

# Determination of Pu, Am, U and Cs in large soil samples in the vicinity of the USDOE Waste Isolation Pilot Plant

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**Abstract** The determination of actinides in environmental soil and sediment samples are very important for environmental monitoring. A rapid actinide separation method has been developed and implemented that allows measurement of U, Pu and Am isotopes in large soil samples (10–15 g) with high chemical yields and effective removal of matrix interferences. The radiochemical procedures involve the total dissolution of soil samples, separation on anion-exchange resin, and separation and purification by extraction chromatography, e.g., UTEVA, TEVA, and TRU with measurements of radionuclides by alpha-spectrometry. The validation of the method is performed through the analysis of reference materials or by participating in laboratory intercomparison programs.

**Keywords** Large soil · Actinide · UTEVA · TEVA · TRU

## Introduction

The Waste Isolation Pilot Plant also known as WIPP is a deep underground geologic nuclear repository permitted to safely and permanently dispose of transuranic waste and mixed waste, generated through defense activities. Located near Carlsbad, New Mexico, an area with less than 30,000 people, the WIPP facility is the world's first underground repository licensed to accept TRU waste ( $>100$  nCi/g, but  $<23$  Ci/liter of  $^{239}\text{Pu}$ -equivalent). Nuclear waste was first received at WIPP on March 26, 1999. Mixed waste was first received by the WIPP in September, 2000 and high

activity waste, called remote handled waste or RH waste (surface dose rates  $>200$  mrem/h or 2 mSv/h), was first received at the beginning of 2007. TRU waste is disposed of 655 m (2,150 ft) below the surface in excavated disposal rooms in the Salado formation, which is a thick sequence of Permian Age evaporite salt beds.

Many factors contributed to the success of this project; an important one being environmental monitoring in the vicinity of the WIPP, both before and after WIPP began receiving nuclear waste. Monitoring is a key component for the development and operation of a nuclear repository and is important to the WIPP performance assessment. The goal of the WIPP-environmental monitoring (WIPP-EM) program is to determine if there is any release of contaminants during the pre-operational and disposal phases of the WIPP. Several monitoring programs are ongoing at WIPP but the Carlsbad Environmental Monitoring and Research Center (CEMRC), an independent monitoring facility, does health and environmental monitoring of the site for the public of Carlsbad. The air, drinking water, surface water, soil, sediments, vegetation and local population around the WIPP facility as well as air entering and exiting the WIPP underground are regularly analyzed at the CEMRC as part of the monitoring program. The baseline data of various anthropogenic radionuclides present in the WIPP environment either from global fallout as a result of nuclear weapons testing or Chernobyl type accidents have been established. These data are then compared against disposal phase data to assess the radiological and ecological effects of radiation on workers and the general public that live and work around the WIPP. The Gnome test site, about 8.8 km southwest of the WIPP site, is also a potential source of radionuclides. At this site a 3.3 kiloton yield nuclear underground detonation was conducted in 1961 as part of the Plowshare Program to demonstrate the peaceful use of

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atomic energy [1]. Following detonation, fission products vented from the underground; however, the plume traveled predominantly toward the northwest and the footprint of the plume suggests that measureable contamination of the WIPP site from the Gnome test is unlikely [2].

The present article is intended to present an overview of the radiochemical procedures that have been developed and used for the determination of the radionuclides present in soil samples in the vicinity of the WIPP site from the prospective of environmental monitoring and radiation protection. The WIPP soils are primarily characterized as sand, with some areas of gravelly loams, sandy loams and loamy sands [3]. The topography is generally monotonous with some areas having dune formations. Hummocks are frequently associated with the shrubs that occur throughout the region. A brief comparison of the radiochemical procedures used for the determination of transuranic nuclides in soil samples is also included to show major trends.

## Experimental

The resins used in this work are TEVA (Aliquot 336), TRU (TBP (tri *n*-butyl phosphate) and (CMPO [*N,N*-diisobutylcarbamoylmethylphosphine oxide])), and UTEVA (dipentyl pentyl phosphonate) obtained from Eichrom Technologies, Inc., (Darien Illinois). An anion exchange resin (Bio-Rad AG1-X8, 100–200 mesh, chloride form) is obtained from Bio-Rad, Hercules, CA, USA. The stock solutions of  $^{242}\text{Pu}$ ,  $^{243}\text{Am}$ , and  $^{232}\text{U}$  were prepared by gravimetric dilution from standards supplied by Analytix, Inc. (Atlanta, GA, USA).  $^{232}\text{U}$  tracer is prepared by removing its  $^{228}\text{Th}$  daughter using barium sulfate precipitation [4]. Nitric, perchloric and hydrochloric acid were prepared from reagent-grade acids (Fisher Scientific, Inc). All other chemicals were ACS reagent grade and dilutions were made with deionized water.

An alpha spectroscopy system (Oxford Oasis System, Oxford Instruments Inc.) equipped with 72 silicon surface barrier detectors (PIPS) connected to an EG&G ORTEC Alpha Vision software system was used for the acquisition, analysis, and storage of alpha spectra. Samples were counted for 5 days. Gamma analysis was conducted using a high purity (HPGe) detector. A set of soil matrix standards procured from Eckert and Ziegler, Analytix (GA) was used to establish matrix-specific calibration and counting efficiencies.

## Sampling procedures

A total of 16 samples were collected at three randomly selected sites within a 25 m radius of a reference point. Individual sampling sites were selected on the basis of

relatively flat topography, minimum surface erosion, and minimum surface disturbance by human or livestock activity. Approximately 4 L of soil were collected from within a 50 × 50 cm area, to a depth of approximately 2-cm for radionuclide analyses. Soil samples were excavated using a trowel and placed in plastic bags for transport and storage. Sampling equipment was cleaned between samples. Samples were sieved through a 1 mm mesh screen to remove rocks, roots, and other large material. The samples were homogenized by mixing and 50 and 450 g aliquots were removed for alpha and gamma-spectroscopy, respectively. The alpha and gamma aliquots were grounded with a ball mill prior to analysis.

## $^{137}\text{Cs}$ in soil

The samples for gamma analysis were sealed in a 300-mL paint-can and stored for at least 21 days to allow radon progeny to reach equilibrium with parent radionuclides before counting. Dried and sieved soil samples were counted for 48 h in a high purity germanium detector, HpGe (Canberra). The counting containers held ~500 g of soil. The samples were placed directly over a coaxial HpGe crystal.

## Dissolution of the solid samples

Soil samples were dried at 110 °C and blended prior to sampling. For actinides analyses, 10 g of sample were heated in a muffle furnace at 500 °C for at least 6 h or more to combust organic material. Each sample was then spiked with a radioactive trace and digested in a Teflon beaker with 30 mL of HCl, 10 mL of HNO<sub>3</sub> and 40 mL of HF. Sea sand was used as a matrix for Laboratory Control Standard (LCS) and reagent blank. The samples were heated at 250 °C for at least 2 h; longer heating does no harm. After digestion is complete, the samples were evaporated to dryness and 40 mL of HClO<sub>4</sub> was added and evaporated to complete dryness. This step was repeated once more with 30 mL of HClO<sub>4</sub>. Then 20 mL of HF were added and evaporated to dryness. To each beaker 80 mL of 8 M HNO<sub>3</sub>, 1.5 g of H<sub>3</sub>BO<sub>3</sub> and 0.5 mL of 30% H<sub>2</sub>O<sub>2</sub> were added, covered with a watch glass and heated to boiling for 30 min. After cooling, samples were transferred to a 50 mL centrifuge tube and centrifuged at 3600 rpm for 10 min. The leachate was filtered through a 0.45 μm filter and transferred to a 250 mL beaker.

## Actinides separation

The oxidation state of Pu was adjusted by adding 1 mL of 1.0 M NH<sub>4</sub>I with a 10 min wait step, followed by 2 mL of

$\text{NaNO}_2$ . The sample solutions were then ready for the purification procedure with anion exchange and by extraction chromatography. Next Pu was separated from Am and U using an anion exchange column. U was separated from Am on UTEVA and the Am subsequently purified from lanthanides with TEVA. Uranium fraction from UTEVA may be purified further (if needed) with anion exchange columns. Finally, Pu, Am and U were micro-coprecipitated on stainless steel discs for alpha spectrometry.

#### Separation of americium and uranium from plutonium

The 8 M  $\text{HNO}_3$  solution was then passed through large anion exchange (AG1-X8, 100-200 mesh,  $\text{Cl}^-$  form) columns (diameter  $\times$  10 cm long), which were pre-conditioned with 50 mL of 8 M  $\text{HNO}_3$ . The columns were washed with  $3 \times 15$  mL of 8 M  $\text{HNO}_3$ . Am(III) and U(VI) passed through the column (1.5 cm diameter  $\times$  10 cm long), and these effluents were kept for Am and U analysis. The columns were then washed with 40 mL of 10 M HCl to remove thorium. Pu(IV) converts to an anionic chloro-complex and was retained on the resin. The Pu was eluted with 30 mL of 0.1 M  $\text{NH}_4\text{I} + 8$  M HCl solution, where the iodide reduces Pu(IV) to Pu(III); then 3 mL concentrated  $\text{HNO}_3$  was added to the Pu strip and heated on a hotplate to expel excess iodine. Approximately, 2 drops of HF was then added and the Pu fraction was evaporated to dryness. The residue was dissolved in 4 mL of 2 M HCl and transferred to a 50 mL polycarbonate centrifuge tube with DI water. The samples were then micro-coprecipitated with Nd-carrier as in [5].

#### Separation of uranium from americium by UTEVA

The Am/U fractions from the 8 M  $\text{HNO}_3$  eluate of the first anion exchange resin column were evaporated to dryness, and then dissolved in 10 mL of 3 M  $\text{HNO}_3$ . An Eichrom-UTEVA column (2 mL, 100–150  $\mu\text{m}$ ) pre-conditioned with 5 mL of 3 M  $\text{HNO}_3$  was used for the separation of U from Am. The samples were then loaded into the column and washed with  $3 \times 10$  mL of 3 M  $\text{HNO}_3$ . The column was then washed with 10 mL of 9 M HCl to remove Np (if present) and this rinse converts resin to the chloride form. Am passed through the column, and these effluents were kept for Am analysis. U was stripped from the UTEVA column with 20 mL of 1.0 M HCl and evaporated to dryness. The residue was dissolved in 4 mL of 2 M HCl and transferred to a 50 mL polycarbonate centrifuge tube with DI water. The alpha sources were prepared by co-precipitation with an  $\text{NdF}_3$  as in [5].

#### Pre-concentration of americium by Ca-oxalate precipitation

The Am fraction from the UTEVA column was evaporated to ca 10 mL and diluted to 100 mL with DI water. Then 1 mL of 100 mg/mL of Ca in the form of  $\text{Ca}(\text{NO}_3)_2$  and 10 g of oxalic acid were added to each sample and the solutions were heated on a hot plate until complete dissolution (2 g for LCS and blank samples). Concentrated  $\text{NH}_4\text{OH}$  was added to pH 2 to form the Ca-oxalate precipitates. The solutions were centrifuged to separate the precipitates at 3600 rpm for 10 min. Finally, Ca-oxalate precipitates were dissolved in 20 mL of conc.  $\text{HNO}_3$  and evaporated to dryness.

#### Purification of americium by TRU

Samples were dissolved in 10 mL of 2 M  $\text{HNO}_3$ . Then 0.5 g of ascorbic acid was added to the solution to convert Fe(III) to Fe(II). The samples were then loaded into TRU column (2 mL, 100–150  $\mu\text{m}$ ) pre-conditioned with 10 mL of 2 M  $\text{HNO}_3$  and washed with  $3 \times 5$  mL of 2 M  $\text{HNO}_3$ . The columns were then washed with 10 mL of 2 M  $\text{HNO}_3 + 0.05$  M  $\text{NaNO}_2$  to oxidize any Pu(III) formed by the reduction of Pu(IV) with ascorbic acid back to Pu(IV). This prevents any Pu(III) from co-eluting with the Am(III) in 4 M HCl. The columns were then washed with 5 mL of 1 M  $\text{HNO}_3$ . Finally, Am was eluted with 2 mL of 9 M HCl followed by 15 mL of 4 M HCl. The Am strip from the TRU column was evaporated to dryness with 1 mL of 50%  $\text{H}_2\text{SO}_4$  to enhance destruction of any extractant in this solution and then with 3 mL of  $\text{HClO}_4$ .

#### Separation of americium from lanthanides by TEVA

The strip Am fraction from the TRU columns was redissolved in 10 mL of 3 M  $\text{NH}_4\text{SCN} + 0.1$  M  $\text{HCOOH}$ , warming gently as needed. The solution was loaded onto a TEVA cartridge (2 mL, 100–150  $\mu\text{m}$ ), previously conditioned with 10 mL of 3 M  $\text{NH}_4\text{SCN}$ . The column was washed with  $3 \times 4$  mL of 1.5 M  $\text{NH}_4\text{SCN} + 0.1$  M  $\text{HCOOH}$  to remove lanthanides present, which interfere with alpha spectrometry peak resolution. Finally Am was eluted with 15 mL of 2 M HCl and the remains of  $\text{NH}_4\text{SCN}$  were destroyed by heating with 8-10 mL of  $\text{HNO}_3$ : HCl (1:3). The solution was then evaporated to dryness with 3 mL of  $\text{HClO}_4$ . The residue was dissolved in 4 mL of 2 M HCl and transferred to a 50 mL polycarbonate centrifuge tube with DI water. The alpha sources were prepared by co-precipitation with  $\text{NdF}_3$  as in [5].

The Am fraction from the UTEVA column was evaporated to dryness and dissolved in 1 M  $\text{HNO}_3$  with Ca and oxalic acid to co-precipitate Am at pH 6 with 10 M NaOH.

The precipitate was dissolved in 2 M HCl and evaporated to dryness; then 10 mL of 6 M  $\text{NH}_4\text{SCN}$  was added and adjusted the solution pH to about 2.5. The solution was then loaded onto a TEVA cartridge (2 mL, 100–150  $\mu\text{m}$ ), previously conditioned with 10 mL of 3 M  $\text{NH}_4\text{SCN}$  + 0.1 M HCOOH. The column was then washed with  $3 \times 4$  mL of 1.5 M  $\text{NH}_4\text{SCN}$  + 0.1 M HCOOH to remove lanthanides present in the samples, which interfere with alpha spectrometry peak resolution. Finally, Am was eluted with 15 mL of 2 M HCl and the remains of  $\text{NH}_4\text{SCN}$  were destroyed by heating with 8–10 mL of  $\text{HNO}_3$ : HCl (1:3). The solution was then evaporated to dryness and re-dissolved in 1 mL of conc.  $\text{HNO}_3$ .

## Results and discussion

The results obtained by this method for simultaneous determination of U, Pu and Am in the soil samples collected during 2009 are presented in Table 1. The detection limit at one sigma limit was 0.004 Bq/kg. The average recoveries of Pu and Am were  $85 \pm 5\%$  and  $95 \pm 6\%$ . The blank analyses were performed to detect possible contamination from reagents, glassware and other sources during analytical procedures. None or only a few counts were observed in the alpha spectra of Pu, Am and U. The high yields indicate the reliability and robustness of the method. Pu and Am are the main constituents of the WIPP wastes. Activity concentrations of  $^{241}\text{Am}$  ranged in the surface soil

from 0.01–0.068 Bq/kg, while that of  $^{238}\text{Pu}$  varied from 0.006–0.035 Bq/kg. The range of  $^{239+240}\text{Pu}$  concentrations (0.021–0.24 Bq/kg) fell within the range reported by Kenney [2] at the WIPP site (0–0.74 Bq/kg). These values are lower than those measured at Hueston Woods and Urbana, Ohio (0.7–1.0 Bq/kg) [6] and between Ft. Collins and Colorado Springs, Colorado (0.6–1.7 Bq/kg) [7]. The concentrations of  $^{239+240}\text{Pu}$ ,  $^{238}\text{Pu}$ , and  $^{241}\text{Am}$  in Gnome soil were in the range 0.007–1550, 0.016–219 and 0.004–346 Bq/kg, respectively with an overall mean of 149, 28.8 and 36.1 Bq/kg [8]. The deposition of radioactive fallout from weapons testing is known to vary with latitude, being greatest in the middle latitudes of the northern hemisphere [9]. Fallout levels have also been shown to be correlated with precipitation [10]. The lower levels of  $^{239+240}\text{Pu}$  at the semi arid WIPP site may likely be due to the lower precipitation levels in this region as compared to the Ohio and Colorado sites, although some effect due to latitude cannot be ruled out. In addition, surface soil may show differences due to spatial variability in site-specific rates of vertical transport, bulk density and disturbances of surface soil after deposition.

Table 2 presents results of  $^{137}\text{Cs}$  measurement in the soil. The one sigma detection limit was 0.17 Bq/kg. Variability among the  $^{137}\text{Cs}$  concentrations is not very significant. Although  $^{137}\text{Cs}$  is a fission product, it is ubiquitous in soils because of global fallout from atmospheric weapons testing and nuclear accidents like Chernobyl [11, 12]. The activity concentrations of  $^{137}\text{Cs}$  ranged from 0.50–5.12 Bq/kg. The Gnome soil samples show elevated concentrations of  $^{137}\text{Cs}$  as compared to WIPP soil. The maximum

**Table 1**  $^{241}\text{Am}$  and  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  concentrations (Bq/kg) in Near Field Grid soil samples

Grid node	$^{241}\text{Am}$ (Bq/kg)	$^{238}\text{Pu}$ (Bq/kg)	$^{239+240}\text{Pu}$ (Bq/kg)
A-1	0.041 ± 0.009	0.141 ± 0.057	0.128 ± 0.018
A-2	0.028 ± 0.009	0.045 ± 0.030	0.106 ± 0.015
A-3	0.012 ± 0.008	0.062 ± 0.041	0.056 ± 0.011
A-4	0.007 ± 0.006	0.068 ± 0.038	0.071 ± 0.011
A-5	0.029 ± 0.007	0.120 ± 0.045	0.075 ± 0.013
A-5	0.036 ± 0.008	−0.114 ± 0.060	0.129 ± 0.017
A-6	0.007 ± 0.006	0.115 ± 0.057	0.021 ± 0.007
A-7	0.014 ± 0.008	0.290 ± 0.082	0.097 ± 0.015
A-8	0.043 ± 0.010	−0.044 ± 0.039	0.115 ± 0.013
B-1	0.027 ± 0.007	0.012 ± 0.026	0.090 ± 0.012
B-2	0.024 ± 0.008	0.073 ± 0.035	0.061 ± 0.010
B-3	0.067 ± 0.010	0.146 ± 0.059	0.238 ± 0.020
B-4	0.048 ± 0.011	0.194 ± 0.052	0.131 ± 0.016
B-4	0.068 ± 0.011	0.086 ± 0.038	0.154 ± 0.016
B-5	0.024 ± 0.008	0.048 ± 0.036	0.066 ± 0.013
B-6	0.003 ± 0.005	0.064 ± 0.034	0.011 ± 0.008
B-7	0.010 ± 0.004	0.081 ± 0.043	0.058 ± 0.011
B-8	0.047 ± 0.009	0.134 ± 0.042	0.133 ± 0.014

**Table 2**  $^{137}\text{Cs}$  concentrations (Bq/kg) in Near Field Grid soil samples

Grid node	Activity (Bq/kg)
A-1	3.45 ± 0.10
A-2	2.62 ± 0.07
A-3	1.72 ± 0.07
A-4	1.05 ± 0.06
A-5	2.02 ± 0.07
A-5	3.73 ± 0.10
A-6	0.50 ± 0.07
A-7	2.43 ± 0.07
A-8	2.80 ± 0.08
B-1	2.09 ± 0.08
B-2	1.66 ± 0.08
B-3	5.12 ± 0.10
B-4	3.33 ± 0.10
B-4	3.56 ± 0.09
B-5	1.33 ± 0.07
B-6	0.19 ± 0.07
B-7	0.80 ± 0.07
B-8	2.48 ± 0.08

observed concentration of  $^{137}\text{Cs}$  for the Gnome soil, 2980 Bq/kg [8], is about 1000 times larger than the largest concentration seen in the WIPP surface soil. Hodge et al. [7] suggest that the ratio of  $^{137}\text{Cs}/^{239+240}\text{Pu}$  from global fallout remains relatively constant through time. Perturbations in this ratio could result if the soil chemistry favored the downward migration of one these radionuclides or if there were a local source of one of the nuclides or both with a very different ratio. The average value of  $^{137}\text{Cs}/^{239+240}\text{Pu}$  for northern-hemisphere fallout is  $36 \pm 4$  (as of July 1995,  $^{137}\text{Cs}$  data in literature has been corrected to the sampling date of current study). Additionally, values of 33 and 30 (as of 1 July 1995) are reported from studies of fallout radionuclides in glaciers in Greenland and Antarctica [13], while “NTS-only” fallout values of 21 and 6 are reported for sediments taken from two reservoirs in Utah [14]. The mean ratio of  $^{137}\text{Cs}/^{239+240}\text{Pu}$  for the WIPP soil,  $24 \pm 2$  is lower than the northern hemisphere value of  $36 \pm 4$ . The lower ratio at the WIPP site suggests

contamination from sources other than fallout. The mean ratio of  $^{137}\text{Cs}/^{239+240}\text{Pu}$  for Gnome soil,  $3591 \pm 1635$ , was significantly greater than the WIPP soil.

The mean ratio of  $^{238}\text{Pu}/^{239+240}\text{Pu}$  from the WIPP samples (0.16) are not significantly different than the mean ratio for the Gnome samples ( $0.14 \pm 0.02$ ). In either case the  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios for both WIPP and Gnome exceed the global fallout ratio of  $\sim 0.061$  [15]. This ratio suggests that the fallout in the vicinity of the WIPP is a mixture of global fallout from thermonuclear devices and the local fallout from the above-ground testing at the Nevada Test Site (NTS).

A few examples of the concentrations of  $^{137}\text{Cs}$  and  $^{239+240}\text{Pu}$  in background and contaminated soils are presented in Table 3. The  $^{239+240}\text{Pu}$  concentrations near the WIPP site is about 0.2 Bq/kg. This is lower than the range reported for soils in Colorado and Utah [7, 14, 16]. Pu concentrations in surface soil from the first nuclear test site are 5 Bq/kg at 0–2.5 cm and 14 Bq/kg at 2.5–5.0 cm [17],

**Table 3**  $^{137}\text{Cs}$  and  $^{239+240}\text{Pu}$  activities in soils at various locations worldwide

Location	Year	Soil depth (cm)	$^{137}\text{Cs}$ (Bq/kg)	$^{239+240}\text{Pu}$ (Bq/kg)	References
Background					
WIPP site	1998	0–2	0.31–5.96	0.01–0.21	[18]
Trinity Site, New Mexico, control	1973	0–2.5	–	0.4	[17]
Searchlight	1995	0–1.5	0.7–13	0.06–0.5	[19]
Colorado, mid-state transect	1994	0–6.4	22–65	0.6–1.7	[7]
Rocky Flats, Colorado, control	1969–1970	0–1	–	0.4–2	[16]
Italy	1997	0–5	6–10	0.05–0.2	[20]
Utah	1979	0–2.5	22–70	0.3–0.8	[14]
Hanford, Washington	1988	0–2.5	12	0.3	[21]
		2.5–5.0	3	0.09	
		5.0–7.5	<1	0.02	
		0–2.5	14	0.3	
2.5–5.0	3	0.07			
Contaminated					
Trinity site, New Mexico	1973	0–2.5	–	5	[17]
		2.5–5.0	–	14	
		5.0–10	–	2	
Rocky Flats, Colorado	1969	0–0.3	–	77	[16]
		0.3–1.3	–	29	
		1.3–2.5	–	1	
Hanford, Washington	1988	0–2.5	56	8	[21]
		2.5–5.0	14	4	
		5.0–7.5	–	<1	
Queen City, Nevada	1995	0–1.5	0.8–41	0.10–51	[18]
Gnome site	2001	0–2.5	46–2980	0.07–1550	[12]
WIPP site	2009	0–2	0.50–5.12	0.02–0.24	PW
Bazagona, Spain	–	0–5	21.7	0.21	[22]
Palomares, Spain	–	0–5	8.2	11400	[22]

PW Present work

**Table 4** The results of measurement and traceability for MAPEP and NRIP soil samples

Nuclide	Massic activity (Bq/g) NIST value	Expanded uncertainty (%, $k = 2$ )	Massic activity (Bq/g) Our value	Expanded uncertainty (%, $k = 2$ )	Diff. ( $\pm\%$ )	Traceability limit ( $\pm\%$ )	ANSI (42.22) traceable
NRIP05-SS							
$^{241}\text{Am}$	1.055	0.63	1.025	9.268	-2.8	14	Yes
$^{238}\text{Pu}$	1.165	0.68	1.127	4.656	-3.3	6.8	Yes
$^{239+240}\text{Pu}$	1.102	0.68	1.078	5.251	-2.2	7.8	Yes
$^{234}\text{U}$	2.619	0.98	2.599	5.425	-0.75	8.2	Yes
$^{235}\text{U}$	0.125	0.62	0.137	14.728	+9.4	24	Yes
$^{238}\text{U}$	2.719	0.60	2.688	5.860	-1.1	8.7	Yes
MAPEP series 22	Reported value		MAPEP value		Evaluation rating		% bias
$^{241}\text{Am}$	0.0252		f		A		N/A <sup>c</sup>
$^{239+240}\text{Pu}$	0.18		0		N		d
$^{238}\text{Pu}$	24.6		24.1		A		2.1
$^{234}\text{U}$	57.2		60		A		-4.7
$^{235}\text{U}$	3.45		f		f		f
$^{238}\text{U}$	61.7		64		A		-3.6

MAPEP Mixed Analyte Performance Evaluation Program, *E* Evaluation rating (*A* acceptable, *W* acceptable with warning, *N* not acceptable), *c* cot applicable statistically zero result per MAPEP, *d* not applicable for non-detect per MAPEP, *f* information not provided by MAPEP

or an average of 10 Bq/kg compared to an average of about 18 Bq/kg in the top 5 cm of Queen City Summit soil (approximately 55 km north of the NTS, Nevada). Similar concentrations, approximately 8 Bq/kg, were found in the top 0–2.5 cm of soil from an inactive fuel reprocessing facility at Hanford, Washington. In addition, the  $^{137}\text{Cs}$  concentrations at the WIPP site are lower than for all sites listed in Table 3. The  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  concentrations in surface soil at WIPP are within the range of background concentrations measured in 1998 [18] and are typical “background soil”; the waste handling activities at the WIPP have not increased the level of these radionuclides. Table 4 shows the performance of the method on 10 g soil samples on MAPEP-10-MaS22 (Mixed Analyte Performance Evaluation Program, Department of Energy DOE-Radiological and Environmental Science Laboratory, Idaho Falls, ID, USA) and NIST-Radiochemistry Intercomparison Program (NIST-NRIP). The average Pu-242 tracer recovery was 77.5% and the average tracer recovery for Am-243 was 85.5%. Only one analysis result, which was for  $^{239+240}\text{Pu}$  in a soil matrix, did not meet the accuracy acceptance criteria. The number of acceptable ratings for the analysis of performance evaluation samples indicates that the procedure is appropriate for the accurate and reliable detection of low concentrations of radionuclides. The FWHM of the peak are about 50 keV each, which is very good for the co-precipitation technique. The radiochemical procedures commonly used for the determination of transuranic nuclides in soil/sediments matrices are listed

in Table 5. Acid leaching/fusion seem to be commonly used methods for the dissolution of large soil samples (>5 g), while for small soil samples (1–2 g), microwave digestion seems to be a method of choice. A combination of anion exchange and chromatography columns for separation followed by counting on alpha spectrometry and/or ICP is the most commonly used process for the determination of transuranic nuclides in the soil samples.

## Conclusion

The sequential method based on the advantages of anion-exchange resin and extraction chromatography is used for the determination of actinides in soil samples. The proposed procedure proved to be a good method for the determination of U, Pu and Am in soil samples. The method is very reliable in terms of overall chemical recovery, alpha spectrum and bias to the reference values. The  $^{137}\text{Cs}/^{239+240}\text{Pu}$  and  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratios in the soil samples suggest that the Pu and Cs in the WIPP environment originated mainly from global fallout from thermonuclear devices and local fallout from above-ground testing at the Nevada Test Site, although contamination of WIPP soil from the Gnome test remains a possibility. The monitoring results indicate that there is no evidence of increased radiological contamination in the region of the WIPP that could be attributed to release from the WIPP.



**Table 5** Comparison of the condition use in the separation of actinides by various ion exchange and chromatography columns

Actinides	Digestion	Co-ppt./ pre-concen.	Analyte	Resin(s)	%Yield	References
Soil, sediment, 5 g	LiBO <sub>2</sub> fusion	–	Pu, Np	TEVA	50–80	[23]
Soil, sediment, 10 g	Dissolution/leaching	DIPHONIX	U, Th, Pu, Am	UTEVA (U, Th) TRU (Pu, Am) TEVA (Am)	85	[24]
Soil, sediment, 1 g	LiBO <sub>2</sub> fusion	(1) Fe(OH) <sub>2</sub> , (2) CaF <sub>2</sub>	U, Th, Np, Pu, Am	(1) UTEVA, (2) TRU	>85 >80	[25]
Soil, 2–50 g	Leaching 8 M HNO <sub>3</sub>	–	Pu	TEVA	89	[26]
Soil, 5–10 g	NaOH fusion	Fe(OH) <sub>3</sub> –BaCO <sub>3</sub> – CeF <sub>3</sub>	Actinides	TEVA–TRU–DGA	ca. 100	[27]
Soil, sediment, 1–5 g	Borate fusion	TOPO extraction	Pu, Am	TEVA (Pu) TEVA–TRU (Am)	93	[28]
Soil, 1 g	Fusion Na <sub>2</sub> CO <sub>3</sub> – K <sub>2</sub> CO <sub>3</sub> + H <sub>3</sub> CO <sub>3</sub>	Chelex resin pH 3.4	Pu	UTEVA	88	[29]
Soil, 30 g	Leaching 7.5 M HNO <sub>3</sub> + 0.2 M HF	–	Pu, Am, Sr	Pu: microtheneTOA Am: HDEHP column with DTPA + LA;	85	[30]
Soil, 10 g	Acid digestion	none	Pu, Am, Sr	Pu: anion Am: Ca-oxalate, TRU	>80	[31]
Soil, sediment, 1–4 g	Conc. HNO <sub>3</sub>	–	Np, Pu	TEVA	86–96	[32]
Soil, sediment, 2 g	Li-borate Fusion LiBO <sub>2</sub> :Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	–	Pu	TEVA UTEVA–TRU	73–83 60–81	[33]
Soil, 0.5–3 g	Microwave	CaF <sub>2</sub> /NH <sub>2</sub> OH	Pu	UTEVA, TRU	>80	[34]
Soil, 0.5–3 g	Microwave	CaF <sub>2</sub> /NH <sub>2</sub> OH	Pu, Am	UTEVA, TRU	81–94	[35]
Soil, 100–200 g	Leaching/NaOH Fusion	–	Pu, Am, Cm	TEVA (Pu) TRU-DGA (Am, Cm)	80–95	[36]
Soil, sediments, 5 g	(1) Leaching (2) Fusion (3) Microwave	Ca-oxalate	Sr, U, Th, Pu, Am	UTEVA (U, Th) Anion(Pu) TRU, anion-cation(Am)	–	[37]
Soil, 25 g	Leaching 8 M HNO <sub>3</sub> NaOH fusion	Fe(OH) <sub>3</sub> Ca-Oxalate	Pu, Am, Sr, Cs	Pu: anion + HTTA extraction. Am: Ca-oxalate, TRU/anion column	–	[38]
Soil, 50 g	Leaching 8 M HNO <sub>3</sub> , then with 6 M HCl	None	Pu	Pu: anion exchange	50–70	[39]
Soil, sediments, 10 g	Leaching, Conc. HNO <sub>3</sub>	Ca-oxalate	Np, Pu, Am Sr	Np, Pu: anion exchange Am: Ca-oxalateTRU Sr: Sr resin	40–61 66 67	[40]
Soil, 2 g	Acid leaching (HNO <sub>3</sub> , HCl, HF)	None	Pu, Am	Pu: microthene-TOA column Am: Gamma spec.	–	[41]

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