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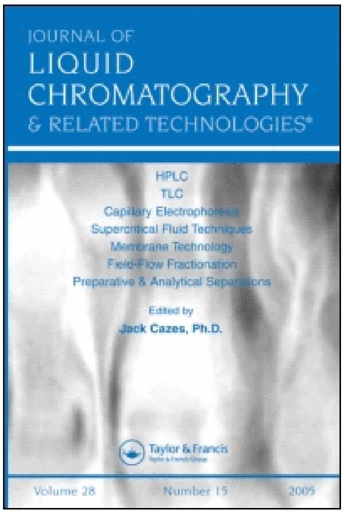

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Determination of Plutonium in Soil by ICP-MS After CCC Preseparation

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ABSTRACT

Environmental plutonium was determined by ICP-MS after countercurrent chromatography (CCC) preseparation with 20% tri-*n*-octylamine in toluene as stationary phase. The matrix elements, thorium and uranium, were eluted by using 7.5 mol/L nitric acid, 10 mol/L hydrochloric acid, and 3 mol/L nitric acid, respectively, and the plutonium was quantitatively stripped by using 0.025 mol/L oxalic acid–0.15 mol/L nitric acid. The spectral interferences due to the tailing of adjacent actinoids, polyatomic ion, and the matrix effect were depleted after the sample was subjected to the CCC preseparation because uranium and thorium were well separated with decontamination factors of 10^4 and 10^5, respectively; the memory effect could be eliminated effectively with a solution with the same composition of plutonium eluant. Isotopic dilution was used to determine ultra-trace ^{239}Pu using ^{242}Pu as the spike. The limit of detection of ^{239}Pu is 6 fg (27 attomoles), and the limit of determination is 25.5 fg for soil.

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The depth profile of ^{239}Pu was revealed with maximum ^{239}Pu concentrations of $\sim 0.08 \times 10^{-12}$ g/g (0.3 femtomole per g) in Xi'an and $\sim 1.6 \times 10^{-12}$ g/g (6.7 femtomole per g) in Gansu, China. The ratio of ^{240}Pu/^{239}Pu in the soil sampled from Gansu differs from the mean value of the global fallout, indicating a different origin.

Key Words: Plutonium; Countercurrent chromatography; Inductively coupled plasma mass spectrometry; Sample purification.

INTRODUCTION

Environmental plutonium is at the ultra-tracelevel; it mainly comes from the fallout of nuclear weapons testing.[1] More localized sources of plutonium in the environment may be produced by leakage from nuclear-powered generating stations, reprocessing plants, or other nuclear facilities. The toxicity and radiotoxicity of plutonium is so high that its determination at ultra-trace levels is of critical interest. The plutonium isotopes in the environment are mainly ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu, of which ^{239}Pu is the most abundant isotope. It is known that the isotopic composition of plutonium varies with source term, so the isotopic ratio, ^{240}Pu/^{239}Pu, can be used to identify different sources of plutonium released.

Alpha spectrometry, hitherto, has been the most widely used in the determination of environmental plutonium, but it is impossible to determine the ^{240}Pu/^{239}Pu ratio precisely because the alpha spectra of the two particles are overlapped, and the measuring time is very long because of the low activity of the plutonium in environmental samples. Mass spectrometry, such as thermal ionization mass spectrometry, resonance ionization mass spectrometry, and accelerator mass spectrometry, can provide the information of isotopic composition, but their low sample throughput and complicated procedure of sample treatment restrict their extensive applications in environmental plutonium analysis. The advent of inductively coupled plasma mass spectrometry (ICP-MS), which has high sensitivity, high throughput, and the ability to measure isotopic ratios, makes the routine analysis of ultra-trace plutonium practical. It has been successfully used in the determination of long-lived radioactive nuclides.[2,3] When ICP-MS is used to determine the ultra-trace plutonium, one should be aware of the interferences during the process of determination. The main interferences are signal suppression caused by matrix elements, polyatomic ion of ^{238}U^{1}H, and the tailing of ^{238}U and ^{232}Th, and further, the mass discrimination and memory effect existing in the process of sample introduction.

Chemical separation is absolutely necessary in order to reduce or suppress these interferences. Ion exchange has been generally used to separate environmental plutonium from the matrix. The typical sample preparation procedure was modified from that described by Talvitie.[4] A spike, such as ^{242}Pu, was added to the soil as a yield tracer for the calculation of total plutonium. The sample was incinerated at 550°C, followed by acid leaching and then is evaporated to dryness; the residue was dissolved in a high concentration of nitric acid or hydrochloric acid, and the resultant solution was passed through a strong anion exchange resin column. The co-adsorbed uranium was removed from the resin with nitric acid. Plutonium was eluted with dilute nitric acid or hydrochloric acid, in the presence of complexant or reductant. There are two disadvantages to ion exchange. First, the column is easily clogged by some fine suspended matter originating from the leaching, even though it was well centrifuged. Second, the recovery may be affected by the irreversible adsorption by the resin and the surface of the column material.

Since no solid support exists in the countercurrent chromatography (CCC), it is free from the loss of trace solute, column clogging, as well as contamination. Moreover, PTFE, the column material of CCC, is a very inert material and its adsorption capability for metal ions is the least among all of the column materials. In addition, the great load capacity of CCC permits large injection volumes of the sample solution. Some authors[5–10] had been dedicated to explore CCC as an enrichment and preseparation technique for the determination of trace elements, e.g., REEs in rocks.[5,6] In this paper, ultra-trace environmental plutonium was determined following CCC separation. The matrix effect and polyatomic interferences were eliminated by CCC preseparation. The concentration of ^{239}Pu, as well as the isotope ratio ^{240}Pu/^{239}Pu in two regional soils was analyzed.

EXPERIMENTAL

Reagents and Standard Solutions

Ultra pure reagents of nitric acid, hydrochloric acid, oxalic acid, and hydrogen peroxide are used in the experiments. The standard solutions were diluted in 2% w/w nitric acid from 18.2 MΩ cm deionized water obtained from an Ultra-Pure Water System (Millipore, USA). ^{242}Pu was produced by the State Scientific Center of Russia, in which the atomic ratios of ^{239}Pu/^{242}Pu, ^{240}Pu/^{242}Pu are 0.0012 and 0.017, respectively.

Analytical Procedure

The layered profile soil samples were collected at Xi'an and in the west of Gansu, China. The program of sample treatment is depicted in Fig. 1. ^{242}Pu

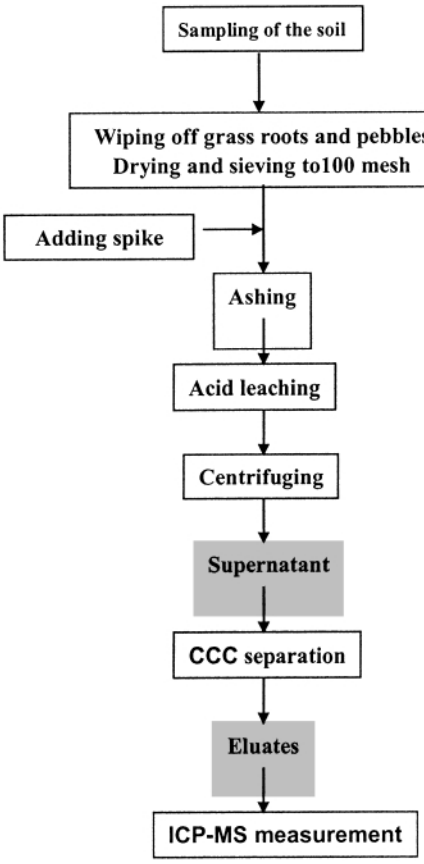

Figure 1. The analytical procedure for the soil.

was added to the soil sample as a yield tracer for the calculation of total plutonium by isotope dilution. The samples were incinerated overnight at 550°C in a muffle furnace, followed by nitric acid–hydrogen peroxide leaching, then evaporated to dryness; the residue was dissolved in 8 mol/L nitric acid, then it was subjected to CCC separation, and the eluates of plutonium were analyzed directly by ICP-MS.

Countercurrent Chromatography Separation

A multilayer coil partition centrifuge, GS-20A HSCCC (Beijing Institute of New Technology Application, Beijing, China), was used in this research.

Its fabrication parameters have been described previously.[11] Because erosive acids are often employed in the inorganic separation, a peek pump, which could resist the erosion of acid, should be used, and a Uniflows Micro Pump (Uniflows Co. LTD, Tokyo, Japan) was employed in the present work. Tri-*n*-octylamine, 20%, (TNOA) in toluene was used as stationary phase, because TNOA is a good reagent for the isolation of plutonium from the nuclear fuel materials and fission products.[12] In order to wipe out the matrix elements, thorium and uranium, step elution with four different kinds of mobile phases was adopted:

1. 7.5 mol/L nitric acid for rinse matrix elements,
2. 10 mol/L hydrochloric acid for rinse matrix elements,
3. 3 mol/L nitric acid to elute uranium, and
4. 0.15 mol/L nitric acid containing 0.025 mol/L oxalic acid. To strip plutonium.

Measurement

All measurements were performed with a Finnigan MAT Element high resolution ICP-MS with Cetac Technologies concentric nebulizer and Aridus membrane desolvating system. This instrument is equipped with a double-focusing magnetic sector mass spectrometer. A mass resolution of 300 was used. The instrument settings are summarized in Table 1. Before a measurement sequence was started, the instrument was carefully mass calibrated, and the argon gas flow rate and the ion lenses were optimized for maximum sensitivity at m/z 238 by using a 10 ng/mL uranium standard solution. The sensitivity can be tuned to approximately 2×10^5 cps per ppb ^{238}U.

A blank procedure was performed in advance of the analysis of the sample and 2% w/w ultra-pure nitric acid was used as the blank between each sample. The formation rate of the m/z 239 ion and the mass bias coefficient was determined before and after the measurement of the sample. The data collecting parameters are also listed in Table 1. The signal intensity at m/z 238 was monitored, in the case unsatisfactory separations of uranium were encountered. The atomic ratio, ^{239}Pu/^{242}Pu, was corrected according to Eq. (1).

$$^{239/242}R_{\mathrm{m}} = \left({}^{239/242}R - \frac{{}^{239}I_{\mathrm{b}} + {}^{238}I \times K_{\mathrm{U}}}{{}^{242}I} \right) \times \frac{{}^{242}I}{({}^{242}I - {}^{242}I_{\mathrm{b}})\eta} \qquad (1)$$

where $^{239/242}R_{\mathrm{m}}$ means the isotopic ratio, ^{239}Pu/^{242}Pu, given by the method, whereas, the $^{239/242}R$ refers to the atomic ratio reported by the instrument. K_{U} means the formation rate at m/z 239 by uranium. I denotes the signal intensity,

Table 1. Instrumental operating conditions measurement parameters for the ICP-MS.

Instrumental operating conditions		Measurement parameters	
Plasma power	1,350 W	Isotopes	^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu
R_f power	<7 W	Acquisition mode	E-scan
Sample uptake rate	0.06 mL/min	No. of scans	30
Plasma gas flow rate	13 L/min	Acquisition points	10
Auxiliary gas flow rate	1.2 L/min	Search window	50%
Nebulizer gas flow rate	0.85 L/min	Integration window	80%
Ion lens settings	Optimized daily	Dwell time per sample	10 ms for ^{238}U; 200 for ^{239}Pu;
Ion sampling depth	Optimized daily		500 ms for ^{240}Pu; 50 ms for ^{242}Pu
Sampler skimmer cone	Nickel	No. of samples per nuclide	20

cps. η means mass bias calibration coefficient; it was determined using standard plutonium solutions before or after ICP-MS measurement. The subscript, b, denotes the blank of 2% nitric acid, and d denotes the dilute.

The concentration of ^{239}Pu was calculated according to Eq. (2).

$$^{239}C = \frac{^{242}\mathrm{Pu}_\mathrm{d}(^{239/242}R_\mathrm{m} - {}^{239/242}R_\mathrm{d})(239/242)}{W} \tag{2}$$

where ^{239}C is the concentration of plutonium in the dry soil, g/g. $^{242}\mathrm{Pu}_\mathrm{d}$ is the amount of ^{242}Pu added to the sample in the dilute, g. W is the weight of the dry soil sample, g. The quantification of ^{240}Pu is similar to that of ^{239}Pu. The isotopic composition of $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ was readily calculated from the concentrations of ^{239}Pu and ^{240}Pu.

RESULTS AND DISCUSSION

Separation of Plutonium

Before the separation process, the mobile phases were saturated with the stationary phase and placed in a thermostat overnight. The coiled column was filled with the eluant (1) firstly, then 15 mL stationary phase was pumped into the column; the beginning revolution speed was set at 1200 rpm and the sample was introduced through the pump. The densities of the mobile phases are different, gradually decreasing from eluant (1) to eluant (4). If the operation parameters are fixed, the stationary phase will leak out when the eluant is changed. This is undesirable in the process of separation. To cope with the leakage of the stationary phase, the rotational speed should be elevated or the flow rate should be decreased; in our experiments, the rotational speed was increased from the beginning speed 1200 rpm for eluant (1) to 1800 rpm for eluant (4). Figure 2 shows the chromatogram when a sample solution containing 20 μg thorium, 10 μg uranium, and 0.04 ng ^{242}Pu in 50 mL 7.5 mol/L nitric acid was introduced to the column. As is shown in the figure, the uranium and thorium are well separated and the decontamination factors for uranium and thorium are 10^4 and 10^5, respectively. Moreover, most of the

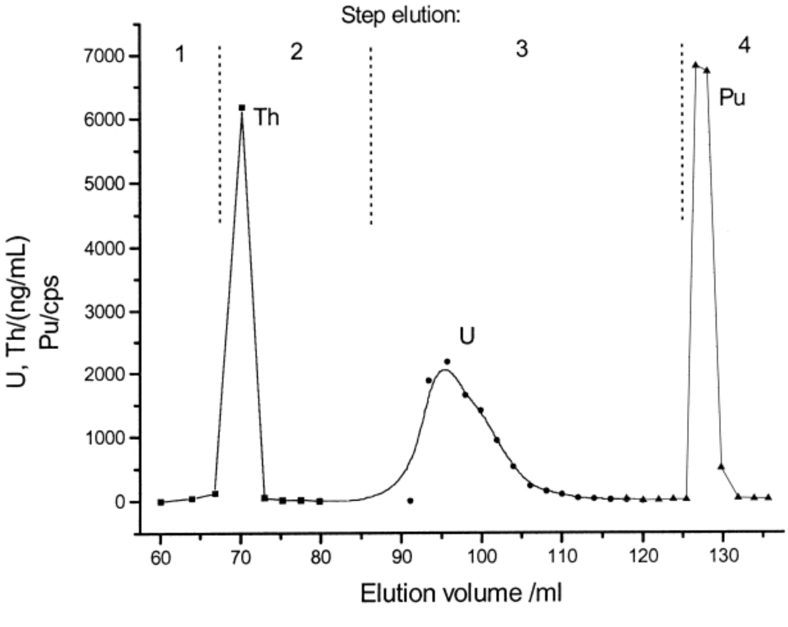

Figure 2. Step elution of Th, U, and Pu using CCC. GS-20A CCC machine, volume 30 mL, stationary phase, toluene with 20% TNOA; mobile phase: acidic aqueous solutions of various pHs, head-to-tail, 1 mL/min flow rate; $S_f = 61\%$. Preconcentration: 50 mL solution containing 20 μg Th, 10 μg U, and 0.04 ng ^{242}Pu in 7.5 mol/L nitric acid. Step elution: (1) 10 mL 7.5 mol/L nitric acid; (2) 20 mL 10 mol/L hydrochloric acid; (3) 40 mL 3 mol/L nitric acid; (4) 0.025 mol/L oxalic acid in 0.15 mol/L nitric acid.

eluted plutonium was concentrated in 3 mL of eluate, which is beneficial for the increase of signal intensity in the ICP-MS measurement.

Interferences

The interferences involved in the ICP-MS determination of environmental plutonium are mainly the matrix effect, spectral interferences, and the memory effect. The matrix effect may suppress the signal intensity, but it can be completely eliminated as long as the sample is subjected to preseparation. The spectral interferences arise from the tailing and molecular ions of neighboring actinoids. When a solution of 10 ppb uranium (10 µg/L or 42 nM) was injected to the plasma, there is significant signal intensity at m/z 239, m/z 240, and m/z 237, as illustrated by Fig. 3. The counting rate at m/z 239 is much larger than that at m/z 237, due to the existence of molecular ion $^{238}U^{1}H$. To reveal the dependency of the signal intensities between m/z 238 and m/z 239, m/z 237, and m/z 240, a series of solutions with different concentrations of uranium were measured. The intensities at m/z 239, m/z 240, and m/z 237 are proportional to that at m/z 238, as illustrated in Fig. 4. This result means that the calibration of the interferences from the ^{238}U could be quantified using K_U, the ratio m/z 239 or m/z 240 to m/z 238. This K_U ratio is

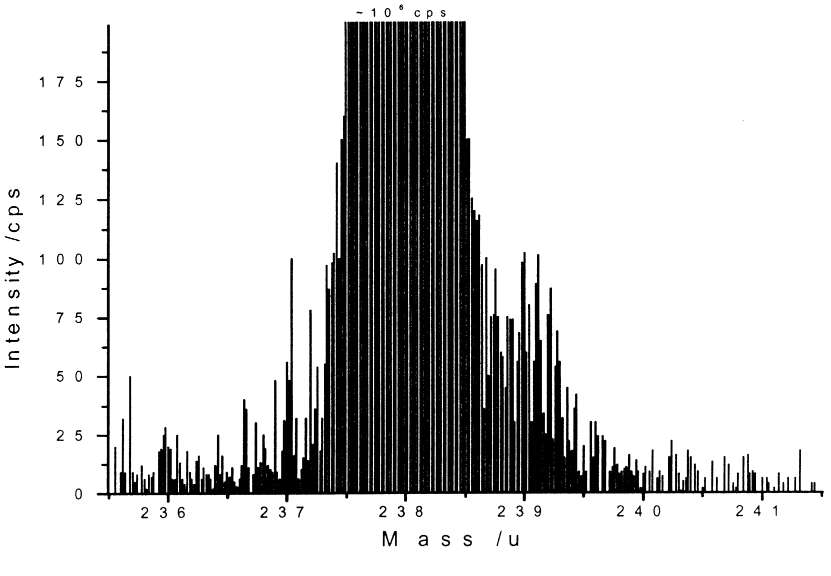

Figure 3. Inductively coupled plasma mass spectrum of uranium (236–241 Daltons).

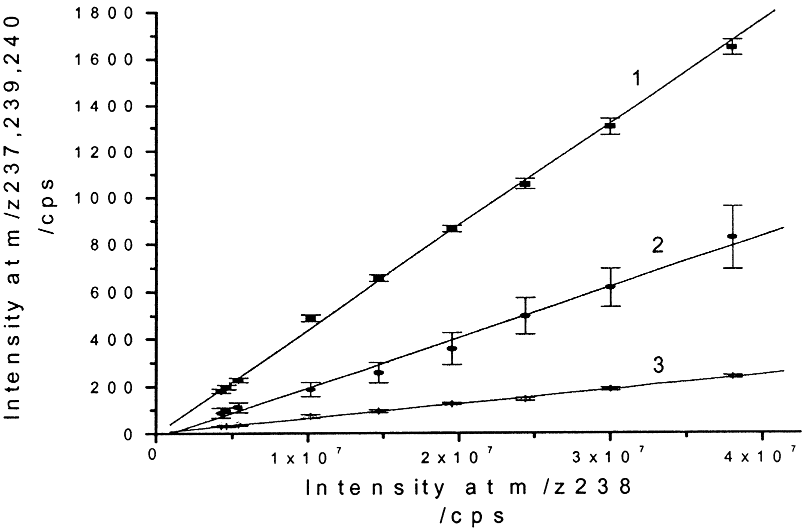

Figure 4. The dependence of signal intensity at *m/z* 237, 239, and 240 with signal intensity at *m/z* 238. Sample: uranium solution of different concentrations. Nebulizer: pneumatic nebulizer. 1, ^{239}I/^{238}I; 2, ^{237}I/^{238}I; 3, ^{240}I/^{238}I.

Table 2. The tailing and uranium hydride in ICP-MS.

K_U		Instrument, sample injection	Refs.
$^{239}I/^{238}I$	$^{240}I/^{238}I$		
7.8×10^{-5}		Quad, PN	13
7.1×10^{-5}		Quad, USN	
0.95×10^{-5}		Quad, USN/MD	
$3.84 \pm 0.15 \times 10^{-5}$	$9.7 \pm 2.5 \times 10^{-7}$	HRICP-MS, PN	14
6.7×10^{-5}		HRICP-MS, PN	15
$3.2 \pm 0.2 \times 10^{-5}$		Quad II, PN	16
$1.8 \pm 0.1 \times 10^{-5}$		Quad II, USN	
$4.4 \pm 0.08 \times 10^{-5}$	$6.17 \pm 0.07 \times 10^{-6}$	HRICP-MS, PN	Present work
$1.6 \pm 0.09 \times 10^{-5}$		HRICP-MS, MD	

Note: PN, pneumatic nebulizer; MD, membrane desolvating system; USN, ultrasonic nebulizer.

related to the instrumental and operation parameters; therefore, it should be determined before or after ICP-MS measurement. K_U at m/z 239 is 4.4×10^{-5}, when the pneumatic nebulizer was used, which is in accord with that reported (Table 2) by other authors.[13–16] The tailing from another actinoid element, thorium, may also affect the ICP-MS determination of environmental plutonium. The corresponding K_{Th} ratio is 1.7×10^{-7}. The amounts of uranium and thorium in the polluted soils are in the ppm (~µg/g) and tens of ppm (~10 µg/g) range, respectively. The ^{239}Pu equivalents caused by tailing and molecular ions from uranium and thorium in one gram of soil were exactly 1.6×10^{-11} g/g and 1.7×10^{-12} g/g. These equivalent ^{239}Pu are much larger than the actual quantities of ^{239}Pu itself in the soils, which is around 10^{-13} g in one gram of surface soil.[17] Therefore, the separation of uranium and thorium, especially uranium, from plutonium before ICP-MS measurement remains essential.

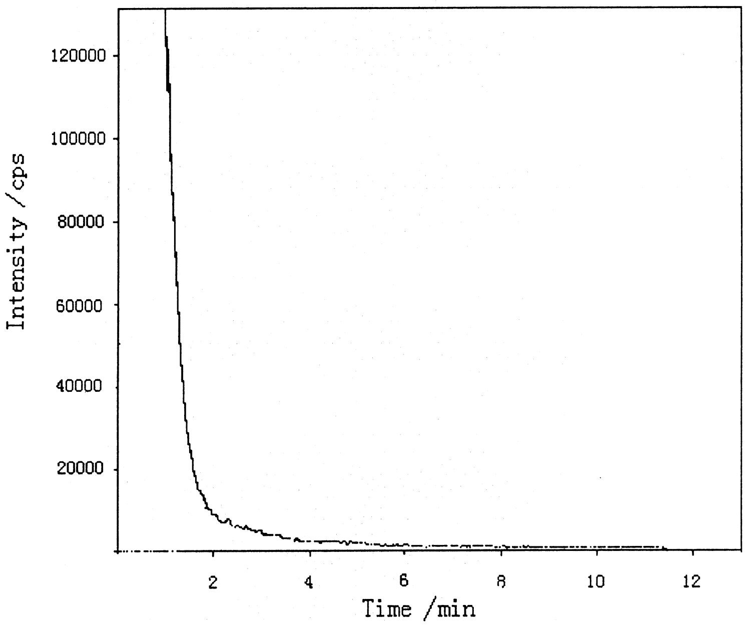

Figure 5. Elimination of memory effect of plutonium by rinsing with 0.025 mol/L oxalic acid in 0.15 mol/L nitric acid. Injection: 1 ng/mL ^{242}Pu solution in 2% m/m nitric acid for 5 min, followed by 2% nitric acid for 2 min and then ($t = 0$ min), rinsing with acidic oxalic solution.

Memory Effect

The memory effect due to the retention of analyte in the sample injection system or the torch will induce additional signal intensity of the subsequent sample or increase the detection limit. The memory effect of plutonium was observed in this work, although memory effects had been previously reported for the more volatile elements like cadmium, iodine, lead, lithium, and mercury.[18] To evaluate it, several experiments were performed.

First, a solution of ^{242}Pu (1 ng/mL in 2% w/w nitric acid) was analyzed for 5 min and then injected with 2% nitric acid for another 10 min, the signal intensity at *m/z* 242 being much larger than the blank. This result shows that the memory effect of plutonium is obvious.

Secondly, in order to assess the locations of plutonium retention, the solution of ^{242}Pu 1 ng/mL in 2% nitric acid was injected for 5 min, followed by rinsing with 2% nitric acid for 2 min, and then a new plastic tubing was used to transmit 2% nitric acid; the signal intensity at *m/z* 242 was equivalent to the background. This result shows that the memory effect of plutonium was caused by the retention of Pu (adsorption) in the plastic tubing.

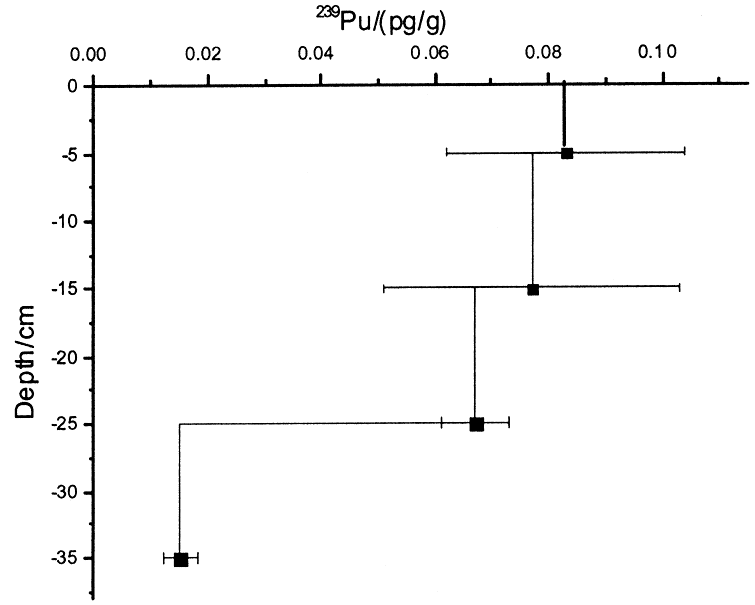

Figure 6. The concentration of ^{239}Pu in the dry soil sampled in Xi'an, China.

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Third, after ^{242}Pu 1 ng/mL in 2% nitric acid was injected for 5 min and rinsed with 2% nitric acid for 2 min, 0.025 mol/L oxalic acid in 0.15 mol/L nitric acid was injected; the counting rate at m/z 242 decreased dramatically, as shown in Fig. 5. That means the eluate of plutonium used in CCC could be employed to remove memory effect.

Limit of Detection

The detection limit (LOD) for the ^{239}Pu was calculated as the equivalent concentration to three times the standard deviation of the 2% nitric acid blank. The LOD is 6 fg for ^{239}Pu, when the micro concentric nebulizer was used. This LOD is a rather good one in comparison with the reported LODs.[2,3,14,19,20] At low levels, background is very important. It is the concomitant of sample treatment and, therefore, the limit of determination, LD3σ, which is based on 3σ criterion of the background, is more useful to characterize the detection capability of an analytical method. The background was 12.5 ± 4.3 fg for the CCC separation; therefore, the limit of determination of ^{239}Pu is 25.5 fg with this method.

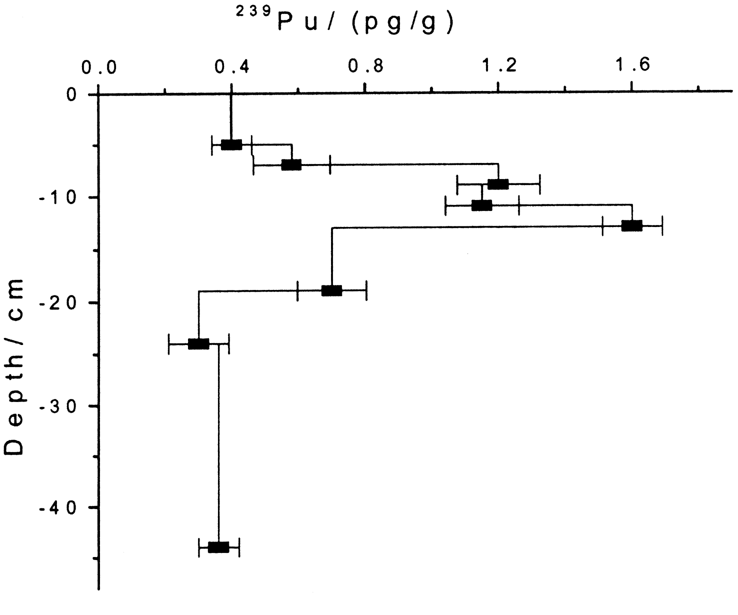

Figure 7. The concentration of ^{239}Pu in the dry soil sampled in Gansu, China.

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Table 3. The atomic ratio, $^{240}Pu/^{239}Pu$, around China.

Site	$^{240}Pu/^{239}Pu$	RSD (%)
From Ref. [21]		
Sapporo, Japan	0.1730	0.5
Tokyo, Japan	0.1720	7.0
Chienhua, Taiwan, China	0.1652	2.7
Lahore, Pakistan	0.1842	0.9
Mean value of global fallout	0.176	7.9
From present work		
Xi'an, China	0.18	15
Gansu, China	0.16	8

Analysis of Plutonium in Soils

A spike solution, containing ~0.04 ng ^{242}Pu, was added to 50 g soil and then incinerated at 550°C for 24 h to decompose the organic matter. Plutonium was extracted by acid leaching, using 150 mL 8 mol/L nitric acid plus 5 mL hydrogen peroxide. The extract was centrifuged, the supernatant was used for CCC separation, and the eluant of plutonium was used directly for ICP-MS measurement. The concentration profile of ^{239}Pu in soil sampled in Xi'an is depicted in Fig. 6. The maximum concentration is $\sim 0.08 \times 10^{-12}$ g/g at a depth of 5 cm. The concentration profile of ^{239}Pu in soil sampled in Gansu is depicted in Fig. 7. Its maximum concentration is $\sim 1.6 \times 10^{-12}$ g/g at a depth of 13 cm. The concentration of ^{239}Pu in the soil sampled in Xi'an is of the background level, while it is higher in the soil sampled in Gansu. The atomic ratios of $^{240}Pu/^{239}Pu$ of the soils adjacent to China as well as that of global fallout[21] and the present work are listed in Table 3. The data in the table show that the ratio for Xi'an coincides with that of the global fallout, whereas the isotopic ratio in the soil from Gansu deviates slightly. In consideration of the ^{239}Pu concentration being also much higher than the mean value of global fallout, it may be concluded that, aside from the global fallout, there is another unidentified source of plutonium in Gansu.

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