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DETERMINATION OF ^{238}Pu, $^{239+240}$Pu, ^{241}Pu AND ^{241}Am IN RADIOACTIVE WASTE FROM IPEN'S REACTOR

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ABSTRACT

Ion exchange resin is a common type of radioactive waste arising from treatment of coolant water of the main circuit of research and nuclear power reactors. This waste contains high concentrations of fission and activation products. The management of this waste includes its characterization in order to determine and quantify specific radionuclides including those known as difficult-to-measure radionuclides (RDM). The analysis of RDMs generally involves expensive and time-consuming complex radiochemical analysis for purification and separation of the radionuclides. The objective of this work is to show an easy methodology for quantifying plutonium and americium isotopes in spent ion exchange resin, used for purification of the cooling water of the IEA-R1 reactor located at the Nuclear and Energy Research Institute, IPEN-CNEN/SP. The resins were destroyed by acid digestion, followed by purification and separation of the Pu and Am isotopes with anionic and chromatographic resins. 238Pu, 239+240Pu, and 241Am isotopes were analyzed in an alpha spectrometer equipped with surface barrier detectors. 241Pu isotope was analyzed by liquid scintillation counting. Chemical recovery yield ranged from 73 to 98% for Pu and 77 to 98% for Am, demonstrating that the methodology is suitable for identification and quantification of the isotopes studied in spent resins.
Keywords: radioactive waste, transuranic, spent ion exchange resin, chromatography and characterization.

1. INTRODUCTION

Ion exchange resin is a common type of radioactive waste arising from treatment of coolant water of the main circuit of research and nuclear power reactors. Resin removes radioactive elements dissolved in the water while the reactor is in operation, becoming radioactive [1].

Resin, 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 directly measure 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, ionic 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}H, ^{14}C, ^{54}Mn, ^{55}Fe, ^{59}Ni, ^{60}Co, ^{63}Ni, and ^{94}Nb), fission products (^{90}Sr, ^{99}Tc, ^{129}I, ^{134}Cs, and ^{137}Cs), transuranics (^{241}Am, ^{242}Cm, and ^{244}Cm) and isotopes of U and Pu. Some of these radionuclides don't 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 four 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's 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 and col. [10] developed a separation process utilizing various organic extraction agents that was later brought to market by Eichrom Technologies in the form of chromatographic resins, such as TRU resin, and several other extractors, can offer actinides in extremely high selectivity.

The objective of this work is to present an easy-to-apply analytical methodology for determining concentrations and activities of ^{238}Pu, $^{239+240}Pu$, ^{241}Pu, and ^{241}Am in five different resin samples collected at the IEA-R1 research reactor at the Institute of Nuclear and Energetic Research, IPEN-CNEN/SP.

2. MATERIALS AND METHODS

2.1. Sample collection

Resin samples were collected at IPEN's Radioactive Waste Management located on the campus of the University of São Paulo.

2.2. Sample preparation

Samples were previously weighed (to determine wet mass) and dried for 24 hours at 70 °C (to determine dry mass).

Decomposition was carried out with approximately 0.3 g of dry sample which was transferred to a 250 mL beaker and then concentrated HNO_3 and 30% H_2O_2 were added. The mixture was heated to 100 °C on a hot plate and before drying several doses of 10 mL of HNO_3 and 2 mL H_2O_2 were added until complete decomposition was verified. The sample was then dried, cooled and reconstituted with 8M HNO_3 in a 100 mL volumetric flask.

A 50 mL aliquot was transferred to a 250 mL beaker and then 5 mL of ^{242}Pu tracer and 2 mL of ^{243}Am tracer were added.

The desired oxidation state of Pu (IV) was adjusted with approximately 0.30 g of $NaNO_2$ and left to rest for 12 hours.

2.3. Determination of ^{241}Am and Plutonium isotopes

The radionuclides present in the resulting solution were separated and purified by the strongly anionic Dowex 1x2 resin (pre-treated with 8M HNO_3 at a drip rate of 2.0 to 3.0 seconds per drop). The column was then washed three-times with 40 mL of 8M HNO_3 and all of the effluent was reserved for Am analysis. Next the column was washed three times with 40 mL of 8M HNO_3 to eliminate interference. For Pu elution, approximately 0.30 g $NH_2OH.HCl$ was added to the resin as were 3 doses of 30 mL 0.5M HCl and all of the effluent was reserved for Pu isotope analysis. The effluent containing Am was heated on a hot plate until it was dry and 20 mL of 2M HNO_3 was added. The sample was percolated through a TRU chromatographic resin that had been pre-treated with 2M HNO_3 and then washed twice with 10 mL of 2M HNO_3. The Am was eluted twice with 20 mL of 0.05M HNO_3. The effluent containing Pu was dried using a hot plate, chilled and reconstituted with 8M HNO_3 in a 25 mL volumetric flask. The sample was divided into two 10 mL parts. The first part was used for electrodeposition and alpha spectrometry while the second was used to determine ^{241}Pu [11]. The first part was transferred to a 100 mL beaker in order to determine ^{238}Pu and $^{239+240}$Pu.

2.4. Eletrodeposition of Plutonium and Americium

The eluates obtained were evaporated and electrodeposited on polished silver plates with a 1.2 A current for one hour.

After electrodeposition, samples were quantified by Alpha Spectrometer with the efficiency of the detector determined by means of a certified standard source of alpha emitters.

2.5. Determination of ^{241}Pu activity

^{241}Pu is a pure low-energy beta emitter and was quantified by liquid scintillation. The second fraction of the sample was transferred to a liquid scintillation vial, brought to a hot plate and evaporated to dryness twice with a few milliliters of concentrated HCl. The residue was dissolved in 2 mL of 0.1M HCl and then 18 mL of Packard Ultima Gold AB Cocktail was added. The measurement was carried out after the vial containing the sample had been stabilized in a cool dark environment [11].

Due to the lack of a certified ^{241}Pu standard, calibration efficiency was determined using a ^{3}H standard [11, 12]. Maximum beta energies of ^{3}H and ^{241}Pu are18.6 KeV and 20.8 KeV respectively and since they are similar the same channel (10 - 250) can be used to determine radionuclides. Equal quenching effects can be assumed for both, at low energies. The counting efficiency curve was determined with a ^{3}H reference solution by external standardization for various levels of quenching. According to this external calibration, a counting efficiency of 37-39% and detection limit of 1.8 Bq kg^{-1} were obtained [11].

The activity of ^{241}Pu in the determination time was calculated by the equation:

$$A_1 = \frac{A_2.R_1}{\varepsilon_1.R_2.\alpha.m.\varepsilon_2} \quad (1)$$

In which:

A_1 – sample activity (Bq g^{-1}),
A_2 – tracer activity ^{242}Pu (Bq g^{-1}),
R_1 – ^{3}H liquid count rate on the beta channel (cpm),
ε_1 – ^{3}H counting efficiency (%),
R_2 – total liquid alpha count rate on the alpha channel (cpm),
α – ratio: ^{242}Pu count over total alpha count by alpha spectrometry measurement,
m – sample mass (g),
ε_2 – alpha count efficiency.

2.6. Analytical and nuclear techniques

A Canberra Alpha Analyst Alpha Spectrometry System with surface barrier semiconductor detectors was used. For beta emitting radionuclides, a Hidex model 300 SL Liquid Scintillation System was employed.

3. RESULTS AND DISCUSSION

Table 1 shows results obtained for plutonium isotopes and ^{241}Am in resin samples collected from the IEA-R1 reactor.

Table 1. Results for Radionuclides in Resins

Samples (Bq g^{-1})	^{241}Am	^{238}Pu	$^{239+240}$Pu	^{241}Pu
R-01	$2.5.10^{-2}\pm2.6.10^{-3}$	$3.7.10^{-2}\pm1.2.10^{-3}$	$1.8.10^{-1}\pm3.9.10^{-3}$	$< 5.11.10^{-1}$
R-02	$4.7.10^{-2}\pm3.6.10^{-3}$	$9.4.10^{-2}\pm4.7.10^{-3}$	$4.5.10^{-1}\pm1.6.10^{-2}$	$2.0.10\pm2.0.10^{-1}$
R-03	$4.1.10^{-2}\pm2.3.10^{-3}$	$1.0.10^{-1}\pm5.4.10^{-3}$	$4.5.10^{-1}\pm1.5.10^{-2}$	$4.5.10^{-1}\pm4.5.10^{-2}$
R-04	$3.5.10^{-2}\pm1.7.10^{-3}$	$8.4.10^{-2}\pm4.2.10^{-3}$	$4.3.10^{-1}\pm1.6.10^{-2}$	$4.1.10\pm4.1.10^{-1}$
R-05	$5.6.10^{-2}\pm3.6.10^{-3}$	$1.1.10^{-2}\pm1.3.10^{-3}$	$6.5.10^{-2}\pm3.3.10^{-3}$	$< 5.11.10^{-1}$

It was observed low activities for ^{241}Am and ^{238}Pu, usually found in environmental samples. $^{239+240}$Pu had slightly higher activities, approximately 10 times that of ^{241}Am and ^{238}Pu radionuclides. The concentration of ^{241}Pu varied considerably, between 0.445 and

4.088 Bq g^{1}, and in two samples the results were below the detection limit of 0.511 Bq g^{-1}. The concentration of ^{241}Pu was approximately a hundred times higher than ^{241}Am and ^{238}Pu.

Tracers are radioactive isotopes with chemical properties similar to the elements of interest. They are introduced into the samples to provide information separation process during a radiochemical analysis. The Fig. 1 presents the chemical recovery values of Pu and Am radioisotopes.

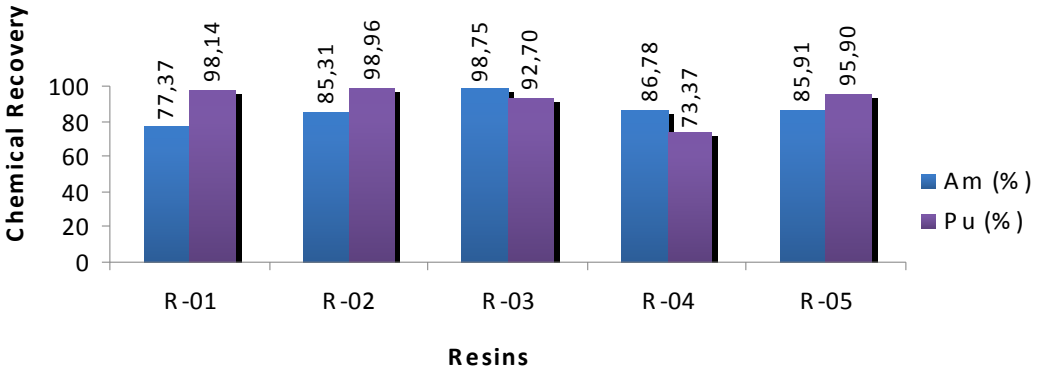

Figure 1. Chemical recovery values of Pu and Am radioisotopes.

The chemical recoveries obtained were from 73 to 98 % for Pu, and 77 to 98 % for Am. These results suggested that the technique adopted in this work is applicable to resins characterization. Similar results are found in the literature. Vajda et al. reviewed and assessed the radiochemical procedures that are currently the state-of-the-art for the determination of Pu, Np and Am nuclides in various matrixes focusing on environmental samples using alpha spectrometry. These authors reported chemical recoveries ranging from 50 to 70 % for Pu and 82 % for Am [13].

4. CONCLUSIONS

The methodology presented in this paper was suitable for characterization of the resins used in the process of purifying water research reactor of IPEN IEA-R1 and it was possible to determine the concentration of Pu and Am isotopes. It is noteworthy that even after several steps to purification and separation of these isotopes, the methodology presented a good tracer recovery, showing that the analytical method is efficient and easy to apply.

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