. However, the precision for measurements at this level was not reported. Rec and Myers [10] used a similar instrument but with solution-evaporated samples overcoated with rhenium by radio-frequency sputtering. They reported steady count rates of 90 per s for 10 min for 0.01-pg sample sizes heated to 1760 °C. Kelly and Fassett [11] used resin bead loading with a mass spectrometer of the National Bureau of Standards (NBS) design and achieved count rates of 2×10^4 for 25 pg of uranium (U) heated to 1650 °C. The precision for measurement of biological and environmental samples in the 100–700-pg range was approximately 2% and was dominated by the chemical blank. Perrin et al. [12] used a platinum (Pt) overcoating technique with an NBS-type mass spectrometer; both the Pu and the Pt were deposited by electrodeposition and heated to 1450 °C for analysis. They reported a precision of 0.06% for 240/239 ratios at the 1-ng level and a detection limit of 2×10^5 atoms. Zhu [13] evaporated Pu into small grains of activated charcoal that were heated to 1675 °C, and reported a precision of 0.04% at the 10-ng level. Application of this technique to subpicogram levels was not reported. Buessler and Halverson [14] used the same technique and instrumentation as Lagergren and Stoffels [9], except that the rhenium filament was carburized prior to sample deposition. They reported precisions of better than 10% for samples in the 2–4-fg range.

We have developed an anion exchange disk technique for high efficiency analysis of actinide isotopes [3, 15]. The technique is very similar to the resin bead

technique [11], except that the disks are much larger, 1-mm diameter, and easier to manipulate. We report here the application of this technique, using a single-sector instrument with electron multiplier detection, to the determination of the isotopic composition of Pu at subpicogram levels in Lake Ontario sediment.

Experimental

Reagents and Materials

Nitric acid solutions were prepared from double sub-boiling distilled nitric acid (Seastar Chemicals, Sidney, BC) diluted with double-distilled water deionized by a millipore ion exchange system. A 45-mg/mL aluminum nitrate solution was prepared from Anachemia (Anachemia Chemicals Ltd., Montreal, PQ), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in 8 M HNO_3 . Sodium nitrite, 0.2 g/mL, was prepared from Anachemia NaNO_2 dissolved in distilled water. The concentrated HCl used was Seastar double subboiling distilled hydrochloric acid.

The resin used in the ion exchange column was analytical-grade macroporous anion resin (BIO.RAD Laboratories, Richmond, CA) AGMP-1, which was 100–200 mesh and was in the chloride form.

Apparatus

The separation procedure was carried out in a laminar-flow clean air hood, Canadian Cabinets Model DND-6-DM, with acid-washed labware. Pyrex beakers were used for leaching the Pu from the papers and for collecting the eluent, and plastic-tipped transfer pipettes were used with all the reagents and solutions. The final evaporation step was carried out in 2-mL polypropylene microvials.

An 11-mL acid-washed polypropylene column connected to 30 cm of 2.25-mm (i.d.) polyethylene tubing was used to isolate Pu. The tubing was used to slow down the flow rate in the column, allowing efficient adsorption and elution of the various components in the solution.

The mass spectrometer was a Nuclide (Nuclide Corporation, State College, PA) 90 °C magnetic-sector instrument equipped with Cathodeon-type 553 triple-filament assemblies, an IBM PC-based automation system, a Cary 401 vibrating-reed electrometer (Cary Instruments, Monrovia, CA), and a Vacumetrics (Vacumetrics, Ventura, CA) ETP AEM 1000 electron multiplier. The original center filament was replaced with Rhenium Alloys (Rhenium Alloys Inc., Elyria, OH) zone-refined Re ribbon. The electron multiplier voltage was set to 2.5 kV, and the gain was 2.5×10^5 . The electron multiplier was used in the analog mode for this work.

Procedure

The Pu in the sediment samples had been previously separated by anion exchange chromatography and

co-precipitated with LaF_3 for α -spectrometry at the Canada Centre for Inland Waters laboratories [16]. This preparation included a ^{242}Pu spike as a recovery monitor. The precipitates were collected on 4.7-cm diameter Tuffryn HT-100 filter papers and sent to Chalk River Nuclear Laboratories for Pu isotopic measurements. To liberate the Pu from the paper and the LaF_3 precipitate the paper was cut into small pieces and transferred to a 10-mL beaker, to which 1.5 mL of hot 8 M HNO_3 and 1 mL of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution were added. These were heated for 10 min and the liquid decanted into a 30-mL beaker. Another 1.5 mL of the hot acid and 1 mL of $\text{Al}(\text{NO}_3)_3$ were added to the paper, heated for 10 min, and the liquid was combined with the first leachate. Ten drops of NaNO_2 solution were added to the leachates and the solution was warmed for 20 min to ensure that all the Pu was oxidized to the Pu(IV) state.

The anion exchange column was prepared and washed with 15 mL of 8 M HNO_3 , which converted the resin to the nitrate form. The Pu solution was added to the column and a slow, controlled flow rate of 0.2 mL/min was established. The sample beaker was washed twice with 2 mL of 8 M HNO_3 , and these washings were added to the column when the solution had dropped to the surface of the resin. The column was then washed with 25 mL of 8 M HNO_3 , followed by 25 mL of 12 M HCl and 1.5 mL of 1.5 M HNO_3 . The Pu was eluted with 10 mL of warm 0.2 M HNO_3 at 0.1 mL/min. The eluate was evaporated to 200 μL in a glass beaker under an infrared lamp, transferred to a microvial and evaporated to dryness with N_2 flow.

The Pu was re-dissolved in the microvial with 2 μL of 6 M HNO_3 . A 1-mm diameter Acropor ion exchange filter paper, which had been conditioned in 1 M HNO_3 , was transferred to 8 M HNO_3 for 10 s and then placed in the 2 μL of Pu solution for at least two hours. The impregnated paper was placed on a rhenium center filament where it was dried by applying 1 A current across the filament and then burned with a steadily increasing current up to 1.8 A. For mass spectrometry, a filament temperature of 1500 $^\circ\text{C}$ was used to focus the signals; this was increased to 1550 $^\circ\text{C}$ for isotopic measurements. Mass discrimination factors were determined by analysis of standards at nanogram levels. As such they may not have been strictly applicable at femtogram levels, but they were very small relative to the measurement uncertainty in the femtogram-to-picogram range.

Results and Discussion

Chemical Preparation

Separation of Pu from the LaF_3 -filter paper matrix was necessary because the matrix suppressed the Pu^+ ion signal in the mass spectrometer. Aluminum nitrate in

nitric acid was used not only to solubilize LaF_3 but also to complex the liberated fluoride (F) so that complexation of Pu^{3+} by F^- would be avoided. Sodium nitrite was subsequently added to oxidize all of the Pu to the tetravalent state. The subsequent anion exchange separation was based on the relatively strong retention of anionic Pu(IV) nitrate complexes in strong nitric acid, and is similar to that described by Wick [17].

Thorium (Th) was present in the samples and followed Pu through the separation. Its presence on the filaments was undesirable because it lowered the ionization efficiency for Pu. The HCl wash of the column was sufficient to remove Th.

A further purification/concentration of the Pu was achieved in the anion exchange disk adsorption step, because of the high distribution coefficient for Pu(IV) [3]. Also, $\sim 88\%$ of the Pu in the final 2 μL of solution was extracted into the disk.

Procedural blanks did not show any Pu at the levels studied in this work. There was a frequent 10-100-pg U blank, which was likely due to trace contaminations during chemical preparations, and which interfered with ^{238}Pu signals. Interference from UH^+ at mass 239 was not observed.

Mass Spectrometry

The accuracy and precision of isotopic analysis of subpicogram quantities of Pu was determined by replicate analysis of NBS SRM 949f. The standards were loaded in the same manner as samples, the loading achieving a high degree of separation of Pu from Am because of the high distribution coefficient for Pu on the anion exchange disk [3]. The precision was dominated by the instrumental noise associated with the minor isotope. The internal, instrumental precision of a single determination was estimated from 30 replicate mass spectra of each sample, and ranged between 10 and 20% *rsd*. The precision of a mean ratio was determined from the means of six or more replicate loadings of the standard, and the results (Table 1) show that this precision was $\leq 7\%$ *rsd* in the 0.07-0.42-pg range. The average measured ratios were corrected for a mass discrimination factor of 0.0029/u, and were in agreement with the certified

Table 1. Accuracy and precision of Pu isotopic ratios at subpicogram levels

Quantity of Pu minor isotope (pg)	Isotopes measured	Isotope ratio	
		Known ^a	Measured $\pm 1 s^b$
0.420	241/240	0.01430	0.0144 \pm 0.0009
0.290	240/239	0.02887	0.0294 \pm 0.0004
0.068	242/241	0.14960	0.1390 \pm 0.01

^aNBS SRM 949f with ^{241}Pu levels corrected for decay.

^bPrecision of mean, estimated from six or more separate loadings.

ratios within the measurement precision. Large isotopic fractionation effects were not observed.

Mass spectra of Pu extracted from sediment showed sufficient signal-to-noise ratio for isotopic composition measurement, even at the 3-fg level for ^{240}Pu (Figure 1). The precision of 240/239 ratio measurement at this level was also between 10 and 20% *rsd* for a single determination, which is comparable to that achieved by the few other laboratories that have reported Pu

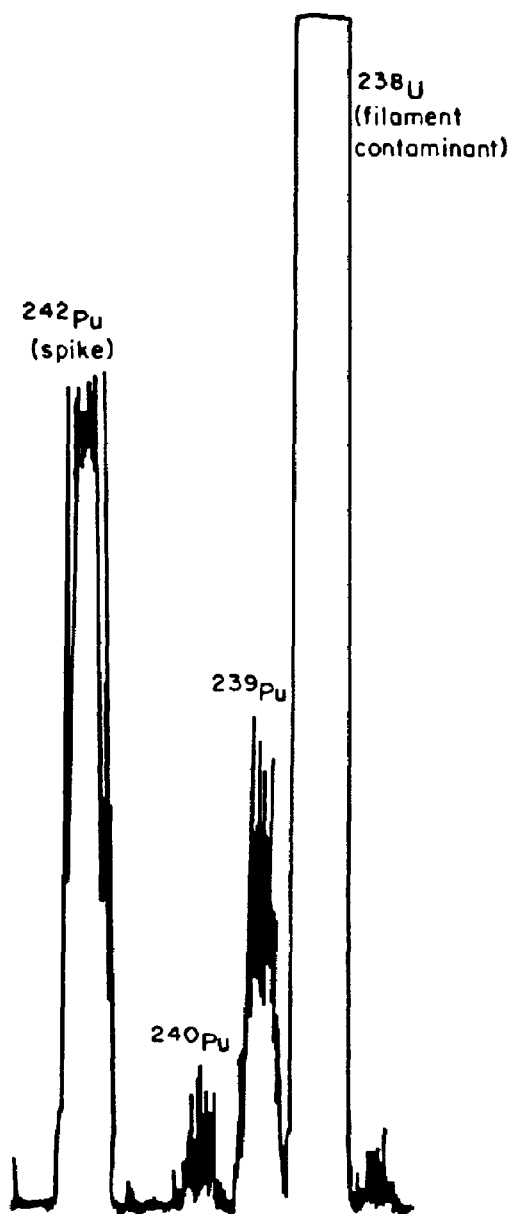


Figure 1. Mass spectrum of trace Pu (0.02 pg ^{239}Pu) in Lake Ontario sediment.

Table 2. Pu 240/239 ratios for sediment core samples from Lake Ontario

Sample no.	Depth (cm)	Quantity of ^{239}Pu (pg)	240/239 ratio
1	0.0-1.1	0.10	0.18
2	1.1-2.3	0.10	0.19
3	2.3-3.5	0.10	0.17
4	3.5-4.7	0.10	0.19
5	4.7-5.9	0.30	0.20
6	5.9-7.1	0.30	0.19
7	7.1-8.2	0.30	0.19
8	8.2-9.4	0.50	0.18
9	9.4-10.7	0.50	0.19
10	10.7-11.9	0.50	0.19
11	11.9-13.1	0.10	0.20
12	13.1-14.2	0.05	0.17
13	14.2-15.4	0.10	0.18
14	15.4-16.6	0.10	0.17
15	16.6-17.8	0.10	0.17
16	17.8-19.0	0.10	— ^a
17	19.0-20.2	0.02	0.17
18	20.2-21.4	0.02	0.14
19	21.4-22.7	0.02	0.16
20	22.7-23.9	0.02	— ^a

^aInsufficient signal.

isotopic data at these low levels [9-14]. The relatively large amount of ^{242}Pu signal in the spectra was due to the addition of this isotope as a recovery monitor for radiochemical separations. The isotope purity of this spike was > 99.99% ^{242}Pu , and thus corrections for spike ^{239}Pu and ^{240}Pu isotopes were not necessary.

Sediment Samples

A 95% confidence interval of 0.18 ± 0.02 for 240/239 ratios in the sediment was estimated from the precision obtained for separate loadings of NBS SRM 949f. Results (Table 2) for 18 samples from the same core showed that for only one sample, 18, was the 240/239 ratio outside this range. This one deviation was not considered to be sufficient evidence for an isotopic anomaly in the sediment, and furthermore, sample 18 was much deeper than expected for West Valley Pu. Hence, if there was measurable leakage of Pu from the reprocessing plant located at West Valley, its isotopic composition was not sufficiently different from the mean global value to cause a significant change in the 240/239 ratios measured in this work. An estimate of the precision required to detect a shift in 240/239 ratio would be possible if the Pu isotopic composition of West Valley effluent were known, but this information, if known, has not been reported and the collection of samples in the Cattaraugus Creek and Lake Erie was beyond the scope of this work. The use of the leakage Pu as a geochronometer in Lake Ontario sediment appears to require a high-precision femtogram-level technique.

References

1. Buesseler, K. O.; Sholkovitz, E. R. *Geochim. Cosmochim.* **1987**, Acta 51, 2623-2637.
2. Krey, P. W.; Hardy, E. P.; Pachucki, C.; Rairke, F.; Coluzza, J.; Benson, W. K. In *Transuranium Nuclides in the Environment*; Report IAEA-SM-199/390; Vienna, 1976; pp. 671-678.
3. Green, L. W.; Elloit, N. L.; Miller, F. C.; Leppinen, J. J. *J. Radioanal. Nucl. Chem.* **1989**, Art. 131, 299-309.
4. Noshkin, V. E.; Gatrousis, C. *Earth Planet. Sci. Lett.* **1974**, 22, 111-117.
5. Beasley, T. M.; Carpenter, R.; Jennings, C. D. *Geochim. Cosmochim.* **1982**, Acta 46, 1931-1946.
6. Koide, M.; Bertine, K. K.; Chow, T. J.; Goldberg, E. D. *Earth Planet Sci. Lett.* **1985**, 72, 1-8.
7. Joshi, S. R. *Water, Air, Soil Pollut.* **1988**, 42, 159-168.
8. Joshi, S. R. *Water, Air, Soil Pollut.* **1988**, 37, 111-120.
9. Lagergren, C. R.; Stoffels, J. J. *Int. J. Mass Spectrom. Ion Processes* **1970**, 3, 429-438.
10. Rec, J. R.; Myers, W. R. *Anal. Chem.* **1974**, 46, 1243-1246.
11. Kelly, W. R.; Fassett, J. D. *Anal. Chem.* **1983**, 55, 1040-1044.
12. Perrin, R. E.; Knobeloch, G. W.; Armijo, V. M.; Efurud, D. W. *Int. J. Mass Spectrom. Ion Processes* **1985**, 64, 17-24.
13. Zhu, F.-R. *Nucl. Instr. Methods Phys. Res.* **1987**, B26, 381-383.
14. Buesseler, K. O.; Halverson, J. E. *J. Environ. Radioactivity* **1987**, 5, 425-444.
15. Green, L. W.; Elliot, N. L.; Longhurst, T. H. *Anal. Chem.* **1983**, 55, 2394-2398.
16. Joshi, S. R. *J. Radioanal. Nuclear Chem.* **1985**, Art. 90/2, 409-414.
17. Wick, O. J., Ed. *Plutonium Handbook*; American Nuclear Society: La Grange Park, IL, 1980.