

## UTILIZATION OF RADIOANALYTICAL METHODS FOR THE DETERMINATION OF ISOTOPES OF U, Pu AND Am IN ACTIVATED CHARCOAL FROM IEA-R1 REACTOR

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### ABSTRACT

Activated charcoal is a radioactive waste arising from the water purification system of the nuclear research reactor. The management of this waste includes its characterization in order to identify and quantify the existing radionuclides, including those known as “difficult-to-measure radionuclides” (RDM). The analysis of these RDM usually involves complex radiochemical costly and time consuming procedures for the purification and separation of them. The objective of this work was to define a methodology of sequential analysis of isotopes of U, Pu and Am, present in activated charcoal, evaluating chemical recovery, analysis time, quantity of radioactive waste generated and cost. Ion exchange and the chromatographic extraction methodologies were compared. Both methods showed high chemical recoveries, ranged from 74 and 100% for U, 76 and 100% for Pu and 87 and 100% for Am, demonstrating that these methods provide accurate and reliable results. However, chromatographic extraction method is more suitable for the determination of the radionuclides because it generates the smaller volume of waste and is more cost-effectively.

Keywords: radioactive waste, transuranic, ion exchange and chromatographic extraction.

### 1. INTRODUCTION

Activated charcoal is a radioactive waste arising from the water purification system of a research reactor nuclear. It removes radioactive elements dissolved in the water while the reactor is in operation, becoming radioactive [1].

The charcoal, like any radioactive waste, needs to be characterized to obtain information about its composition, keeping in mind its chemical pre-treatment and subsequent disposal [2].

Waste radioisotope characterization is carried out by means of identifying the radionuclides contained in the packaged waste and determining their concentration. The inability to measure directly the pure alpha and beta emitting radionuclides has been a major problem. Sophisticated radiochemical techniques that are difficult to implement on a regular basis are involved in determining these radionuclides. Techniques such as precipitation, ion exchange or solvent extraction have been used to separate and quantify different elements; however, these methods are complex, time consuming and generate large quantities of chemical waste.

The precipitation technique for determining analytes, for example, is not as selective as ionic exchange or solvent extraction, and the process is also labor-intensive. The ionic exchange technique is more selective and less labor-intensive, but requires a large volume of acid and resins in the elution and regeneration processes. Solvent extraction is the most selective, but it is very labor-intensive and generates large volumes of secondary waste.

The most important radionuclides present in waste generated in nuclear reactors are: activation products ( $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{54}\text{Mn}$ ,  $^{55}\text{Fe}$ ,  $^{59}\text{Ni}$ ,  $^{60}\text{Co}$ ,  $^{63}\text{Ni}$ , and  $^{94}\text{Nb}$ ), fission products ( $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ ,  $^{134}\text{Cs}$ , and  $^{137}\text{Cs}$ ), transuranics ( $^{241}\text{Am}$ ,  $^{242}\text{Cm}$ , and  $^{244}\text{Cm}$ ) and isotopes of U and Pu. Some of these radionuclides do not emit measurable gamma radiation in their decay process and consequently are considered difficult to measure, since their concentrations can only be measured by means of radiochemical separation techniques [3, 4].

These techniques consist of five main steps: sample pre-treatment; dissolution; separation of the analyte from the matrix; transformation of the fraction separated into a source adequate for measurement; and determination of sample activity. In the separation process, it is important to take into consideration that elements with high valence states have a significant ability to form anionic complexes. Thus, anionic resins are very selective and adequate for separation. Literature describes many viable techniques that reduce the waste generation during the process [5-9] and in the 1990s Horwitz et al developed a separation process utilizing various organic extraction agents that was later brought to market by *Eichrom Technologies* in the form of chromatographic resins [10]. These resins impregnated with organic extractants have agents which are specific for separating a radionuclide or a set of radionuclides are very efficient and selective [6]. It is a common application of these techniques in isolation or combined, which obviously depends on the radionuclides present in the waste.

The objective of this study was to define a methodology for sequential analysis of isotopes of U, Pu and Am present in activated charcoal, evaluating chemical recovery, analysis time, the amount of radioactive waste generated and the cost.

## 2. MATERIALS AND METHODS

To define the optimal method of analysis for charcoal, selected radionuclides were determined according to the procedures described by Rodriguez *et al.* [11] and ASTM C1561-10 [12], and some modifications on methods were made for improve performance.

### 2.1. Sample Collection

The charcoal samples were collected from the research reactor IEA-R1, located on the campus of the University of São Paulo, Institute of Energy and Nuclear Research (IPEN).

### 2.2. Sample Preparation

The samples were pre-weighed (to determine the wet weight) and dried in an oven for 24 hours at 70 °C (for dry mass determination). Then the samples were weighed and kept in oven for 48 hours at 450 °C (for removal of organic matter).

The total mass of sample (0.3 g) was dissolved in a 250 mL beaker, adding 3 portions of 10 mL of 65% HNO<sub>3</sub> and 3 portions of 5 mL of 30% H<sub>2</sub>O<sub>2</sub>, under heating at 250 °C on a hot plate, so that each portion was added just after the sample has been dried. Tracers were previously added with the sample. Then, 5 mL of 69-72% HClO<sub>4</sub>, 5 mL of 48% HF, 10 mL of 65% HNO<sub>3</sub> were added and brought to dryness. For the elimination of HF and HClO<sub>4</sub> 3 parts of 6 mL of 65% HNO<sub>3</sub>, 2 mL 30% H<sub>2</sub>O<sub>2</sub> and 2 mL of deionized water were added. Then, the samples were completely dried, cooled and the salts were dissolved with approximately 20 mL of 8 M HNO<sub>3</sub> or oxalic acid in 2 M HNO<sub>3</sub> (in accordance with each method).

### 2.3. Radiochemical Separation

#### 2.3.1. Ion Exchange followed by Extraction Chromatography (EI + EC)

This methodology was based on the work described by Rodriguez *et al.* (1997) who studied the interferences in determination of Pu, Am and Cm in extraction chromatography for radioactive waste.

The analysis solution was obtained by dissolving the salts with 20 mL of 8 M HNO<sub>3</sub> and adding the following tracers: 2 mL of <sup>242</sup>Pu (44.92 Bq.L<sup>-1</sup>), 2 mL of <sup>232</sup>U (19.01 Bq.L<sup>-1</sup>) and 2 mL of <sup>243</sup>Am (23.35 Bq.L<sup>-1</sup>). The state of oxidation of Pu [+3] is set to [+4] with sodium nitrite.

The sample was percolated into a column containing *Dowex* 1 x 2, previously conditioned with 50 mL of 8 M HNO<sub>3</sub>. After percolation of the sample, 3 portions of 40 mL of 8 M HNO<sub>3</sub> were added and all effluent that should contain U and Am was collected. Then, three 40 mL portions of 37% HCl were added to eliminate possible interferences and to modify the medium acidic of resin, the effluent was discarded. Only Pu was retained on the resin, and its oxidation state reduced with hydroxylamine hydrochloride in [+4] to [+3] and then eluted with three 30 mL portions of 0.5 M HCl. The effluent containing U and Am was dried, diluted with 20 mL of 3 M HNO<sub>3</sub>, and the solution was percolated in columns UTEVA and TRU, previously conditioned with 20 mL of 3 M HNO<sub>3</sub> and mounted one above another, respectively. Two portions of 20 mL of 3 M HNO<sub>3</sub> were added and the effluent was discarded. The columns were separated and Am retained in the TRU column was eluted with two 15 mL portions of 0.05 M HNO<sub>3</sub>. The UTEVA column was conditioned with 10 mL of 9 M HCl to modify the medium, this effluent was discarded and U was then eluted with two 15 mL portions of 0.01 M HCl.

#### 2.3.2. Extraction Chromatography (EC)

The determination of the isotopes of U, Pu and Am was based on the standard *American Society for Testing and Materials* (ASTM) C1561-10 "Determination of plutonium and neptunium in uranium hexafluoride matrix and enriched uranium by alpha spectrometry" adapted to the laboratory conditions. Basically, the method uses UTEVA chromatographic columns for the purification of the isotopes of U followed by a column TRU for the purification of isotopes of Pu and Am. For quantification of isotopes by alpha spectrometry, electrodeposition was adopted instead of microprecipitation, because provides sources of isotopes with uniform thin layers, and also exhibit high spectral resolution.

The solution was prepared by dissolving the salts of the samples with 20 mL of oxalic acid in 2 M HNO<sub>3</sub> and adding the following tracers: 2 mL of <sup>242</sup>Pu (44.92 Bq.L<sup>-1</sup>), 2 mL of <sup>232</sup>U (19.01 Bq.L<sup>-1</sup>) and 2 mL of <sup>243</sup>Am (23.35 Bq.L<sup>-1</sup>). A UTEVA chromatographic column,

previously conditioned with 20 mL of oxalic acid in 2 M HNO<sub>3</sub>, was used for each sample. The solution was percolated into this column and then two 20 mL portions of oxalic acid in 2 M HNO<sub>3</sub> were added. All effluent (Pu and Am) was collected. The U retained in the UTEVA column was eluted with two 20 mL portions of 0.1M ammonium oxalate. The effluent was collected and dried under heating at 200 °C. The residue was dissolved with 20 mL of 3 M HNO<sub>3</sub> and the state of oxidation of Pu [+4] is set to [+3] with iron (III) nitrate solution (10 mg Fe/mL) and ascorbic acid solution (saturated).

The effluent containing Pu and Am was percolated in a TRU chromatographic column previously conditioned with 20 mL of 3 M HNO<sub>3</sub>. The state of oxidation of Pu was restored with a freshly prepared solution of 100 mg.mL<sup>-1</sup> sodium nitrite. The column was washed with 20 mL of 2 M HNO<sub>3</sub> and conditioned with 10 mL of 9 M HCl. All effluent was discarded. The Am was eluted with 10 mL of 4 M HCl, then 35 mL of 1.5 M HCl was added to eliminate possible interferences, isotopes of Pu were eluted subsequently with 15 mL of oxalic acid in 1 M HCl.

#### **2.4. Electrodeposition**

The eluates obtained were dried in a hot plate and then dissolved with 3 M H<sub>2</sub>SO<sub>4</sub> and 0.8 M ammonium sulphate. The samples were transferred to the electroplating cell with 0.8M ammonium sulphate and the pH was adjusted with 28% NH<sub>4</sub>OH and 3 M H<sub>2</sub>SO<sub>4</sub>, using 0.1% thymol blue as indicator. The electrodeposition was conducted under current of 1.20 A for 1 hour on polished silver plates and analyzed on an alpha spectrometer, calibrated previously [11].

#### **2.5. Quantification of Radionuclides**

An Alpha Spectrometry System (Model *Alpha Analyst of Canberra Industries*) was used with semiconductor detectors surface barrier.

### **3. RESULTS AND DISCUSSION**

The parameters observed and used to define the radioanalytical method are presented in Table 1. Comparing the results of chemical recovery obtained with two methods in the literature, it was observed that the methodology EI + EC, the results for Pu and Am were 90% and 80% respectively. In other words, very close to the values observed in this study, 84% (Pu) and 94% (Am). The results obtained by EC were also very similar, 103% (U) and 98% (Pu) against 86% (U) and 94% (Pu).

Comparing the methods EI + EC and EC, it was observed that, despite the differences between the chemical recoveries, there was no significant difference in the concentrations of the elements of activities, demonstrating that the application of the technique's EC is feasible to determine the isotopes U, Pu and Am, as well as the technique EI + EC.

All liquid waste, radioactive or not, generated during the analysis was collected and properly treated. The final volume of radioactive waste generated in each analysis was measured and the average values were 383 and 230 mL for methods EI + EC and EC, respectively. The EC method presented a volume of waste smaller than the EI + EC, which makes it a more economical and environmentally viable. It was observed a significant reduction of the time of

analysis. In general, EC method was the most practical and smaller volumes of reagents with low concentrations were employed.

To evaluate the cost of analysis the cost and maintenance of equipment, power consumption, glassware and regeneration of columns were not taken into consideration. To calculate the volume of radioactive waste generated, we considered all steps from sample dissolution to electrodeposition.

**Table 1: Parameters used in the radioanalytical method definition**

Parameters	EI + EC	EC
RC (%)	76 – 100	74 – 100
Analysis time (days)	6.9	6.5
Waste radioactive (mL)	383	230
Cost/sample (R\$)	R\$ 1,085.83	R\$ 967.73

The analysis time was the same for both methods, about 7 days. The volume of radioactive waste generated by the method EI + EC was about 67% higher when compared with the volume generated by the EC. In terms of cost, were 12% higher than the EC. These results suggest that the EC method is the most efficient for the determination of U, Pu and Am found in radioactive wastes.

#### 4. CONCLUSIONS

Two separation techniques for the determination of isotopes of U, Pu and Am using *Dowex 1 x 2*, produced by *Sigma-Aldrich* and resins TRU and UTEVA, produced by *Eichrom Technologies*, were tested and compared. From the results obtained it was possible to conclude that:

- ✓ The analysis time spent in the two methods was similar, about seven days;
- ✓ Methods EI + EC and EC provide similar results;
- ✓ All radioactive waste generated during the work was properly treated;
- ✓ The EC method is most suitable for determination of selected elements for generating the smaller volume of radioactive waste and being less expensive.

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