

INTERCOMPARISON STUDY ON ^{241}Pu DETERMINATION IN SEQUENTIALLY EXTRACTED FRACTIONS OF TRANSURANICS IN SAMPLES ARISING FROM DECOMMISSIONING ACTIVITIES

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ABSTRACT. Activity concentrations of ^{241}Pu and other transuranics were determined in different fractions (water soluble, readily available or physically bound, carbonate bound or specifically adsorbed, bound to organic matter, bound to Fe and Mn sesquioxides, and residual) of mud taken from a radioactive waste storage deposit and from solid residue accumulated in a pipe of the liquid effluent system. Two sets of extractants were used at the Department of Radiochemistry and Colloid Chemistry of Maria Curie Skłodowska University (UMCS) and CIEMAT laboratories, along with different procedures concerning reagent concentrations, shaking time, temperature, and order of reagent extraction. ^{241}Pu measurements in the fractions were performed directly by liquid scintillation counting (LSC) and indirectly via alpha spectrometry by quantifying ^{241}Am ingrowth from old Pu discs. In addition to these investigations, alpha-emitting plutonium and americium isotopes were also determined and compared. The results show that direct measurement of beta-emitting plutonium via LSC yields more accurate results than indirect calculation via its descendant, ^{241}Am . The distribution percentages of transuranics bound to the extracted fractions are presented, indicating that iron and manganese oxides are the most important phases for Pu fixation. The influence of the extraction procedure employed on radionuclide distribution among the different fractions is also discussed.

INTRODUCTION

Recently, some of the nuclear and radioactive facilities from CIEMAT, which were used in the past for nuclear energy production, were decommissioned as part of a global dismantling project. This project involves several phases, including radiological characterization activities, removal of contaminated materials as radioactive waste, and site clean-up.

One of the places affected by this dismantling project is a former laboratory where transuranics were handled. During its radiological characterization, a significant contamination of actinide elements was found in the old liquid effluents system. The most contaminated locations were several metal pipes and an underground brick-built liquid deposit, in which a dry mud enriched in transuranics had accumulated over several years.

Samples from these pipes and the liquid deposit were collected and analyzed using various sequential leaching procedures to obtain information about the actinide association with certain geochemical phases with different solubility, and thus to choose the most suitable clean-up method. The proposed cleaning protocol would be applied to the brick walls once the majority of the contaminated mud is removed from the deposit.

The methods presented in this paper provide information about the availability of a given element without further knowledge of its chemical speciation (Tessier et al. 1979; Rauret 1998). The following phases were isolated: exchangeable or adsorbed ion fraction (which are released by neutral salts, such as MgCl_2 or CaCl_2 , i.e. ion-exchange competition reactions); carbonate-bound fraction (extractable with acetic acid or acetic buffer); organic matter-bound fraction (separated by oxidizing destruction with H_2O_2 or complexing with alkaline solution of sodium pyrophosphate); a fraction bound to hydrous sesquioxides of Fe and Mn (released by means of ammonium oxalate or by reduction with hydroxyl-amine hydrochloric); and finally, a residual fraction (almost insoluble silicates,

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such as clay minerals). The fractions obtained via the different exchange/dissolution steps are also strongly dependent on i) the ratio of solid:extractant, ii) the extraction temperature, iii) the extractant employed in each phase, iv) the contact time between solid/liquid phase, v) the stirring method used, vi) the environmental conditions (oxic-anoxic), and vii) the reagents for stabilizing transuranics in the extractant, among other factors.

This paper presents part of a collaborative study between the Department of Radiochemistry and Colloid Chemistry of the Marie Curie Skłodowska University (UMCS) and CIEMAT laboratories, carried out with the objective of intercomparing transuranic sequential leaching methods applied to samples from dismantling operations. This research focuses on comparing the ^{241}Pu determination methods in the extracted fractions. Even though ^{241}Pu is not the main contributor to the radioactive dose, its high activity concentration in the selected samples, “mud” and “pipe residue,” allows us to take small aliquots for analysis in each extraction step and to test the measurement techniques.

EXPERIMENTAL

Two samples were taken from 2 locations of the liquid effluent system: a dry mud stuck to the walls of the collecting tank (200 g) and a solid residue from the inside of a pipe (50 g) that transported the liquids from the laboratory to the tank.

Pretreatment

The samples were milled in 2 different porcelain mortars and stored. Before splitting the sample for the labs (A and B), several experiments were performed in CIEMAT to i) test a rapid procedure for Pu, Am, and total alpha determination (10 g); ii) check the total ^{241}Am concentration activity in the whole sample (50–200 g) by nondestructive analysis; and iii) prove total dissolution in a microwave oven with different acids (Álvarez et al. 2005; Gascó et al. 2003). The transuranic contents are shown in Table 1. A set of these samples was analyzed by each of the laboratories mentioned above, following different analytical and sequential extraction procedures.

Table 1 Analysis results of different aliquots of the mud and pipe residue samples.

Sample	Aliquot size	$^{239,240}\text{Pu}$ Bq/g $\pm 1 \sigma$	^{241}Am Bq/g $\pm 1 \sigma$
Mud	Whole (200 g)	—	38.0 ± 1.0
	Aliquot (50 g)	—	19.0 ± 0.9
	Totally dissolved (0.38 g)	55.70 ± 3.9	20.1 ± 0.6
	Totally dissolved (0.9 g)	5.15 ± 0.72	—
	Sequential leaching (Total) 0.5 g	3.45 ± 0.19 (Lab A) 18.37 ± 0.38 (Lab B)	6.18 ± 0.21 (Lab B)
Pipe	Whole (50 g)	—	7.9 ± 0.6
	Totally dissolved (0.5 g)	20 ± 1	6.3 ± 0.3
	Sequential leaching (Total) 1.2 g	4.43 ± 0.44 (Lab A) 18.9 ± 0.6 (Lab B)	5.15 ± 0.36 (Lab A) 6.31 ± 0.14 (Lab B)

Sequential Leaching Methods

Two sequential extraction procedures (Method A and Method B) were applied to the radioactive samples of mud and pipe residue. Method A is currently used by the UMCS (Komosa 2002) and Method B is used by the Radioecology Laboratory of CIEMAT (Antón et al. 1994).

A summary of both methods is shown in Tables 2 and 3. They differ in the type of extractants employed, the extraction sequence (Method A obtains the oxide fraction prior to the organic phase and vice versa for Method B), the temperature, the solid:extractant ratios, and the means of extraction. Method A is based on the modified Tessier procedure (Tessier et al. 1979; Rauret 1998; Komosa 2002; Haque and Nakanishi 1999) and Method B on the procedure by Cook et al. (1984).

After sequential extraction, Pu and Am isotopes were analyzed in each fraction by alpha spectrometry. ^{242}Pu and ^{243}Am were added as tracers to each aliquot of the extracted fractions.

Table 2 Summary of the sequential leaching method (Method A) applied at the UMCS laboratory for the mud and pipe residue samples.

Fraction	Order	Time (hr)	Temp (°C)	Extracting reagent ^a (shaking)	Solid:liquid ratio
Water soluble	1	0.5	20	H ₂ O	1:60
Available	2	1	20	a) 1M MgCl ₂	1:20
		1	20	b) 1M MgCl ₂	1:20
Exchangeable/carbonates	3	5	20	a) 1M HAc/1M NaAc	1:20
		5	20	b) 1M HAc/1M NaAc	1:20
Oxides Fe/Mn	4	6	96	a) 0.04M NH ₂ OH.HCl/25% HAc	1:20
		2	96	b) 0.04M NH ₂ OH.HCl/25% HAc	1:20
Organic matter	5	2	85	a) 0.02M HNO ₃ /H ₂ O ₂	1:32
		2	85	b) H ₂ O ₂	1:12
		0.5	20	c) 3.2 M NH ₄ Ac/20% HNO ₃	1:12
Residual	6	1	100	6M HCl	1:200

^aHAc = acetic acid; NaAc = sodium acetate.

Table 3 Summary of the sequential leaching methods applied at the CIEMAT laboratory for the mud and pipe residue samples. Results for the mud sample are in parentheses.

Fraction	Order	Time (hr)	Temp (°C)	Extracting reagent ^a (stirring)	Solid:liquid ratio; pipe (mud)
Water soluble	1	6 (18)	20–25	H ₂ O	1:80 (1:200)
Available	2	6 (20)	20–25	0.05M CaCl ₂	1:80 (1:70)
Exchangeable/carbonates	3	6 (6)	20–25	0.5M HAc	1:80 (1:70)
Organic matter	4	6 (7)	20–25	0.1M Na ₄ P ₂ O ₇	1:80 (1:80)
Oxides Fe/Mn	5	6 (14)	20–25	0.1M H ₂ C ₂ O ₄ /0.175M (NH ₄) ₂ C ₂ O ₄	1:80 (1:80)
Residual	6	48	>100	8M HNO ₃ (3×)	1:100 (1:200)

^aHAc = acetic acid; NaAc = sodium acetate.

Radiochemical Procedures

Different radiochemical standard procedures for transuranic determination were employed by the 2 laboratories involved.

^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am Determination Methods

CIEMAT. Purification of Pu was carried out via 2 columns: one containing an anion-exchange resin AG 1×8 (20–50 mesh) in 8M HNO₃ medium and the second one with AG 1×8 (50–100 mesh) in 10M HCl (Gascó 1992). Am was then isolated using TRU and TEVA extraction chromatography resins or directly measured in every fraction by means of its gamma emission at 59.5 keV, using an HPGe detector with a 20% relative efficiency.

UMCS. Plutonium was initially coprecipitated with $\text{Fe}(\text{OH})_3$ and separated from the remaining transuranics and alpha emitters using an ionic resin Dowex 1×8 (50–100 mesh) in 8M HNO_3 , 12M HCl, and 12M HCl/0.1M NH_4I media (Komosa 1999). Am was then isolated utilizing 2 Dowex 1×8 columns for removing Fe ions (elution with 8M HNO_3) and for Am purification with 1M HNO_3 /93% methanol dissolutions. The rare earth metals were removed by means of a 80% methanol/0.1M HCl/0.5M NH_4SCN solution and the Am was eluted in a 86% methanol/1.5M HCl medium. Finally, these radionuclides were electroplated onto stainless steel discs and counted by high-resolution alpha spectrometry with PIPS detectors in both methods.

²⁴¹Pu Determination Methods

Determining ²⁴¹Pu is complicated due to the presence of a complex mix of radionuclides and the elapsed time that is needed to wait for its indirect determination. ²⁴¹Pu measurements in the extracted fractions were performed by direct liquid scintillation counting (LSC) and indirectly by alpha spectrometry, quantifying the ²⁴¹Am ingrowth from old plutonium discs.

CIEMAT. Beta-emitting ²⁴¹Pu was determined indirectly by the ingrowth of ²⁴¹Am in the old plutonium discs from each extracted fraction. The ²⁴¹Am growth could not be directly determined on the old discs via a second measurement after enough time lapsed. The impossibility of detecting a significant increase of ²⁴¹Am—and therefore quantifying it with enough sensibility—made it necessary to carry out a chemical separation once plutonium and americium were recovered from the discs. This was achieved using a 8M HNO_3 hot solution (4×). Americium was isolated from plutonium by extraction chromatography using TRU resin (Eichrom) (Gascó 1994; Gascó et al. 1997). The ingrowth elapsed time was 6 months for the mud sample and 1 yr for the pipe residue sample.

UMCS. The electroplated plutonium was removed from the sample discs using 8M nitric acid according to procedure described by Pimpl (1992). The obtained solution was evaporated to dryness and plutonium was extracted with 0.2M TOPO dissolved in cyclohexane (from 4M HNO_3). The organic phase was transferred into a Teflon®-coated scintillation vial (Zinsser) for LSC measurement.

Measuring Equipment and Quantification

Alpha Spectrometry

CIEMAT. The plutonium and americium discs obtained in each fraction were counted for 600,000 s in a CANBERRA Alpha-Analyst spectrometer with a 450-mm² PIPS detector (10% counting efficiency) and Genie™ 2000 software (www.canberra.com).

The activity concentration of ²⁴¹Pu (A_{Pu-241}) was calculated via the ²⁴¹Am ingrowth, applying the progeny/progenitor disequilibrium relationship valid for the boundary condition, which states that insignificant daughter nuclides were present initially at time $t = 0$:

$$A_{Pu-241} = \frac{\lambda_{Am-241} - \lambda_{Pu-241}}{\lambda_{Am-241}} \cdot \frac{A_{Am-241}}{(e^{-\lambda_{Pu-241} \cdot t} - e^{-\lambda_{Am-241} \cdot t})}$$

where A_{Am-241} = activity concentration of ²⁴¹Am found after separation from plutonium in an old disc; t = elapsed time between separation of plutonium and americium in an AG 1×8 (20–50 mesh) column and separation of americium with TRU resins in the old disc; and λ = decay constant.

The ^{241}Pu detection limit ranges from 0.05 to 106 Bq/g depending on the aliquot taken for the analysis of each fraction, the elapsed time between both separations, and the chemical recovery.

UMCS. Determination of alpha-emitting isotopes was performed by 2 alpha spectrometers, Model 7401 with 300-mm² PIPS detectors (counting efficiency 35%), mixer/router 1520, and Genie 2000 software. The counting time was 600,000 s for the MDA of ~0.2 mBq per sample.

Liquid Scintillation Spectrometry

UMCS. The ^{241}Pu activity concentration and total alpha activity concentration were determined by means of an ultra low-level liquid scintillation (LS) spectrometer, Quantulus 1220TM. Permablend[®] III (Packard) dissolved in scintillation-grade toluene (Merck) (7 g·dm⁻³) was used as the scintillation cocktail. The quenching was corrected according to the tritium curve, with improvements done by E Günter (private communication, 2001). The activity concentration of ^{241}Pu (Bq/g) was calculated using the following equation:

$$A_{\text{Pu-241}} = \frac{N_{LSC\beta} \cdot N_{SP\alpha} \cdot A_{242}}{N_{LSC\alpha} \cdot m \cdot E_{LSC} \cdot N_{242SP\alpha}}$$

where $N_{LSC\beta}$ = count rate of beta radiation by LS spectrometer in the channel range 2–265 (cpm); $N_{LSC\alpha}$ = count rate of alpha radiation by LS spectrometer in the channel range 600–805 (cpm); $N_{SP\alpha}$ = total count rate of alpha radiation as measured by alpha spectrometry with a PIPS detector (cps); E_{LSC} = counting efficiency of ^{241}Pu by LS spectrometer, calculated with tritium standard; $N_{242SP\alpha}$ = count rate of alpha radiation of the tracer ^{242}Pu by alpha spectrometry (cps); m = mass of sample (g); A_{242} = tracer ^{242}Pu activity (Bq). Background was subtracted from all count rate values.

We assumed that the LS counting efficiency of alpha-emitting Pu isotopes was equal to 100% and the chemical loss of plutonium during redissolution of electroplated material and transferring it into the LS vial was negligible. The chemical yield and counting efficiency of alpha spectrometry, in the equation above, was eliminated by relating it to the activity of the ^{242}Pu tracer added and the count rate of the tracer measured by alpha spectrometry.

RESULTS AND DISCUSSION

The ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Pu , and ^{241}Am sequential leaching results (pipe residue sample) and ^{241}Pu (mud sample) are presented in this section. A similar sequential extraction analysis was carried out on the mud sample. The results corresponding to the transuranic concentration levels in each of the extraction fractions were shown previously (Álvarez et al. 2005; Gascó et al. 2003).

The transuranic content in the analyzed samples is likely heterogeneous. For this reason, the discussion of results is based on the transuranic percentages associated with each phase and their activity concentrations in the extracted fractions.

The plutonium distribution among different phases from the pipe residue sample is shown in Tables 4, 5, and 6. The percentages of the extracted plutonium in each phase were different depending on the method.

The sum of the percentages of plutonium associated with the “water-soluble,” “easily available,” and “carbonates” fractions were 12% ($^{239,240}\text{Pu}$), 10% (^{238}Pu), and 3% (^{241}Pu) for Method A and 7.5% ($^{239,240}\text{Pu}$), 8% (^{238}Pu), and 7.5% (^{241}Pu) for Method B. Considering their uncertainties, it can be noted that both methods extract approximately the same quantity of “easily extractable” plutonium.

By analyzing the plutonium linked to the oxides phase (iron and metals oxides are the main compounds of the matrix), we found that 40% of $^{239,240}\text{Pu}$, 29% of ^{238}Pu , and 61% of ^{241}Pu were associated with this fraction (Method A), as well as up to 52% of the 3 plutonium isotopes in Method B. Both methods are in good agreement for the oxide phase when their uncertainties are taken into account.

The percentage of plutonium isotopes associated with the organic phase is 4–6 times higher when Method A is applied: 34.7% ($^{239,240}\text{Pu}$), 41% (^{238}Pu), and 22% (^{241}Pu) for Method A and 5.2% ($^{239,240}\text{Pu}$ and ^{241}Pu) and 6.5% (^{238}Pu) for Method B.

The incorporated plutonium in the residual phase was 14.1% ($^{239,240}\text{Pu}$), 18.8% (^{238}Pu), and 14.6% (^{241}Pu) for Method A and 36% ($^{239,240}\text{Pu}$), 35% (^{238}Pu), and 36% (^{241}Pu) for Method B. Method B recognizes double the quantity of plutonium linked to the residual phase.

The protocol utilized here should extract the whole plutonium existing in the tested matrix and, therefore, allows us to compare its effectiveness on the radionuclide leaching. Thus, we can compare the capability of each extractant for stripping the plutonium of a specific phase. Assuming that methods A and B are strong enough for removing them—even though the total plutonium was not the same in the 2 aliquots—a certain possibility of cross-contamination occurs in the main phases. Method A overvalues the plutonium linked to the organic phase and underestimates the plutonium associated with the residual phase when compared to Method B; both methods quantify approximately an equal amount of plutonium associated with the oxide fraction and more “soluble” fractions.

The obtained activity concentrations in each fraction are comparable except in the oxide and residual fractions. Method A leaches 1.743 ± 0.080 ($^{239,240}\text{Pu}$) Bq/g and 0.035 ± 0.011 (^{238}Pu) Bq/g in the oxide phase, and Method B leaches 9.73 ± 0.80 Bq/g ($^{239,240}\text{Pu}$) and 0.373 ± 0.068 Bq/g (^{238}Pu). Method B would extract 1 order of magnitude more plutonium than Method A. This happens also in the residual phase, where the concentrations for plutonium isotopes are 0.623 ± 0.080 Bq/g ($^{239,240}\text{Pu}$) and 0.022 ± 0.001 Bq/g (^{238}Pu) for Method A, and 6.80 ± 0.78 Bq/g ($^{239,240}\text{Pu}$) and 0.261 ± 0.064 Bq/g (^{238}Pu) for Method B—also an order of magnitude higher. Something similar but in lower proportion (double the quantity for Method B in the oxide phase and 5 times the quantity extracted by Method B in the residual fraction) can be observed for ^{241}Pu concentrations in both phases: oxide fraction (10.1 ± 7.0 Bq/g for Method A and 21.4 ± 7.0 Bq/g for Method B) and residual fraction (2.4 ± 0.7 Bq/g for Method A and 15.0 ± 5.6 Bq/g for Method B).

Table 4 $^{239,240}\text{Pu}$ concentrations in the pipe residue sample following 2 different sequential extraction methods.

Extracted fraction	Method A		Method B	
	$^{239,240}\text{Pu} \pm 1 \sigma$ (Bq/g)	$^{239,240}\text{Pu} \pm 1 \sigma$ (%)	$^{239,240}\text{Pu} \pm 2 \sigma$ (Bq/g)	$^{239,240}\text{Pu} \pm 2 \sigma$ (%)
Water soluble	0.009 ± 0.002	0.20 ± 0.07	0.083 ± 0.016	0.440 ± 0.089
Easily available	0.011 ± 0.002	0.25 ± 0.07	0.125 ± 0.020	0.66 ± 0.11
Carbonate	0.504 ± 0.029	11.4 ± 1.8	1.21 ± 0.21	6.4 ± 1.2
Oxides Fe/Mn	1.743 ± 0.080	39.4 ± 5.9	9.73 ± 0.80	51.4 ± 5.2
Organic	1.537 ± 0.080	34.7 ± 5.3	0.99 ± 0.12	5.20 ± 0.71
Residual	0.623 ± 0.020	14.1 ± 1.8	6.80 ± 0.78	35.9 ± 4.6
<i>Total</i>	4.43 ± 0.44	<i>100</i>	18.9 ± 1.1	<i>100</i>

Table 5 ^{238}Pu concentrations in the pipe residue sample following 2 different sequential extraction methods.

Extracted fraction	Method A		Method B	
	$^{238}\text{Pu} \pm 1 \sigma$ (Bq/g)	$^{238}\text{Pu} \pm 1 \sigma$ (%)	$^{238}\text{Pu} \pm 2 \sigma$ (Bq/g)	$^{238}\text{Pu} \pm 2 \sigma$ (%)
Water soluble	0	0	0.0084 ± 0.0033	1.13 ± 0.47
Easily available	0	0	0.0082 ± 0.0029	1.10 ± 0.42
Carbonate	0.013 ± 0.003	10.5 ± 4.4	0.043 ± 0.031	5.8 ± 4.2
Oxides Fe/Mn	0.035 ± 0.011	29 ± 15	0.373 ± 0.068	50.0 ± 11
Organic	0.049 ± 0.007	41 ± 13	0.048 ± 0.022	6.5 ± 3.1
Residual	0.022 ± 0.001	18.8 ± 4.5	0.261 ± 0.064	35.2 ± 9.8
<i>Total</i>	<i>0.119 ± 0.018</i>	<i>100</i>	<i>0.74 ± 0.10</i>	<i>100</i>

Assuming that the sample had the same quantity of plutonium, the extractants (Method B) are strong enough to remobilize the plutonium existing in the residual and oxide fractions, and Method A would only leach 25% of the total plutonium present in the matrix. The extraction with 6M hydrochloric acid (1×) is not as effective as hot 8M nitric acid (3×) in stripping the plutonium. The existence of highly “unleachable” plutonium cannot be discarded in this type of sample.

Two different explanations (or both) are possible when the extraction percentages and concentration activities are jointly analyzed:

a) Both laboratories analyzed a heterogeneous sample (different plutonium content). The plutonium would have been deposited heterogeneously in the matrix (iron and metals oxides are the main compounds in the pipe residue) and associated with identical phases. The total activities are different (4.43 ± 0.44 Bq/g and 18.9 ± 1.1 Bq/g [$^{239,240}\text{Pu}$]), but the extraction percentages would be comparable in all the fractions. Method B extracts the plutonium associated with the residual phase more efficiently than Method A does with the organic fraction; this is likely due to a cross-contamination among the main phases (organic/oxide, organic/residual) when analyzing.

b) Both laboratories analyzed a homogeneous sample with the same plutonium content (18.9 Bq/g). The plutonium existing in the sample would have been homogeneously spread in the matrix and would be in a chemical form that would not be easily removable. Method A would only extract 25% of the total plutonium, and the remaining 75% in the residue could not be leached with hydrochloric acid. Method B is more effective in removing the plutonium from the residual phase in this particular matrix. The hypothesis of the presence of “hot particles” or “highly insoluble” plutonium cannot be rejected in these kinds of samples due to their origin.

Table 7 shows the ^{241}Am sequential leaching extraction results. An analogous interpretation can be done when analyzing the americium distribution in the different phases, although in this case the total content of americium is similar (5.15 ± 0.36 Bq/g for Method A and 6.31 ± 0.28 Bq/g for Method B).

The americium linked to each phase is in a better agreement for both methods (A and B) compared to plutonium. Americium was associated with the sum of “water soluble,” “easily available,” and “carbonate” phases: 21% for Method A and 19% for Method B. Americium was linked to the oxide phase, 62% for Method A and 41% for Method B, and to the organic phase as 6.9% (A) and 7.9% (B). The main difference is found in the residual phase (9% for Method A and 32% for Method B), pointing once again to the strength of the different acids used to strip the americium in this final step.

Table 6 ^{241}Pu concentrations in the pipe residue sample following 2 different sequential extraction methods and 2 different measurement techniques (reference date: Feb 2005).

Extracted fraction	Method A (direct LSC measurement)		Method B (by ^{241}Am ingrowth)	
	$^{241}\text{Pu} \pm 1 \sigma$ (Bq/g)	$^{241}\text{Pu} \pm 1 \sigma$ (%)	$^{241}\text{Pu} \pm 2 \sigma$ (Bq/g) (calculated) ^a	$^{241}\text{Pu} \pm 2 \sigma$ (%)
Water soluble	0.007 ^b	0.04	0.18 ± 0.07	0.43 ± 0.20
Easily available	0 ^b	—	0.27 ± 0.11	0.66 ± 0.30
Carbonate	0.44 ± 0.50	2.6 ± 3.0	2.7 ± 1.1	6.4 ± 2.9
Oxides Fe/Mn	10.1 ± 7.0	60.8 ± 42	21.4 ± 7.8	51 ± 22
Organic	3.7 ± 3.4	22 ± 21	2.18 ± 0.82	5.2 ± 2.3
Residual	2.4 ± 0.7	14.6 ± 4.2	15.0 ± 5.6	36 ± 16
<i>Total</i>	<i>17 ± 16</i>	<i>100</i>	<i>41.7 ± 9.7</i>	<i>100</i>

^aThese values were calculated by applying the $^{241}\text{Pu}/^{239,240}\text{Pu}$ ratio of the Fe/Mn oxide-bound fraction to the extracted aliquots; ^{241}Pu was detected only in this fraction.

^bValue below the minimum detectable amount.

Table 7 ^{241}Am concentrations in the pipe residue sample following 2 different sequential extraction methods.

Extracted fraction	Method A (alpha spectrometry)		Method B (gamma spectrometry)	
	$^{241}\text{Am} \pm 2 \sigma$ (Bq/g)	$^{241}\text{Am} \pm 2 \sigma$ (%)	$^{241}\text{Am} \pm 2 \sigma$ (Bq/g)	$^{241}\text{Am} \pm 2 \sigma$ (%)
Water soluble	0	0	0.082 ± 0.051	1.3 ± 0.8
Easily available	0	0	<0.09	
Carbonate	1.108 ± 0.073	21.5 ± 2.8	1.1 ± 0.1	17.5 ± 1.8
Oxides Fe/Mn	3.22 ± 0.15	62.6 ± 6.9	2.59 ± 0.18	41.1 ± 3.4
Organic	0.358 ± 0.029	6.9 ± 1.0	0.50 ± 0.07	7.9 ± 1.2
Residual	0.460 ± 0.031	8.9 ± 1.2	2.04 ± 0.17	32.4 ± 3.0
<i>Total</i>	<i>5.15 ± 0.36</i>	<i>100</i>	<i>6.31 ± 0.28</i>	<i>100</i>

Method A underestimates the content of ^{241}Am in the residual phase and slightly overvalues the percentage in the oxide phase.

When studying the americium concentration activity concentrations, the ^{241}Am content is similar in all phases except in the residual phase (0.460 ± 0.031 Bq/g in Method A and 2.04 ± 0.17 Bq/g in Method B). Only 4 times more americium is leached with Method B, far from the 1 order of magnitude observed in the plutonium extraction experiments. This can happen because the americium would be more “leachable” than plutonium for both types of acid attack of the residual fraction. Method A would extract the americium less efficiently (82%) from the sample, although better than the plutonium (25%), assuming that the sample was homogenous in americium content. The results of the ^{241}Pu sequential leaching in the mud sample are presented in Table 8.

The total quantities of ^{241}Pu obtained for the 2 laboratories in the mud sample are 14 ± 9 Bq/g for UMCS and 32 ± 7 Bq/g for CIEMAT. The arguments explaining the percentages of $^{239,240}\text{Pu}$ and

Table 8 ²⁴¹Pu concentrations in the mud sample following 2 different sequential extraction methods and 2 different measurement techniques (reference date: January 2002).

Extracted fraction	Method A (direct LSC measurement)		Method B (by ²⁴¹ Am ingrowth)	
	²⁴¹ Pu ±1 σ (Bq/g)	²⁴¹ Pu ±1 σ (%)	²⁴¹ Pu ±2 σ (Bq/g) (calculated) ^a	²⁴¹ Pu ±2 σ (%)
Water soluble	0.6 ± 0.5	4.3 ± 1.8	0.045 ± 0.015	0.14 ± 0.06
Easily available	0.9 ± 0.8	6.6 ± 5.6	0.038 ± 0.015	0.12 ± 0.05
Carbonate	1.5 ± 1.1	11.0 ± 7.4	0.45 ± 0.15	1.4 ± 0.6
Oxides Fe/Mn	9.6 ± 3.5	69 ± 26	10.6 ± 3.5	34 ± 13
Organic	1.1 ± 0.9	7.9 ± 6.1	18.5 ± 6.1	59 ± 23
Residual	0.103 ^b	0.74	1.92 ± 0.65	6.1 ± 2.5
<i>Total</i>	<i>13.9 ± 8.8</i>	<i>100</i>	<i>31.6 ± 7.1</i>	<i>100</i>

^aThese values were calculated by applying the ²⁴¹Pu/^{239,240}Pu ratio of the residual fraction to the extracted aliquots; only in this fraction was ²⁴¹Pu detected.

^bValue below the minimum detectable amount.

²³⁸Pu associated with each phase can be repeated here, highlighting that in this sample, the concentration activity rates in the organic and residual phases are 1 order of magnitude higher for Method B than for Method A (organic: 18.5 ± 6.1 Bq/g ²⁴¹Pu [A] and 1.1 ± 0.9 Bq/g ²⁴¹Pu [B]; residual: 0.103 Bq/g ²⁴¹Pu [A] and 1.92 ± 0.65 Bq/g ²⁴¹Pu [B]). ²⁴¹Pu would be more leachable for both methods if the ²⁴¹Pu content is homogenous; thus, Method A would extract 44% of the plutonium existing in the mud and 25% in the pipe residue.

The plutonium isotopic ratios and Pu/Am ratios for both types of samples are shown in Table 9. The differences between americium and plutonium ratios can be explained by the differences in the extractability of the plutonium and americium or by the plutonium heterogeneities.

Table 9 Ratios obtained by the 2 laboratories for the pipe residue and mud samples.

	²³⁸ Pu/ ^{239,240} Pu ±2 σ		^{239,240} Pu/ ²⁴¹ Am ±2 σ		²⁴¹ Pu/ ^{239,240} Pu ±2 σ		²⁴¹ Pu/ ²⁴¹ Am ±2 σ	
	UMCS	CIEMAT	UMCS	CIEMAT	UMCS	CIEMAT	UMCS	CIEMAT
Pipe	0.0269 ± 0.0098	0.0390 ± 0.0120	0.86 ± 0.21	3.00 ± 0.44	3.8 ± 7.1	2.2 ± 1.1	3.2 ± 1.6	6.6 ± 3.1
Mud	0.0220 ± 0.0052	0.0347 ± 0.0018	1.26 ± 0.31	2.97 ± 0.44	4.0 ± 5.1	1.7 ± 0.8	5.1 ± 1.8	5.1 ± 2.3

Previous investigations with different leaching procedures (Gascó and Antón 2002), applied to an Irish Sea sediment with a homogenous content of plutonium, also resulted in different percentages for the extracted fractions, implying that cross-contamination among phases, the influence of order, temperature, and the ratio of solid:liquid were important factors when leaching transuranics.

The results of these experiments and those obtained by others (Napoles et al. 2004; Lucey et al. 2004) have proven the difficulties in validating sequential leaching protocols. In spite of the different percentages and concentration activities found in each phase, methods A and B can be used to assess the potential remobilization of transuranics, and consequently could be useful tools to suggest a cleaning method for the tank and pipes during dismantling activities.

The results obtained for the different types of ²⁴¹Pu measurement (by scintillation and indirectly via its daughter ²⁴¹Am growth in old discs) and 2 types of samples are shown in Tables 6 and 8 and presented in Figures 1 and 2.

²⁴¹Pu percentages in each extracted fraction "mud"

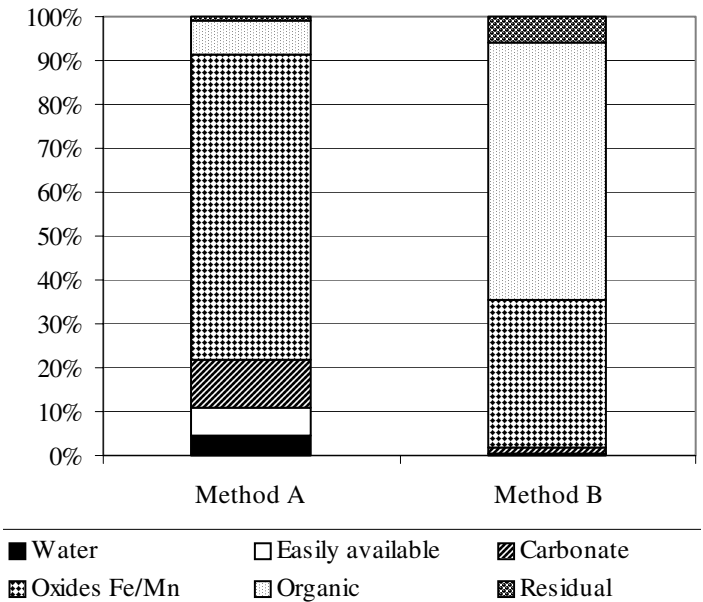


Figure 1 Distribution of ²⁴¹Pu concentration in the mud sample treated by the 2 sequential leaching methods (A and B).

²⁴¹Pu percentages in each extracted fraction "pipe residue"

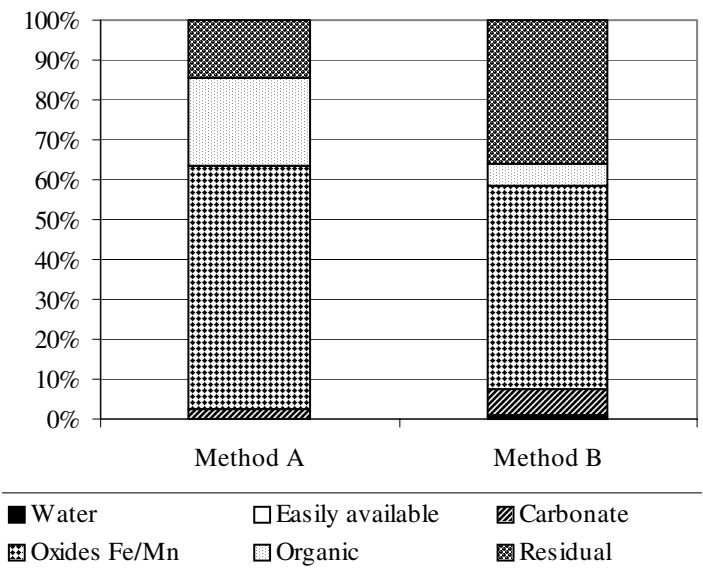


Figure 2 Distribution of ²⁴¹Pu concentration in the pipe residue sample treated by the 2 sequential leaching methods (A and B).

Determination of ^{241}Pu via its daughter ^{241}Am is a time-consuming method (from 6 months to 1 yr after plutonium and americium separation) that requires radiochemical separation. Due to the aliquot used to determine the alpha-emitting Pu isotopes, the concentration of ^{241}Am accumulated on the old discs provided a limit of detection for ^{241}Pu slightly higher than that obtained by its direct measurement by LSC.

^{241}Pu direct determination via LSC (after extraction from the discs) has the advantage of being a less time-consuming method; it can be analyzed just after the $^{239,240}\text{Pu}$ counting, but the laboratory has to have access to this instrumental technique. The uncertainties determined in the direct measurement are due to the calibration factors and the low-level ^{241}Pu concentration activity in the aliquot. In spite of this, the percentage of the extracted fraction is in good agreement—when considering uncertainties—with those found for the other isotopes.

The main differences between the methods are their uncertainties. The aliquot size was not big enough to allow for an optimal determination, although its quantification was possible by both methods.

CONCLUSIONS

The comprehension of the cross-contamination among extracted fractions and the accuracy of the sequential leaching extractions requires intercomparison exercises among laboratories that use these techniques and for laboratories to improve the methods for preparing artificial matrices containing the radionuclides in a determined phase.

The sequential extraction techniques are suitable tools for predicting the association of transuranics to the sediment/soil geochemical phases and for suggesting a way for extracting radionuclides in clean-up processes. The intercomparison between the two ^{241}Pu determination methods has allowed us to know the advantages and disadvantages of using the methods when low-level samples are measured, and to calculate indirect detection limits and decision thresholds for ^{241}Pu through its daughter ^{241}Am at different times and aliquot sizes.

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