

# Development of an Automatic Method for Americium and Plutonium Separation and Preconcentration Using an Multisyringe Flow Injection Analysis-Multipumping Flow System

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A new procedure for automatic separation and preconcentration of <sup>241</sup>Am and <sup>239+240</sup>Pu from interfering matrixes using transuranide (TRU)-resin is proposed. Combination of the multisyringe flow injection analysis and multipumping flow system techniques with the TRU-resin allows carrying out the sampling treatment and separation in a short time using large sample volumes. Americium is eluted from the column with 4 mol L<sup>-1</sup> hydrochloric acid, and then plutonium is separated via on-column Pu(IV) reduction to Pu(III) with titanium(III) chloride. The corresponding  $\alpha$  activities are measured off-line, with a relative standard deviation of 3% and a lower limit of detection of 0.004 Bq mL<sup>-1</sup>, by using a multiplanchet low-background proportional counter.

Environmental actinide concentration is usually very low, excepting cases of accident or nuclear power plant releases. Current radioactivity monitoring programs have regulations for limiting the total  $\alpha$  activity in different samples. Thus, in the case of drinking waters, the European Union has established a limiting value of 0.1 Bq L<sup>-1</sup> as a new guideline for total  $\alpha$  activity.<sup>1</sup> When this value is exceeded, a study of the isotopes responsible for the increased activity must be carried out. Among the different identification techniques,  $\alpha$  spectrometry is one of the most frequently used.<sup>2</sup> Recently, inductively coupled plasma-mass spectroscopy (ICPMS)<sup>3,4</sup> has also been utilized as a reliable, although very expensive technique for this purpose. Alternatively, low-background proportional counter, a classical detection technique for total activities, has potential advantages in the analysis of a great number of environmental samples. Obviously, in this case and in order to determine analyte activity, its isolation from other  $\alpha$  emitters present in the sample must be guaranteed.

In environmental samples, in addition to the use of large sample volumes, the development of one or several preliminary steps of separation and preconcentration will be needed in order to eliminate the possible interferences present in the matrix of the analyzed sample. Most traditional methods of actinide separation include ion-exchange,<sup>5–9</sup> liquid–liquid extraction,<sup>10–12</sup> chromatographic extraction,<sup>3,11,13</sup> HPLC and ion chromatography,<sup>14–16</sup> or a combination of these techniques.<sup>17,18</sup> The former methods involve a great consumption of reagents and time. In addition, the continuous contact with aggressive reagents and potentially hazardous samples must be considered as an important risk factor for the analyst.

In the early 1990s, Horwitz et al. developed new chromatographic compounds with a high potential capacity for retention of different elements. These resins (Sr-resin,<sup>19</sup> transuranide (TRU)-resin,<sup>20,21</sup> TEVA,<sup>22</sup> UTEVA<sup>23</sup>), currently used in routine procedures,

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improve significantly the actinides and other radioisotopes separation processes. TRU-resin is composed of octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphate oxide (CMPO) dissolved in tri-*n*-butyl phosphate and retained in an inert polymeric substrate (Amberchrom CG-71ms). Such resin allows the transuranide separation modifying the concentration of the nitric acid medium.<sup>21</sup>

On the other hand, the development of flow injection techniques<sup>24–28</sup> has enabled researchers to simplify many analytical methodologies. Several have been applied to the analysis of nuclear waste and biological and environmental samples.<sup>29,30</sup> Aldstadt et al.<sup>31</sup> described the use of flow injection analysis (FIA) to automate a separation on a TRU-resin column for U analysis with ICPMS detection. Later, Egorov et al.<sup>32</sup> and Grate et al.<sup>33</sup> optimized the Pu redox reactions with the former FIA technique to obtain its separation from Am.

Grate et al.<sup>34</sup> demonstrated that sequential injection analysis (SIA) is a more versatile technique than FIA and also that chromatographic extraction can be easily implemented for radioisotope isolation and analysis. This methodology has been applied by the authors to carry out the Pu–Am separation and subsequent detection by liquid scintillation counting<sup>35</sup> and by ICPMS.<sup>4</sup> These procedures have been tested on high-activity samples (~1700 Bq).

Multisyringe flow injection analysis (MSFIA) developed in 1999 by Cerdà et al.<sup>26</sup> profits simultaneously from the advantages offered by FIA and SIA methodologies. Using this technique, several radioisotope automatic separations have been applied to environmental and biological samples.<sup>36–38</sup> Recently, Lapa et al.<sup>27</sup> and Lima et al.<sup>28</sup> proposed a new way of impelling sample and reagents by using a multipumping flow system (MPFS).

In this work, an MSFIA-MPFS method is proposed with the aim to carry out the americium and plutonium separation and their determination in different type of samples, as well as to be applied in environmental monitoring programs. This possibility involves important savings of sample and reagents as they are only added when required by the automatic method.

The described method allows obtaining a throughput of 2 samples/h, which largely improves the sampling frequencies of

the classical batchwise methodologies.

## EXPERIMENTAL SECTION

**Reagents and Standards.** All solutions were prepared from analytical grade reagents with Millipore quality water: HNO<sub>3</sub> 69% (Panreac, Barcelona, Spain); HCl 37% (Scharlau, Barcelona, Spain); TiCl<sub>3</sub> 30 wt % solution in 2 mol L<sup>-1</sup> HCl, (Acros Organics); 0.1 mol L<sup>-1</sup> ammonium hydrogen oxalate (obtained from 6.31 g of oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) + 7.11 g of ammonium oxalate [(NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O] in distilled water up to 1 L of solution); L(+) ascorbic acid (Panreac); NaNO<sub>2</sub> (Panreac); Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck, Darmstadt, Germany); 143 ± 1 Bq g<sup>-1</sup> <sup>241</sup>Am (*T*<sub>1/2</sub> = 432.2 years) and 47.38 ± 0.18 Bq g<sup>-1</sup> <sup>239+240</sup>Pu (*T*<sub>1/2</sub> = 24 360 and 6500 years, respectively) standards in 1 mol L<sup>-1</sup> HCl, prepared and certified by CIEMAT (Madrid, Spain). In the case of Pu, the certified standard is presented as a mixture of its 239 and 240 isotopes because of their similar emission energies, which cannot be distinguished by α spectrometry; transuranide resin (TRU-resin) 50–100 μm (Eichrom Technologies, Darien, IL); glass wool for chromatography.

**Samples.** Soil and vegetable ashes (originating from the combustion of ilex, oak, and pine wood): Sample is dried in an oven at 110 °C, sieved using a 1-mm mesh, and subsequently calcinated at 550 °C for 8 h. Next, an acid digestion is carried out (50 g of calcinated sample + 300 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> for soil sample and 100 mL for vegetable ashes).

Synthetic samples of biological type were prepared in the laboratory (urine<sup>39</sup> and blood<sup>40</sup>).

All samples were prepared in a final solution of 0.1 mol L<sup>-1</sup> ascorbic acid, 0.25 mol L<sup>-1</sup> Al(NO<sub>3</sub>)<sub>3</sub>, and 2 mol L<sup>-1</sup> HNO<sub>3</sub>.

**Equipment and Software.** The hyphenated MSFIA-MPFS system used is shown in Figure 1. MSFIA setup is constituted basically of a multisyringe buret (BU4S, Crison Instruments, Alella, Barcelona, Spain) with programmable flow rates. This buret is equipped with four syringes (Hamilton) of 1 (S<sub>1</sub>) and 10 mL (S<sub>2–4</sub>), which are used as liquid drivers. Each syringe has a three-way solenoid valve (N-Research, Caldwell, NJ) at the head, which facilitates the application of multicommutation schemes. In order to avoid the intake of acid solutions into the syringes, two coils (HC<sub>1</sub> and HC<sub>2</sub>) with a holding volume of 14 mL each (1.5 mm of internal diameter and 8 m of length) are placed between syringes S<sub>3</sub> and S<sub>4</sub> and valves V<sub>1</sub> and V<sub>2</sub> (MTV-3-N 1/4 UKG, Takasago, Japan). HC<sub>1</sub> (S<sub>3</sub>–HC<sub>1</sub>–V<sub>1</sub>) coil loads 4 mol L<sup>-1</sup> HCl solution and HC<sub>2</sub> (S<sub>4</sub>–HC<sub>2</sub>–V<sub>2</sub>) coil loads 0.02 mol L<sup>-1</sup> TiCl<sub>3</sub>/4 mol L<sup>-1</sup> HCl solution. The remaining reagents are loaded and supplied directly with syringes. The automatic control of the module is carried out via PC through an RS232C interface. The manifold is constructed with 0.8-mm-internal diameter polytetrafluoroethylene tubes. All connections were carried out by means of PVC connectors, except the cross-junctions, which were made with poly(methyl methacrylate).

The MPFS setup consists of three solenoid micropumps (Bio-Chem Valve Inc., Boonton, NJ) with a stroke volume of 20 (M<sub>1–2</sub>) and 8 μL (M<sub>3</sub>). Each one allows the injection of a certain volume of reagent or sample, varying the number of pulses. The flow rate

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**Table 1. Automatic Procedure for the Separation and Preconcentration of  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$** 

step	flow rate (mL min <sup>-1</sup> )	MSFIA <sup>a</sup>						MPFS <sup>b</sup>		
		S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	V <sub>1</sub>	V <sub>2</sub>	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>
1. loading coils HC <sub>1</sub> and HC <sub>2</sub>	10.0	off	off	on 15 mL	on 15 mL	off	off	off	off	off
2. column conditioning	3.0	off	off	off	off	off	off	on 3 mL	off	off
3. sample	0.5	off	off	off	off	off	off	off	on 1 mL	off
4. elimination of interferences	3.0	off	off	off	off	off	off	on 1 mL	off	off
5. Pu <sup>c</sup> oxidation.	1.0	on 0.125 mL	off	off	off	off	off	on 1 mL	off	off
6. $^{241}\text{Am}$ elution	1.0	off	off	on 15 mL	off	on 15 mL	off	off	off	off
7. $^{239+240}\text{Pu}$ elution	1.0	off	off	off	on 15 mL	off	on 15 mL	off	off	off
8. column cleaning	3.0	off	on 10 mL	off	off	off	off	off	off	off
9. sample change	5.0	off	off	off	off	off	off	off	o 0.5 mL	on 2 mL

<sup>a</sup> MSFIA: S<sub>1</sub>, 0.2 mol L<sup>-1</sup> NaNO<sub>2</sub>; S<sub>2</sub>, 0.05 mol L<sup>-1</sup> HNO<sub>3</sub>; S<sub>3</sub>, H<sub>2</sub>O; S<sub>4</sub>, H<sub>2</sub>O; V<sub>1</sub>, 4 mol L<sup>-1</sup> HCl; V<sub>2</sub>, 0.02 mol L<sup>-1</sup> TiCl<sub>3</sub>/4 mol L<sup>-1</sup> HCl. <sup>b</sup> MPFS: M<sub>1</sub>, 2 mol L<sup>-1</sup> HNO<sub>3</sub>; M<sub>2</sub>, sample; M<sub>3</sub>, H<sub>2</sub>O. <sup>c</sup> Repeat 3 times the sequence HNO<sub>3</sub>/NaNO<sub>2</sub>/HNO<sub>3</sub>.

a reduction reaction of Pu(IV): S<sub>4</sub> (S<sub>4</sub>-on); the additional valve V<sub>2</sub> (V<sub>2</sub>-on) is activated and 15 mL of the 0.02 mol L<sup>-1</sup> TiCl<sub>3</sub>/4 mol L<sup>-1</sup> HCl solution is passed through the column at a flow rate of 1.0 mLmin<sup>-1</sup>. (8) *Final cleaning.* Elimination of those isotopes that have not been eluted in the previous steps but remain in active sites in the resin, decreasing its retention capacity and, therefore, the resin lifetime. Thus, 10 mL of 0.05 mol L<sup>-1</sup> HNO<sub>3</sub> is dispensed with S<sub>2</sub> in the on position at a flow rate of 3.0 mLmin<sup>-1</sup>. (9) *Change of sample.* In order to avoid contamination between samples, 0.5 mL of the next sample is introduced with M<sub>2</sub> in the on position at a flow rate of 5.0 mLmin<sup>-1</sup>. Simultaneously, 2 mL of H<sub>2</sub>O is passed through the column with M<sub>3</sub> in the on position to guarantee a low concentration of nitrates in the resin.

Once the separation of the isotopes has been concluded, preparation of the emitting source is carried out from the eluted fractions corresponding to step 6 for  $^{241}\text{Am}$  and step 7 for  $^{239+240}\text{Pu}$ . Solutions (15 mL) are taken to almost complete dryness, and next, ~5 mL of distilled water is added repeating the evaporation. Once this procedure has been concluded, through which HCl is eliminated, the precipitate is swept out by a small volume of distilled water toward a steel planchet of 50-mm diameter, which is subsequently placed under an infrared (IR) lamp, and the solution is once more evaporated to dryness. Finally, the sample activity is determined with the multiplanchet proportional counter.

## RESULTS AND DISCUSSION

**Flow System.** The use of micropumps (MPFS) allows the system to dispense in a continuous way large sample or reagent volumes without needing reiterative loading and unloading processes of the syringes as it happens in MSFIA methodology. This aspect is considered of great importance when designing automatic methods for separation of radioactive isotopes in environmental samples, where the low concentrations present require the preconcentration of the analyte of interest. Thus, propulsion with micropumps allows solving this inconvenience as well as reducing the execution time.

Nevertheless, the dispensed volume by micropumps is not totally repetitive for different working sessions, and each micropump should be initially recalibrated. Moreover, to minimize back pressure, a resin mass (0.08 g) smaller than the column capacity was used so that when the resin is soaked it can easily move inside the column.

By contrast, MSFIA is a robust system that does not need to be recalibrated and can be subjected to a higher overpressure degree without altering its functioning. The working flow rate range is much wider (0.57–30 mL min<sup>-1</sup>) than that of micropumps. This feature of the MSFIA system is exploited in the step corresponding to the Pu oxidation. The small NaNO<sub>2</sub> volume (0.125 μL) is propelled by syringe S<sub>1</sub> with a flow rate of 1.0 mL min<sup>-1</sup>, merging inside the column with a 2 mol L<sup>-1</sup> HNO<sub>3</sub> solution, which is impelled as sandwich injection fashion by the micropump (turbulent flow). This type of injection provides an adequate mixing between both reagents and, therefore, a high uniformity in the formation in situ of the oxidant (HNO<sub>2</sub>). The contact time between the oxidant and the resin is long enough to ensure that all the Pu(III) passes to Pu(IV) without damaging the retention process of the former or the structure of the polymeric matrix. With the help of the three-way solenoid valves, the reagents' flow is directed toward the separation column or toward the waste, as required, with great precision and reproducibility.

In this way, both flow techniques (MSFIA-MPFS) complement each other, improving their individual advantages according to the required analytical needs. This allows reducing drastically the consumption of reagents and saving of time in relation to manual methodologies in which operations can last days against 40 min of the automated method.

**Column Conditioning.** The distribution relationship between the aqueous and organic phase, for the isotopes studied, increases from a HNO<sub>3</sub> concentration of 1 mol L<sup>-1</sup> onward. In the case of Am(III), this increase remains only up to a concentration value of 2 mol L<sup>-1</sup>, whereas Pu(IV) can be extracted at a considerably higher acid concentration (10 mol L<sup>-1</sup>).<sup>20</sup> Taking into account the

former data, column conditioning was studied within an acid nitric concentration ranging between 1 and 2 mol L<sup>-1</sup>. For concentration values up to 1.5 mol L<sup>-1</sup>, the recovery results did not exceed 90%, Am being the most affected. However, for a concentration of 2 mol L<sup>-1</sup>, the recovery of both analytes surpassed 90%. This last value was selected in order to use the same solution for the requirements of the conditioning, cleaning, and Pu oxidation steps. Whenever the resin is changed, it is left in contact with the 2 mol L<sup>-1</sup> HNO<sub>3</sub> solution.

**Separation Scheme.** The study of the retention and further elution of <sup>241</sup>Am and <sup>239+240</sup>Pu is based on the properties presented by the nitro and chlorine complexes of the actinides in the valence states (III), (IV), and (VI) against the extracting agent CMPO. The retention capacity of each element varies with the concentration of the acid, the best results being obtained for high values (>1 mol L<sup>-1</sup>). The retention degree of such nitro and chlorine complexes varies with the capacity factor (*k'*) of the TRU-resin as well as the cation oxidation state. Thus, tetravalent and hexavalent actinides are strongly retained from nitric or hydrochloric acid concentrated solutions with a *k'* value higher than 10<sup>4</sup>. Nevertheless, trivalent actinides show, in nitric medium, a considerably lower retention (*k'* ≈ 100) and in hydrochloric medium is practically negligible (*k'* < 1)<sup>20</sup> as long as the HCl concentration does not exceed 5 mol L<sup>-1</sup>. Combining acid solutions, complexing agents, or redox reagents, the sequential elution of these isotopes can be achieved in an individual or sequential way, depending on the oxidation state they are in.

First, the retention and elution process of each isotope was optimized separately. Thus, the flow system represented in Figure 1 was used, eliminating in each case the steps corresponding to the separation process of the other isotope (oxidation and elution of Pu for Am and elution of Am for Pu).

The activity of each isotope is determined with a low-background proportional counter, which may be provided with up to 16 detectors, allowing one to obtain in a fast way the activity of samples with low contents in α emitters. Nevertheless, the main limitation of this detection technique lies in the fact that it cannot discriminate the emitter energies, and therefore, in the optimization process the use of α spectrometry has been also resorted to to evaluate the behavior of the variables in each step. In a summarized way, the steps for the application of each of these two detection procedures are as follows:

**(a) Determination of the Total α Activity with a Low-Background Proportional Counter.** The eluted fraction is almost completely dried, and the process is repeated with small volumes of distilled water to remove the HCl medium. Then, the precipitate is swept out toward a planchet, the solution is evaporated, and its activity is further measured.

**(b) Determination of the α Activity by α Spectrometry.** Preparation of the planchet, of 25-mm diameter, is carried out by means of an electrodeposition process. The planchet is degreased with trichloroethylene and preserved in distilled water until further use in the electrolytic cell. To the eluted fraction, 1 mL of 0.3 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> is added. It is taken to complete dryness, and next, 0.3 mL of concentrated H<sub>2</sub>SO<sub>4</sub> and 4 mL of distilled water are added. The resulting solution is passed to the electrolytic cell, cleaning the beaker carefully with a total of 5 mL of 1% H<sub>2</sub>SO<sub>4</sub>, and pH is readjusted with concentrated ammonia within the range

2.1–2.4. The electrolysis is carried out for 1 h with a current intensity of 2 A. One minute before removing the electrolyte anode, the electrodeposition time being considered finished, 1 mL of concentrated ammonia is added and next the current is cut off. Finally, the planchet is cleaned with 1% ammonia and acetone and dried under an IR lamp to further obtain the spectrum of the sample. Electrodeposition yields, using standards of Am and Pu, provided average results of 100%.

α Spectrometry allows us to know the spectra of the analyzed isotope in each of the emerging fractions of the column, the different parameters being able to be adjusted in order to integrate the individual separation procedures in only one sequential methodology.

**(1) Retention and Elution of Am.** The quantitative study of each of the fractions eluted in the individual procedure for <sup>241</sup>Am revealed that, in spite of the acceptable recovery of the isotope in the elution step with losses close to 3%, the final recovery happened to be limited (<50%). Analyzing each of the emerging fractions in each of the procedure steps, we found that the α spectrum corresponding to the elimination of interferences (initially with 5 mL of 2 mol L<sup>-1</sup> HNO<sub>3</sub>) showed a considerable presence of <sup>241</sup>Am (20%), whereas in the remaining fractions, losses did not exceed 1%. Possibly, the retention of the isotope was not strong enough and when the cleaning HNO<sub>3</sub> was passed through the column it swept with a part of the retained isotope. For improvement purposes, Al(NO<sub>3</sub>)<sub>3</sub> was added to the sample and the HNO<sub>3</sub> volume was diminished in this step to 1 mL. Different Al(NO<sub>3</sub>)<sub>3</sub> concentrations were studied (0.1–1 mol L<sup>-1</sup>), demonstrating that with 0.125 mol L<sup>-1</sup> of such salt, and by decreasing the acid volume, the final recovery of the isotope improved substantially (>90%).

After passing the sample through the column, the resin is in a medium whose concentration in nitrates is high, thus enhancing the stabilization of the complex formed between the resin and Am(III). Diminishing the acid concentration to 0.05 mol L<sup>-1</sup> and breaking the ion pair formed is enough to recover the analyte. However, with this solution, the elution of trivalent actinides is not selective, since the former is also effective for the remaining actinides.<sup>20</sup> The selective elution of trivalent actinides is attained by changing the system of nitrates to chlorides. Previously, 2 mL of 9 mol L<sup>-1</sup> HCl was passed through a column and after 6 mL of 4 mol L<sup>-1</sup> HCl, thus achieving the total elution of Am(III). In order to avoid the use of such high acid concentrations, the elution process was also carried out directly with 10 mL of the latter solution. The results were similar to those obtained with both hydrochloric solutions. In view of the above-mentioned, the selective elution of <sup>241</sup>Am was carried out with 10 mL of 4 mol L<sup>-1</sup> HCl.

**(2) Retention, On-Column Oxidation, and Elution of Pu.** Plutonium in nitric medium presents a distribution relationship much higher than that of americium, within a wide range of acid concentration. Bearing this in mind together with the fact that our final goal is to unify both separation procedures into only one, 1 mL of 2 mol L<sup>-1</sup> HNO<sub>3</sub> was selected to be used directly in the sample preparation and in the cleaning step. However, the fairly good retention obtained (with no evidence of Pu) did not imply a good recovery of the isotope (60%) after its elution. When analyzing the subsequent steps, significant amounts of Pu were not detected (losses smaller than 2%).

HNO<sub>2</sub> is a very efficient reagent to quickly oxidize Pu(III) to Pu(IV).<sup>44</sup> However, due to its low stability, it must be obtained in situ by means of the reaction between NaNO<sub>2</sub> and HNO<sub>3</sub>. Grate et al.<sup>33</sup> proposed an on-line procedure to prepare such oxidant impelling first HNO<sub>3</sub> toward the column and next the NaNO<sub>2</sub> solution. The total volume of both reagents is divided into three fractions, which are injected in segments between them, thus assuring both the freshness of the oxidant and that the total HNO<sub>3</sub> concentration when passing through the resin is not lower than 1 mol L<sup>-1</sup>. Taking into account that the irreversible interactions which take place between nitrite ions and the polymeric support are not negligible,<sup>33</sup> it is important that the amount of NaNO<sub>2</sub> to be used and the contact time between these ions and the resin remain minimal. This will avoid the temporary oxidizing characteristics remaining permanently in the resin memory, which would require a more frequent replacement of the column filling, and would also imply a higher cost per analysis.

Initially Pu(III) oxidation was carried out with a NaNO<sub>2</sub> concentration of 0.5 mol L<sup>-1</sup> as recommended in the separation method with disposable cartridges described by Eichrom.<sup>45</sup> The injection sequence used (3 × (1 mL of HNO<sub>3</sub> / 125 μL of NaNO<sub>2</sub> / 1 mL of HNO<sub>3</sub>)) is executed after Pu has been retained on the column and the former is cleaned with 2 mol L<sup>-1</sup> HNO<sub>3</sub>. With this nitrite concentration, oxidation of Pu(III) to Pu(IV) occurs very fast; however, the subsequent elution with 0.02 mol L<sup>-1</sup> TiCl<sub>3</sub> and 4 mol L<sup>-1</sup> HCl is incomplete and the Pu recovered does not surpass 60%. In none of the previous and subsequent steps to elution are significant losses detected. The 0.05 mol L<sup>-1</sup> HNO<sub>3</sub> solution was replaced by a 0.1 mol L<sup>-1</sup> ammonium hydrogenoxalate solution, whose elution capacity in relation to a great number of actinides, regardless their oxidation state, has been demonstrated by other authors.<sup>20</sup> The α spectrum registered for this fraction showed the presence of Pu. Nevertheless, the total yield was not 100%, thus, apparently remaining part of Pu retained on the column. Under these conditions, the retained plutonium is not eluted even if the eluent volume is considerably increased.

When Pu is eluted part of the nitrite ions, generated during the oxidation process, may remain retained between the organic phase and the polymeric support of the TRU-resin, interacting in an irreversible way with the former. Apparently, the nitrite ions are totally eluted; however, these results suggest that the resin continues exhibiting oxidizing properties. As a consequence, part of Pu(IV) is not reduced to Pu(III) and, therefore, is not eluted with the 4 mol L<sup>-1</sup> HCl solution ( $k'_{\text{Pu(IV)}} \text{ in HCl} > 10^5$ ). The optimal recovery (~100%) in the absence of Am(III) is reached by decreasing the NaNO<sub>2</sub> concentration up to 0.2 mol L<sup>-1</sup>.

After oxidizing Pu(III) to Pu(IV), the next step is elution, either by reduction to Pu(III) or as Pu(IV). If the isolation of the analyte from the remaining actinides is of interest, it should be carried out. Among the reducing agents studied, TiCl<sub>3</sub> is that providing a faster and more reproducible elution, with narrow peaks and a small tail.<sup>33</sup>

In our case, elution of Pu(III) was carried out with a mixed solution of TiCl<sub>3</sub> and HCl, thus combining in the same step the

reduction and elution of the analyte. The efficiency of TiCl<sub>3</sub> as a reducing agent was studied within the concentration range between 0.01 and 0.04 mol L<sup>-1</sup> in a 4 mol L<sup>-1</sup> HCl medium, the best results being achieved with a concentration of the reducing agent of 0.02 mol L<sup>-1</sup>.

On the other hand, the low penetration power of the α particles compels us to obtain very thin and homogeneous deposits, in order to minimize the self-absorption phenomenon of such emission. The presence of 4 mol L<sup>-1</sup> HCl in the elution fraction makes the preparation of the planchet difficult due to the reaction of hydrochloric acid with steel, giving rise to the formation of very thick residues. In order to solve this problem and since in the proposed procedure the use of a multiplanchet proportional detector is of interest, it was decided to prepare the planchets previously carrying out a double evaporation, which assured the total elimination of HCl. This simple treatment allowed the use of this detector without any problem. As in all previous cases, this result was corroborated by α spectrometry.

With the aim to avoid the use of highly corrosive solutions, the possibility of substituting the TiCl<sub>3</sub>/HCl solution by a 0.1 mol L<sup>-1</sup> ammonium hydrogenoxalate solution was studied. An evident disadvantage of this alternative is the low selectivity of this compound, which does not allow isolating Pu from the remaining tetravalent and hexavalent actinides present in the real sample, and which are potentially retained on the TRU-resin, even though the main inconvenience is the thick deposits obtained, considerably surpassing the recommended limit. Therefore, the capacity of TiCl<sub>3</sub>/HCl to carry out the Pu elution was demonstrated, since besides being a selective eluent, it allows the preparation of the planchets in an adequate way.

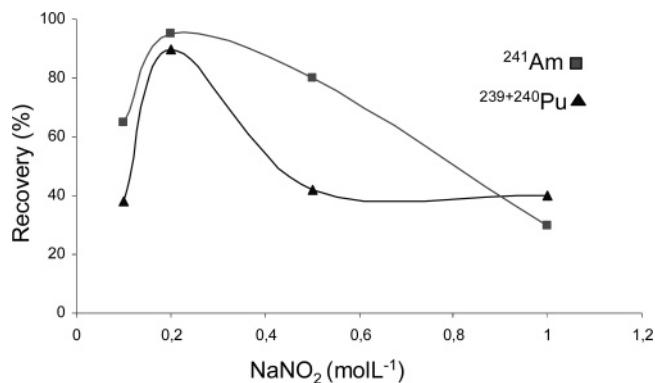
**(3) Sequential Separation of Am and Pu.** Integration of the two individual procedures was performed from the results obtained with each of them. Although these results were optimized adequately and the yields obtained were close to 100%, several parameters needed to be adjusted for unification purposes.

Thus, in the initial retention study, it was found that both Am and Pu recoveries in the eluent phase were remarkably lower (<60%) than those of the individual procedures. By analysis of the elutions of each step by α spectrometry, the presence of <sup>241</sup>Am in the sample loading, cleaning, and elution of <sup>239+240</sup>Pu steps was found in an amount equivalent to its recovery decrease. In the case of Pu, the main losses were detected in steps 3 and 8 of the procedure. This drawback was solved increasing the Al(NO<sub>3</sub>)<sub>3</sub> concentration to 0.25 mol L<sup>-1</sup>. With the aim to use the same solution in every step in which HNO<sub>3</sub> was employed, only one solution of 2 mol L<sup>-1</sup> HNO<sub>3</sub> was used.

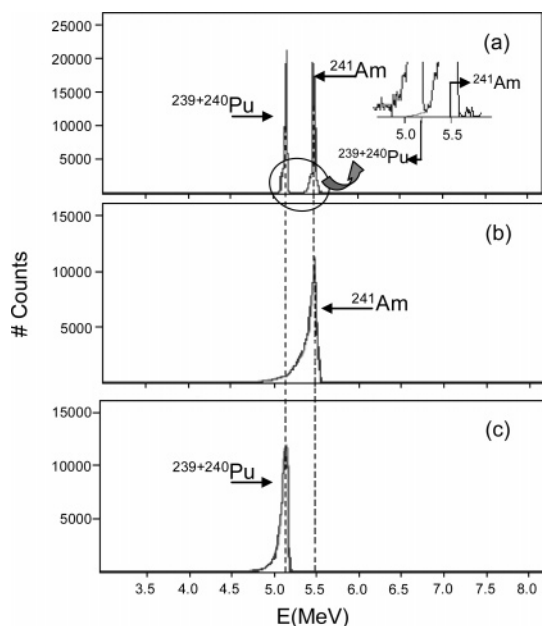
On the other hand, in the elution study it was proved that, whereas in the individual procedure, elution is carried out with 10 mL of 4 mol L<sup>-1</sup> HCl for <sup>241</sup>Am and 10 mL of 0.02 mol L<sup>-1</sup> TiCl<sub>3</sub>/4 mol L<sup>-1</sup> HCl for Pu, in the sequential separation procedure, this same volume does not achieve total elution or, therefore, complete separation of the isotopes. A fraction of <sup>241</sup>Am (5.5 MeV) appears in the α spectrum corresponding to the elution of <sup>239+240</sup>Pu (5.2 MeV). This could be due to the fact that when the procedures were unified a delay was produced in the elution times. In both cases, an eluent volume of 15 mL re-established the former recoveries.

(44) Cleveland, J. M. *The Chemistry of Plutonium*; Gordon and Breach Sci. Pub.: New Cork, 1970.

(45) Analytical Procedures ACW03, Americium, Plutonium and Uranium in water; Eichrom Technologies Inc., 2002; p 14.



**Figure 2.** Variation of the recovery of the isotopes according to  $\text{NaNO}_2$  concentration.



**Figure 3.**  $\alpha$  Spectrum: (a) before separation; (b) and (c) after separation. Counting time: (a)  $6 \times 10^5$  s and (b) and (c)  $3 \times 10^5$  s.  $^{241}\text{Am}$  activity  $1 \text{ Bq mL}^{-1}$  and  $^{239+240}\text{Pu}$  activity  $1 \text{ Bq mL}^{-1}$ .

With regard to the Pu oxidation step, Figure 2 depicts the recovery dependence of each isotope in relation to  $\text{NaNO}_2$  concentration. For Pu activities higher than  $0.5 \text{ Bq mL}^{-1}$ , the increase of the  $\text{NaNO}_2$  concentration to  $0.25 \text{ mol L}^{-1}$  was required, since otherwise Pu(III) oxidation was not being completed, appearing in the Am  $\alpha$  spectrum as a small concentration corresponding to Pu(III) (<10%).

The study of each of the fractions by  $\alpha$  spectrometry revealed, as observed in Figure 3, the efficient separation of both isotopes, thus assuring unequivocally the use of the multiplanchet detector for the counting of  $\alpha$  particles. The use of this detection system allows reducing considerably the counting times with regard to  $\alpha$  spectrometry, from days to hours. Table 2 summarizes the optimized process for separation of  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$ .

Table 3 shows the results obtained with both individual and sequential separation methods, for different  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$  activities once all the experimental parameters have been optimized. Comparing both methods, i.e., individual and sequential

separation, it can be observed that the recovery of each isotope is practically the same and in all cases higher than 90%. In addition, it is proved that the methodology is applicable at low  $\alpha$  activity levels ( $0.025 \text{ Bq mL}^{-1}$ ).

**Lower Limit of Detection.** Taking into account that the described separation method is applied to environmental sample analysis, the isotope activities were always lower than  $2 \text{ Bq mL}^{-1}$ . It should be outlined that  $\alpha$  spectrometry allows much lower detection limits with a detection efficiency higher than that of a proportional counter. However, in our case, the objective aimed at is fulfilled since the lower limit of detection (LLD) with this counter, calculated according to the Currie criterion,<sup>46</sup> for a confidence level of 95% was of  $0.004 \text{ Bq mL}^{-1}$  with an average background of 0.06 cpm. In all cases, the mass of the obtained deposits was always smaller than 1 mg.

**Preconcentration Ratio.** Automated preconcentration enables us to decrease the detection limit in a remarkable and reproducible way. Traditional methods such as evaporation of large sample volumes, besides being more tedious, are less reproducible when it comes to analyzing minority elements at trace levels.

In our case, we started from a standard solution from which preconcentration of the analyte of interest was carried out automatically and on column, assuring a high reproducibility between replicates. As observed in the results shown in Table 4, up to a volume of 5 mL, the recovery of each isotope is higher than 90%. For 10 mL, the largest studied concentration volume, we found that Pu recovery is considerably diminished and at the same time Am recovery is increased. By  $\alpha$  spectrometry, it was proved that Pu was present in the Am fraction, which may have originated from the incomplete oxidation of this isotope, a significant part of the former remaining in the oxidation state +3. This drawback can be solved by increasing the concentration of nitrites with the risk of increasing the interaction of these ions with the polymeric matrix, which would reduce the separation process. Preconcentration of the sample by a 5:1 factor can be considered a fairly good result for this type of analysis. Evidently, the larger the volume capable of being preconcentrated, the lower the LLD attained. However, the preconcentration process can compromise the resin lifetime as well as raise the cost per analysis; thus, the use of this procedure is only recommended when the detection limit without preconcentration is close to the detector background value. The method is developed for 1 mL of sample and 0.08 g of resin; however, the amount of retained analyte can be increased using a larger column with a greater amount of resin.

**Reproducibility, Repeatability, and Lifetime of the Column.** The separation column lifetime is intimately linked to the repeatability of the methodology and is indicative of the number of the consecutive analysis feasible to be carried out without changing the column filling. The results obtained up to the fifth repetition reveal a recovery for both analytes higher than 90% with a RSD ( $n = 5$ ) of 3.0% for  $^{241}\text{Am}$  and 2.1% for  $^{239+240}\text{Pu}$ . In the sixth repetition,  $^{241}\text{Am}$  recovery decreases up to 80%, whereas that of  $^{239+240}\text{Pu}$  decreases up to 64%. The latter is the most affected possibly due to the redox conditions of the resin. In this way, we estimate that the lifetime is of five analyses, after which the replacement of the column is recommended.

(46) Currie, L. A. *Anal. Chem.* **1968**, *40*, 586–593.

**Table 2. Optimization of the MSFIA-MPFS Methodology for the Sequential Separation of  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$** 

step	$^{241}\text{Am}$	$^{239+240}\text{Pu}$
2. column conditioning	3 mL, 2 mol L <sup>-1</sup> HNO <sub>3</sub>	3 mL, 2 mol L <sup>-1</sup> HNO <sub>3</sub>
3. sample (in 0.1 mol L <sup>-1</sup> ascorbic acid + 2 mol L <sup>-1</sup> HNO <sub>3</sub> + 0.25 mol L <sup>-1</sup> Al(NO <sub>3</sub> ) <sub>3</sub> )	1 mL	1 mL
4. eliminate interferences	1 mL, 2 mol L <sup>-1</sup> HNO <sub>3</sub>	1 mL, 2 mol L <sup>-1</sup> HNO <sub>3</sub>
5. Pu oxidation		0.125 mL, 0.25 mol L <sup>-1</sup> NaNO <sub>2</sub> + 1 mL, 2 mol L <sup>-1</sup> HNO <sub>3</sub>
6. $^{241}\text{Am}$ elution	15 mL, 4 mol L <sup>-1</sup> HCl	
7. $^{239+240}\text{Pu}$ elution		15 mL, 0.02 mol L <sup>-1</sup> TiCl <sub>3</sub> /4 mol L <sup>-1</sup> HCl

**Table 3. Individual and Sequential Separation of  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$  Using the MSFIA-MPFS Methodology**

	$^{241}\text{Am}$ activity (Bq mL <sup>-1</sup> )		$^{239+240}\text{Pu}$ activity (Bq mL <sup>-1</sup> )	
	added	found	added	found
individual separation <sup>a</sup>	0.025	0.024 ± 0.001		
	0.25	0.23 ± 0.01		
	2.5	2.4 ± 0.1		
sequential separation <sup>a</sup>			0.025	0.024 ± 0.001
			0.05	0.047 ± 0.002
			0.53	0.50 ± 0.02
	0.025	0.024 ± 0.001	0.025	0.025 ± 0.001
	0.85	0.84 ± 0.03	0.34	0.35 ± 0.02
	1.00	1.03 ± 0.03	1.00	0.98 ± 0.03
	1.65	1.62 ± 0.05	0.78	0.75 ± 0.02

<sup>a</sup> In all cases, the number of analyzed replicates is  $n = 3$ .

**Table 4. Activities Obtained According to the Preconcentration Volume. Total Activity: 1Bq of  $^{241}\text{Am}$  and 1Bq of  $^{239+240}\text{Pu}$ .**

$^{241}\text{Am}$ and $^{239+240}\text{Pu}$ (Bq mL <sup>-1</sup> )	preconcn vol (mL)	$^{241}\text{Am}$ found (Bq)	$^{239+240}\text{Pu}$ found (Bq)
0.5	2	0.95	0.93
0.2	5	0.96	0.94
0.1	10	1.15	0.65

The reproducibility of the method was determined using an activity of 1.65 Bq mL<sup>-1</sup> for  $^{241}\text{Am}$  and of 0.78 Bq mL<sup>-1</sup> for  $^{239+240}\text{Pu}$ .

**Application to Complex Matrixes.** The high Fe(III) concentrations frequently found in different type of samples can give rise to a remarkable decrease in the Am(III) retention.<sup>33</sup> Thus, the elimination of Fe(III) is recommended prior to carrying out the separation procedure, reducing the former to the oxidation state +2. In this way, each aliquot of different matrixes (i.e., soil leachate, vegetable ashes leachate, urine, and blood) was prepared in the presence of 0.1 mol L<sup>-1</sup> ascorbic acid, a concentration high enough to achieve the proposed objective. In all cases, the final solution was prepared in 0.25 mol L<sup>-1</sup> Al(NO<sub>3</sub>)<sub>3</sub> and 2 mol L<sup>-1</sup> HNO<sub>3</sub>.

Evaluation of the automatic methodology was carried out by analyzing four different matrixes. The procedure was applied to spiked samples with known  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$  activities, obtained from the corresponding certified standards. The results of the

**Table 5. Analysis of  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$  in Different Types of Samples<sup>a</sup>**

sample ( $n = 3$ )	$^{241}\text{Am}$ (Bq mL <sup>-1</sup> )		$^{239+240}\text{Pu}$ (Bq mL <sup>-1</sup> )	
	added	found	added	found
soil	0	<LLD	0	<LLD
	1.00	0.96 ± 0.02	1.00	0.94 ± 0.01
vegetable ashes	0	<LLD	0	<LLD
	1.00	0.95 ± 0.01	1.00	0.99 ± 0.02
synthetic urine	0	<LLD	0	<LLD
	1.00	0.92 ± 0.01	1.00	0.95 ± 0.01
synthetic blood	0	<LLD	0	<LLD
	1.00	0.97 ± 0.03	1.00	0.91 ± 0.02

<sup>a</sup> LLD, 0.004 Bq mL<sup>-1</sup>.

analyses for three replicates ( $n = 3$ ) are shown in Table 5, revealing a fairly good separation of the analytes, with recoveries of the two isotopes higher than, in all cases, 90%.

## CONCLUSIONS

Combination of the MSFIA-MPFS techniques provides a new automatic methodology for the chemical separation of Am and Pu.

Also, the use of this combined technique allows impelling the liquids in a continuous way, obtaining a high analysis throughput. The system presents a very simple manifold design providing both versatility and flexibility. Furthermore, the automatic control of the manifold by computer guarantees a good reproducibility and repeatability. The detection system, based on a low-background proportional counter with multiple detectors, permits analyzing a large number of samples with a reduced detection limit.

The procedure has been satisfactorily applied to complex matrixes as well as to samples of environmental interest with low analyte activities.

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