



Radioanalytical methods for sequential analysis of actinide isotopes in activated carbon filter-bed waste

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Abstract

In this work, we compare methods for the sequential determination of U and the transuranium elements Np, Pu, Am, and Cm. The chemical yield, the time spent in the analysis, the amount of secondary waste, and the costs of each method are the aspects of interest. Two methods were compared: extraction chromatography (EC) and ion exchange plus extraction chromatography (IE + EC). The chemical yields of (EC) and (IE + EC) were similar for all radionuclides. The (EC) method is the more effective with respect to time of analysis, the amount of secondary waste and costs.

Keywords Radioactive waste · Radiochemistry · Difficult to measure radionuclides · Cost–benefit analysis

Introduction

IEA-R1 is a nuclear research reactor situated at the Nuclear and Energy Research Institute (IPEN) in Sao Paulo, Brazil. Various radioactive wastes are routinely generated, including replaced filter beds with activated carbon used in the cooling water primary circuit purification system. This filter is used to remove the radioactive material dissolved in water that is retained neither in the cartridge filters nor the ion-exchange resins, the other two filter types of the system.

The control of the water quality is made by measurements of water conductivity and the concentration of radioactive material. When the parameters are outside the established limit, the ion-exchange resins are regenerated and the carbon beds backflushed. If these treatments fail in restoring

operational conditions, the filter beds are replaced and collected as solid radioactive waste.

The radionuclides of most radiological significance, that are present in the wastes generated by the nuclear research reactor, are a) fission products such as ³H, ¹⁴C, ⁹⁰Sr, ⁹⁹Tc, ¹²⁹I, ¹³⁴Cs, and ¹³⁷Cs; b) activation products such as ⁵⁴Mn, ⁵⁵Fe, ⁶⁰Co, ⁵⁹Ni and ⁶³Ni; c) the natural isotopes of U; and d) the actinides ²³⁷Np, ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Am, ²⁴²Cm and ²⁴⁴Cm.

Many of them are known as Difficult To Measure Radionuclides (DTM). There are two main reasons for such denomination. Firstly, they do not emit measurable gamma radiation in their nuclear decay process. They are pure alpha, pure beta or low-energy photon emitters not tractable to direct measurement [1]. Secondly, the determinations of their activities require expensive and time-consuming radiochemical analysis. DTMs are considered important from the point of view of radiation safety in the long term management of radioactive waste [1].

The radiochemical methods currently applied to waste characterization are difficult to implement on a routine basis. Historically, techniques such as precipitation, ion exchange or solvent extraction have been used for the separation and quantification of various elements, but these methods are complex, time-consuming and generate large amounts of chemical waste [2].

The precipitation technique, for example, is not selective for certain analytes compared to ion exchange or solvent

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extraction and requires intensive work in the process [3]. Other drawbacks are the extensive use of chemicals to reduce metals, excessive sludge production, high salt load or high suspended solids content, slow metal precipitation, and aggregation tendency [4, 5].

The ion exchange technique is selective and is less laborious, although requires large volumes of acids and resins in their elution, washing and extraction processes. Solvent extraction is the most selective; however, it has drawbacks to be considered. Firstly, the solvent may dissolve unwanted products depending on the target matrix. This may interfere with the subsequent analysis. Secondly, evaporation of the solvent may also cause evaporation of some of the volatile components present in the prepared solutions [6].

In order to streamline the separation process and reduce waste generation during the process, various alternatives or improvements of these methods have been proposed. Examples in radiochemistry are (1) flow injection techniques [7–9], (2) selective precipitation under alkaline conditions [10], and (3) extraction resin, known as DGA Branched from Eichrom [11]. The latter technique has been improved since the 1990s, when Horwitz [12] developed separation processes using various organic extracting agents. These extraction resins were later commercially available from Eichrom Technologies as chromatographic resins. These resins have impregnated organic extracting agents that are specific for the separation of a chemical element or a set of elements and that allow the measurement of a radionuclide or set of related radionuclides. These resins are very selective and efficient [13].

Methods related to the sequential determination of actinides in radioactive waste samples have been described in the literature. Ion exchange resin was the method of choice for Kastner et al. [14], who employed the Dowex 1 × 8 resin and alpha spectrometry to determine U, reaching an average chemical yield of 95%. Osváth et al. [15] determined ^{237}Np and other long-lived isotopes of Sr, Zr, Nb, U, Pu, Am, and Cm. For that, the separation of the isotopes was done using the resins: UTEVA (Zr, U, Np, and Pu), TRU (Am and Cm), Sr (Sr) and anion exchange resin (Nb). The determination of chemical yields was carried out by liquid scintillation counting (LSC) (Sr), alpha spectrometry (U, Pu, Am, and Cm), inductively coupled plasma mass spectrometry (ICP-MS) (Zr and Np), gamma spectrometry and X-ray spectrometry (Nb). The chemical yields of Sr, Zr, Nb, U, Np, Pu, Am were 62–74%, 31–99%, 30–89%, 65–83%, 66–99%, 36–92%, 55–89%, respectively.

Shimada et al. [16] used the chromatographic extraction technique to analyze Th, U, Pu, Am and Cm. UTEVA and TRU resins were used to separate the radionuclides (Th and U) and (Pu, Am and Cm), respectively. The concentrations were determined by alpha spectrometry (Pu, Am and Cm) and ICP-MS (Th and Pu). The chemical yields obtained were

superior to 85% for all radionuclides, and especially high for Pu (97%) and Am (91%).

Desideri et al. [17] developed a simple, fast method for sequential separation of actinide elements from aqueous solutions and their determination by alpha spectrometry. The technique used for the separation was chromatographic extraction using microporous polyethylene as a support, tri-n-octylamine (TNOA) as stationary phase and hydrochloric acid (with and without reducing agents) as mobile phase. The chemical yields obtained were 64% for U, 79% for Np, 82% for Pu, and 75% for Am and Cm.

Dulanská et al. [18] studied the application of solid phase extraction (SPE) products for sample pre-concentration, preparation and separation. Resins were used: AnaLig Pu02 for the isotopes of Pu, AnaLig Sr01 for ^{90}Sr and TRU for the separation of ^{241}Am in samples of radioactive sludge. The isotopes of Pu and Am were determined by Alpha Spectrometry and the ^{90}Sr was determined by LSC. The authors observed high chemical recoveries, 92% for Sr, 89% for Pu and 84% for Am and effective removal of interferents.

Macsik et al. [19] developed a radioanalytical method based on the use of a single TRU extraction chromatographic column and on-column oxidation state adjustment of actinides. The system was designed to determine Th, U, Np, Pu and Am(Cm) in environmental samples. By using alpha spectrometry and ICP-MS, they were able to gather trustworthy information over a wide range of isotopes. In one sample, the following isotopes were determined: ^{228}Th , ^{230}Th , ^{232}Th , ^{234}U , ^{235}U , (^{236}U), ^{238}U , ^{237}Np , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{241}Am , ^{242}Cm , ^{243}Cm and ^{244}Cm .

Faye et al. [20] applied a five-step sequential extraction procedure for the determination of the actinides ^{232}Th , ^{238}U , $^{239,240}\text{Pu}$ and ^{241}Am from sediment. For that, the authors employed a NaOH fusion procedure followed by sequential leaching, which was able to completely dissolve insoluble species.

Luo et al. [21] employed sequential analyses of actinides in environmental samples. Analyzed material was large-size samples of soil and sediment. The authors totally dissolved the samples by employing a dissolution method based on lithium metaborate fusion, with subsequent chromatographic separation. The method allowed the simultaneous determination of Pu, Am, Cm isotopes by alpha spectrometry and ICP-MS. For that, the authors spiked known amounts of ^{239}Pu and ^{241}Am in the samples, besides using certified reference materials.

The establishment of the radiochemical analysis protocols for activated carbon waste from nuclear reactors is a difficult task, not only because of the separation techniques required but also as a result of the large number of radionuclides that must be analyzed. Furthermore, guidelines and reports on the characterization of activated carbon from nuclear reactors are scarce in the literature and the available works do

not take into consideration aspects such as time, costs and secondary waste.

The elements U, Np, Pu, Am, and Cm were selected for study in activated carbon filter beds because they are long-lived radiotoxic radionuclides that pose a high risk to human health if not managed and disposed of properly. The particular concern about these elements in the United States has led to the creation of a special waste class called transuranic wastes (TRUW), which are managed differently from low- and intermediate-level wastes [22, 23].

To the best of our knowledge, a comparison of methods considering chemical yield, time of analysis, the amount of secondary waste generated and costs has not been previously performed, considering two methodologies. These methodologies are extraction chromatography (EC), and ion exchange plus extraction chromatography (IE + EC), which were compared and validated.

Experimental

Materials and equipment

To define the optimal method for carbon analysis, selected radionuclides were assessed according to procedures described elsewhere [24, 25]. Some modifications to these methods were carried out to improve analysis performance of the current matrix.

Sample collection and preparation

The samples were collected from fourteen 200 L drums containing a slurry of activated carbon with variable water content. Samples with approximately 1 mL of water and carbon were weighed and dried in an oven for 24 h at 70 °C for the determination of dry mass. They were then calcinated in a muffle furnace for 48 h at 450 °C.

Samples with approximately 0.3 g each were dissolved in a 250 mL beaker by adding 3 × 10 mL of 65% HNO₃ and 3 × 5 mL of 30% H₂O₂ and evaporated to dryness on a hot plate each time at 250 °C. Likewise, 5 mL of 69–72% HClO₄, 5 mL of 48% HF, and 10 mL of 65% HNO₃ were added. For the elimination of HF and HClO₄, 3 × 6 mL of 65% HNO₃, 2 mL of 30% H₂O₂ and 2 mL of deionized water were added. The samples were completely dried, cooled and the salts were dissolved with approximately 20 mL 8 mol L⁻¹ HNO₃ or oxalic acid with 2 mol L⁻¹ HNO₃, in accordance with each radiochemical determination method.

Appropriate tracers were added into the carbon sample before dissolution. The ²³²U, ²³⁶Pu, ²⁴²Pu, and ²⁴³Am tracers were selected for the analysis, considering the maximum alpha-ray energies of each one, to avoid spectral overlap. According to the basic nuclear properties, ²³⁶Pu and ²⁴²Pu are

typically used as radioactive tracers in the determination of ²³⁸Pu and ^{239,240}Pu, and ²³²U is used in the determination of U isotopes. ²³⁷Np does not have an appropriate yield tracer. ²³⁹Np (β/γ) could be used, but it has a very short half-life (2.4 d), and regular weekly preparation and normalization is also necessary, which is time-consuming and very expensive. ²³⁶Np is not easy to prepare because it is produced by bombarding the ²³⁵U with deuterons [17]. ²³⁵Np could also be used as a tracer, but it contains some ²³⁷Np impurities. For that reason, we employed ²³⁶Pu and ²⁴²Pu as the tracers, since both have the similar chemical behavior of ²³⁷Np. It is noteworthy that various oxidation states of the elements Pu and Np co-exist simultaneously [17]. These states are: Pu⁴⁺, Pu³⁺, PuO₂⁺, PuO₂²⁺, Np⁴⁺, NpO₂⁺ and NpO₂²⁺. Also, modifications in the redox conditions of the solutions can be turned to a particular state.

For the determination of ²⁴¹Am and often for Cm isotopes, ²⁴³Am is used as a tracer. The ²⁴³Am tracer was used in the isotope analysis of Cm because they present the same chemical behaviors. A sequential method for all radionuclides was not possible with the same sample. Firstly, the alpha-ray energy of the ²⁴²Pu (4.86 MeV) tracer is close to the ²³⁷Np (4.79 MeV) energy. Secondly, the resolution of the equipment (0.02 MeV) does not allow the distinction between these two energy peaks. Finally, when using ²³⁶Pu (*t*_{1/2} = 2.87 years) its decay to ²³²U should be considered, which makes it impossible to determine U isotopes simultaneously with Pu isotopes.

The purification of the ²³⁶Pu tracer would be an option, but it would require a calibration laboratory [25]. For these reasons, 2 × 0.3 g samples were dissolved for both methods. In total, 4 × 20 mL solutions were generated, namely: Solution 1 and Solution 2 for the (IE + EC) method; and Solution 3 and Solution 4 for the (EC) method.

Column preparation

Strongly Basic Dowex®1 × 2 anion exchange resin columns were assembled from a 10 mm diameter × 300 mm high glass column in addition to the reservoir (40 mm diameter × 130 mm height). Columns were mounted by adding a pre-conditioned amount of resin in 8 mol L⁻¹ HNO₃ sufficient to reach 130 mm in height.

UTEVA and TRU chromatographic columns produced by Eichrom Technologies are commercially available as cartridges containing 2 mL each with particle size 100–150 μm. Both were used in combination with a vacuum extraction system.

Radiochemical separation

Determination of Np, U, Pu, Am and Cm isotopes—(IE + EC)

Solutions 1 and 2 were obtained by dissolving the salts with 20 mL of 8 mol L⁻¹ HNO₃. The preparation of both

solutions is then described in detail. Solution 1 contains the following tracers: 2 mL of ^{242}Pu (45 Bq L^{-1}), 2 mL of ^{232}U (19 Bq L^{-1}) and 2 mL of ^{243}Am (23 Bq L^{-1}). The oxidation state of Pu [+3] was adjusted to [+4] with about 0.30 g of sodium nitrite. The sample was percolated on a column containing Dowex[®]1 × 2 resin, previously conditioned with 50 mL $8 \text{ mol L}^{-1} \text{ HNO}_3$ in 1.5 mL min^{-1} .

After sample percolation, $3 \times 40 \text{ mL}$ portions of $8 \text{ mol L}^{-1} \text{ HNO}_3$ were added following the same flow rate; all effluent was collected as it contained U, Am, and Cm. $3 \times 40 \text{ mL}$ portions of 37% HCl were added to eliminate possible interfering elements and change of acid resin medium. At this stage, flow control was unnecessary and the effluent was discarded. Only Pu was retained in the resin, followed by a decrease in oxidation state with hydroxylamine hydrochloride from [+4] to [+3] and then eluted with $3 \times 30 \text{ mL}$ portions of $0.5 \text{ mol L}^{-1} \text{ HCl}$ in 1.5 mL min^{-1} . Note that depending on the solutions (1 or 2), different approaches were considered. Np was retained in the resin when Solution 1 was employed. In that case, ^{242}Pu (which has energy very close to ^{237}Np) was used. As a result, Np was not analyzed in Solution 1. On the other hand, with Solution 2, ^{236}Pu was used and ^{237}Np was analyzed.

The effluent containing U, Am, and Cm was heated to dryness and then dissolved with 20 mL of $3 \text{ mol L}^{-1} \text{ HNO}_3$, percolated in the UTEVA and TRU columns sequentially, previously conditioned with 20 mL of $3 \text{ mol L}^{-1} \text{ HNO}_3$. Two 20 mL portions of $3 \text{ mol L}^{-1} \text{ HNO}_3$ were added to the columns and the effluent was discarded.

The columns were separated, and Am and Cm were eluted from the TRU column with $2 \times 15 \text{ mL}$ portions of $0.05 \text{ mol L}^{-1} \text{ HNO}_3$. The UTEVA column was conditioned with 10 mL of $9 \text{ mol L}^{-1} \text{ HCl}$ for medium change. This effluent was discarded and the U was then eluted with $2 \times 15 \text{ mL}$ portions of $0.01 \text{ mol L}^{-1} \text{ HCl}$. The flow rate was not controlled in these elution steps.

For Solution 2, the second mass of that same sample was weighed, and the same preparation procedure was performed to obtain ^{237}Np analysis. A simultaneous and sequential analysis for the five radionuclides was not possible due to the fact that ^{237}Np had energy very close to the energy of the ^{242}Pu tracer, which required a second sample using the ^{236}Pu tracer. It has energy far from the energy of ^{237}Np , thus making its determination possible.

Solution 2 was prepared with 2 mL of ^{236}Pu (35.74 Bq L^{-1}) and 2 mL of ^{243}Am (23.35 Bq L^{-1}) as tracers. The oxidation states of Pu [+3] and Np [+4] were adjusted to [+4] and [+5], respectively, with about 0.30 g of sodium nitrite.

The sample was percolated on a column containing Dowex[®]1 × 2 resin, previously conditioned with 50 mL of $8 \text{ mol L}^{-1} \text{ HNO}_3$ in 1.5 mL min^{-1} . After sample percolation, $3 \times 40 \text{ mL}$ portions of $8 \text{ mol L}^{-1} \text{ HNO}_3$ were added

following the same flow rate. All effluent was collected as it contained Am and Cm. $3 \times 40 \text{ mL}$ portions of 37% HCl were added to eliminate possible interfering elements and change of acid resin medium. At this stage, the flow was not controlled and the effluent was discarded. Only Pu and Np were retained in the resin, and their oxidation states reduced with hydroxylamine hydrochloride, Pu [+4] to [+3] and Np [+5] to [+4], later eluted with $3 \times 30 \text{ mL}$ portions of $0.5 \text{ mol L}^{-1} \text{ HCl}$ at 1.5 mL min^{-1} .

The procedure of sample preparation and percolation in columns for Solution 2 was very similar to that of Solution 1. The only difference is that in Solution 2, U was not analyzed. In short, the effluent was heated to dryness, diluted with 20 mL of $3 \text{ mol L}^{-1} \text{ HNO}_3$, and percolated in the columns, previously conditioned and mounted. After columns were separated, the radionuclides were eluted from the columns.

The detailed procedure is presented in the flow charts of the Supplementary Material (Fig. S3 and S4). This method was based on the work described by [24], in which they applied a method for the study of interferences in the determination of Pu, Am, and Cm in radioactive waste by chromatographic extraction.

Determination of Np, U, Pu, Am, and Cm isotopes—EC

U, Np, Pu, Am and Cm isotope determination was based on a standard [25] adapted to laboratory conditions. In sum, the method uses UTEVA chromatographic columns for U isotope purification followed by a TRU column for Np, Pu, Am, and Cm isotope purification. For the quantification of isotopes by alpha spectrometry, the electrodeposition technique was employed, instead of microprecipitation, to provide sources with uniform and thin isotope layers, and also to present high-resolution spectra.

Solutions 3 and 4 were prepared by dissolving the sample salts with 20 mL of a solution of oxalic acid in $2 \text{ mol L}^{-1} \text{ HNO}_3$. Solution 3 contains the following tracers: 2 mL of ^{242}Pu (45 Bq L^{-1}), 2 mL of ^{232}U (19 Bq L^{-1}) and 2 mL of ^{243}Am (23 Bq L^{-1}). A previously conditioned UTEVA chromatographic column with 20 mL of oxalic acid in $2 \text{ mol L}^{-1} \text{ HNO}_3$ was used for each sample. In this method, the control of the flow was unnecessary. Solution 3 was percolated into this column, then $2 \times 20 \text{ mL}$ portions of oxalic acid in $2 \text{ mol L}^{-1} \text{ HNO}_3$ were added. The effluent containing Pu, Am, and Cm was collected. The U was eluted with $2 \times 20 \text{ mL}$ portions of 0.1 mol L^{-1} ammonium oxalate. The collected effluent was dried under heating at $200 \text{ }^\circ\text{C}$, the residue was dissolved with 20 mL of $3 \text{ mol L}^{-1} \text{ HNO}_3$ and the oxidation state of Pu [+4] was adjusted to [+3] with 1 mL of $10 \text{ mg mL}^{-1} \text{ Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 2.5 mL saturated ascorbic acid solution.

The effluent containing Pu, Am, and Cm was percolated on a pre-conditioned TRU chromatographic column with 20 mL of 3 mol L⁻¹ HNO₃. The oxidation state of Pu was restored with 5 mL of a freshly prepared 100 mg mL⁻¹ sodium nitrite solution. The column was washed with 20 mL of 2 mol L⁻¹ HNO₃ and conditioned with 10 mL of 9 mol L⁻¹ HCl and all effluent was discarded. Am and Cm were eluted with 10 mL of 4 mol L⁻¹ HCl, then 35 mL of 1.5 mol L⁻¹ HCl were added to eliminate possible interfering elements. Pu isotopes were further eluted, with 15 mL of oxalic acid in 1 mol L⁻¹ HCl.

Solution 4 was prepared with 2 mL of ²³⁶Pu (35.74 Bq L⁻¹) and 2 mL of ²⁴³Am (23.35 Bq L⁻¹) as tracers. A previously conditioned UTEVA chromatographic column with 20 mL of oxalic acid in 2 mol L⁻¹ HNO₃ was used for each sample. Solution 4 was percolated on this column, then 2 × 20 mL portions of oxalic acid in 2 mol L⁻¹ HNO₃ were added. The effluent containing Pu, Np, Am, and Cm was collected. 2 × 20 mL portions of 0.1 mol L⁻¹ ammonium oxalate were added to the column to remove U residues from the ²³⁶Pu tracer. The collected effluent was dried under heating at 200 °C and the residue was dissolved with 20 mL of 3 mol L⁻¹ HNO₃ and the oxidation states of Pu [+4] and Np [+5] were adjusted to [+3] and [+4], respectively, with 1 mL of 10 mg mL⁻¹ Fe solution (Fe(NO₃)₃·9H₂O) and 2.5 mL of saturated ascorbic acid solution.

The effluent containing Pu, Np, Am, and Cm was percolated on a pre-conditioned TRU chromatographic column with 20 mL of 3 mol L⁻¹ HNO₃. The oxidation states of Pu and Np were restored with 5 mL of a freshly prepared 100 mg mL⁻¹ sodium nitrite solution. The column was washed with 20 mL 2 mol L⁻¹ HNO₃ and conditioned with 10 mL of 9 mol L⁻¹ HCl and all effluent was discarded. Am and Cm were eluted with 10 mL of 4 mol L⁻¹ HCl, then 35 mL of 1.5 mol L⁻¹ HCl were added to eliminate possible interferences. Pu and Np isotopes were eluted consequently with 15 mL of oxalic acid in 1 mol L⁻¹ HCl. The detailed procedure is presented in Fig S5 and S6.

U, Np, Pu, Am, and Cm electrodeposition

The following description is the method employed for both (IE + EC) and (EC). The obtained eluates were dried on a hot plate and then dissolved with 3 drops of 3 mol L⁻¹ H₂SO₄ and 3 mL of 0.8 mol L⁻¹ ammonium sulfate. Samples were transferred to the electrodeposition cells with 5 mL 0.8 mol L⁻¹ ammonium sulfate and the pH was adjusted with 28% NH₄OH and 3 mol L⁻¹ H₂SO₄ using 3 drops of thymol blue 0.1% as an indicator. Electrodeposition was conducted under current of 1.20 A for 1 h on polished silver plates and analyzed on a previously calibrated alpha spectrometer [24].

Radionuclide quantification

The Alpha Spectrometry System (model Alpha Analyst from Canberra Industries) consists of Passivated Implanted Planar Silicon (PIPS) surface barrier semiconductor detectors with an area of 450 mm². The detector has a resolution of approximately 0.020 MeV (FWHM), counting efficiency of 17–19% for a 0.5 cm source-detector distance calibrated for 3 to 10 MeV energy. Genie™ 2000 software was used for data acquisition and processing. The counting time was 200040.0 s for each radionuclide (Canberra, 2011).

Equipment calibration—count efficiency

To ensure correct identification and quantification of alpha-emitting radionuclides, the system was calibrated for energy, resolution and counting efficiency using a standard electrodeposited mixed source containing 1.602 Bq ²³⁸U, 1.573 Bq ²³⁴U, 1.685 Bq ²³⁹Pu, and 1.647 Bq ²⁴¹Am, certified by Analytix Inc. and NIST traceable material, model SRS 63997-121. Radionuclide chemical yield was calculated by applying Eq. (1 to 3).

$$CY = \frac{\text{Determined}}{\text{Added}} \quad (1)$$

$$\text{Determined} = \frac{\text{Area}}{t\varepsilon} \quad (2)$$

$$\text{Added} = A_t V \quad (3)$$

where CY is the chemical yield (%); determined is the activity determined; added is added activity; area is the total peak area of the tracer; *t* = counting time (s); *ε* = equipment counting efficiency; *A_t* = tracer activity concentration (Bq L⁻¹); *V* = tracer volume added (L).

Radionuclide activity concentration was calculated by applying Eq. (4).

$$A_1 = \frac{A_2}{CY \times \varepsilon \times t \times m} \quad (4)$$

where *A₁* is the activity concentration (Bq g⁻¹) of the calculated isotope (i.e. ²³⁷Np); *A₂* is the total area of the calculated isotope (i.e. ²³⁷Np); *m* is the mass of the dry sample (g), mass held in solution.

The isotope limit of detection (LD) was calculated by applying Eq. (5) (Fernando et al. 2013):

$$LD = \frac{K^2}{t} + 2\sqrt{2KS_B} \quad (5)$$

where K is the dimensionless constant; t is the counting time (s), and S_b is the background (BG) standard deviation (blank).

Reference material

To assess the methods for reliability and traceability, a reference material supplied by the International Atomic Energy Agency (IAEA) was used, the IAEA-368 (Pacific ocean sediment) [26].

Statistical analysis of data

The paired t test was used to compare the two quantification techniques, which had the same form of sample preparation but diverged in the final step of the methods. The value of t was calculated by Eq. (6):

$$t = \frac{\bar{d}}{\frac{S_d}{\sqrt{n}}} \quad (6)$$

where \bar{d} is the mean of differences between pairs; S_d is the standard deviation of differences, and n is the number of observations.

The p values were also utilized as a statistical test for a better understanding of the radiochemical process. For both tests, 95% confidence was set as the critical value for the null hypothesis (H_0) to be accepted or rejected.

The linear regression was the chosen technique to evaluate the found activity concentrations of all radionuclides herein studied by the methods (EC) versus (IE + EC), and was employed by the application of the Eqs. (7–9) [27, 28].

$$y = ax + b \quad (7)$$

$$\bar{x} = \sum_{i=1}^n \frac{x_i}{N} \quad (8)$$

$$r = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{(\sum (x - \bar{x})^2 \sum (y - \bar{y})^2)}} \quad (9)$$

$$r^2 = \frac{\sum x_i y_i - (\sum x)(\sum y)}{\sqrt{[n \sum x^2 - (\sum x)^2][n \sum y^2 - (\sum y)^2]}} \quad (10)$$

where y is the analytical signal strength; a is the angular coefficient; b is the linear coefficient; x is the analyte activity concentration; and n is the number of curve points.

In Eq. (7), a and b were defined by plotting and comparing the values of each method. By linear regression, the values of these parameters were obtained. The Pearson correlation coefficient (r) and the residual sum of squares

Table 1 Activity concentrations for the ^{234}U and ^{235}U in carbon samples for the two methods: (IE + EC) and (EC). Activity mean \pm activity uncertainty

Sample	$^{234}\text{U} \times 10^{-3}$ (Bq g $^{-1}$)		$^{235}\text{U} \times 10^{-3}$ (Bq g $^{-1}$)	
	(IE + EC)	(EC)	(IE + EC)	(EC)
1	111.0 \pm 6.0	113.0 \pm 11.0	8.71 \pm 1.07	11.00 \pm 3.30
2	83.90 \pm 6.50	71.90 \pm 7.10	6.08 \pm 1.36	6.40 \pm 1.95
3	173.0 \pm 8.0	206.0 \pm 14.0	13.10 \pm 1.20	14.00 \pm 2.80
4	187.0 \pm 9.0	152.0 \pm 9.0	15.60 \pm 1.40	22.50 \pm 2.60
5	44.60 \pm 3.10	23.80 \pm 2.70	3.13 \pm 0.66	3.93 \pm 1.06

Table 2 Activity concentrations for ^{238}U and ^{237}Np in carbon samples for the two methods: (IE + EC) and (EC). Activity mean \pm activity uncertainty

Sample	$^{238}\text{U} \times 10^{-3}$ (Bq g $^{-1}$)		$^{237}\text{Np} \times 10^{-3}$ (Bq g $^{-1}$)	
	(IE + EC)	(EC)	(IE + EC)*	(EC)*
1	76.60 \pm 4.30	78.00 \pm 9.40	< 4.000	< 4.550
2	42.70 \pm 4.10	49.30 \pm 5.70	< 4.000	< 3.300
3	156.0 \pm 7.0	183.0 \pm 13.0	< 4.000	< 3.340
4	172.0 \pm 8.0	120.0 \pm 7.0	< 4.000	< 4.040
5	6.630 \pm 0.990	6.890 \pm 1.440	< 4.000	< 4.410

* < LD

using linear regression (r^2) were used to evaluate the quality of the obtained curve.

Results and discussion

In the following paragraphs, we discuss the results of the radiochemical analyses performed with the carbon samples by the two methods (IE + EC) and (EC). Tables 1, 2, 3 and 4 show the results obtained by the aforementioned analysis, grouped by isotope. Chemical yields are shown in Table 5.

The highest activity concentrations found were for the Pu, U and Am isotopes, except ^{235}U . Np and Cm activity concentrations were low, especially for Np, which presented activities lower than its LD ($\text{LD}_{\text{Np}} = 4.000 \text{ Bq g}^{-1}$). Taddei et al. [29] also demonstrated that the amount of Np in carbon samples is lower than the LD for the methods used, corroborating with the present study. The detection values for Cm are specified in Table 4. Since the alpha-ray energy of the ^{243}Cm (5.74 MeV) is close to the ^{244}Cm (5.76 MeV) energy, the resolution of the equipment (0.02 MeV) does not allow the distinction between these two energy peaks. Therefore, the concentration of activity presented is the sum of the two isotopes of Cm ($^{243+244}\text{Cm}$).

Table 3 Activity concentrations for ^{238}Pu and $^{239+240}\text{Pu}$ in carbon samples for the two methods: (IE + EC) and (EC). Activity mean \pm activity uncertainty

Sample	$^{238}\text{Pu} \times 10^{-3}$ (Bq g $^{-1}$)		$^{239+240}\text{Pu} \times 10^{-3}$ (Bq g $^{-1}$)	
	(IE + EC)	(EC)	(IE + EC)	(EC)
1	475.0 \pm 26.0	497.0 \pm 15.0	2.890 \pm 0.130	2.780 \pm 0.070
2	289.0 \pm 11.0	250.0 \pm 10.0	1.980 \pm 0.060	1.720 \pm 0.040
3	969.0 \pm 32.0	913.0 \pm 26.0	4.580 \pm 0.140	4.170 \pm 0.100
4	1.130 \pm 0.040	1.070 \pm 0.030	5.790 \pm 0.180	5.560 \pm 0.160
5	281.0 \pm 12.0	338.0 \pm 12.0	1.130 \pm 0.040	1.400 \pm 0.040

Table 4 Activity concentrations for ^{241}Am and $^{243+244}\text{Cm}$ in carbon samples for the two methods: (IE + EC) and (EC). Activity mean \pm activity uncertainty

Sample	$^{241}\text{Am} \times 10^{-3}$ (Bq g $^{-1}$)		$^{243+244}\text{Cm} \times 10^{-3}$ (Bq g $^{-1}$)	
	(IE + EC)	(EC)	(IE + EC)	(EC)
1	642.0 \pm 23.0	711.0 \pm 27.0	2.240 \pm 0.530	1.240 \pm 0.510
2	545.0 \pm 20.0	514.0 \pm 24.0	5.320 \pm 0.830	2.640 \pm 1.080
3	1.090 \pm 0.040	1.160 \pm 0.050	5.120 \pm 0.760	11.70 \pm 2.10
4	905.0 \pm 46.0	877.0 \pm 40.0	5.750 \pm 1.380	9.260 \pm 1.890
5	140.0 \pm 6.0	213.0 \pm 10.0	0.580 \pm 0.260	6.560 \pm 1.260

Table 5 Chemical yields: U, Np, Pu, Am, and Cm in carbon samples for the two methods: (IE + EC) and (EC)

Sample	Method	U (%)	Pu/Np (%)	Am/Cm (%)
1	(IE + EC)	100	87	93
	(EC)	84	100	99
2	(IE + EC)	100	94	90
	(EC)	74	100	92
3	(IE + EC)	100	82	100
	(EC)	100	97	87
4	(IE + EC)	100	76	92
	(EC)	94	89	100
5	(IE + EC)	100	80	95
	(EC)	80	85	95

Table 5 highlights that high yields were found in the (IE + EC) and (EC) methods. In these cases, the minimum observed value was 74% for U in (EC).

In the (IE + EC) methodology used by Rodríguez et al. [24], the results for Pu and Am were 90% and 80% respectively, which is very close to the values observed in this work: 84% (Pu) and 94% (Am). In the (EC) method [25], the values were also close, 103% (U) and 98% (Pu), against 86% (U) and 94% (Pu).

The two methods were statistically analyzed by the *t*-Student test, considering a 95% confidence level, paired data, and isolated isotopes. Tables 6 and 7 list the *p*-values obtained.

P-values lower than 0.05 were observed, i.e., the hypothesis of the difference of means was accepted only for the (EC) method (^{234}U and ^{238}U), (IE + EC) and (EC) ($^{239+240}\text{Pu}$) and (EC) (^{237}Np). Thus, data analysis by linear

Table 6 *p*-values for U isotopes obtained from the Student *t*-test. 95% confidence level, paired data, and isolated isotopes

Isotope	Methods	
	(IE + EC)	(EC)
^{234}U	(IE + EC)	0.59
^{235}U	(IE + EC)	0.13
^{238}U	(IE + EC)	0.81

Table 7 *p*-values for Pu and Cm isotopes and ^{241}Am obtained from the Student *t*-test. 95% confidence level, paired data, isolated isotopes

Isotope	Methods	
	(IE + EC)	(EC)
^{238}Pu	(IE + EC)	0.56
$^{239+240}\text{Pu}$	(IE + EC)	0.04
^{241}Am	(IE + EC)	0.28
$^{243+244}\text{Cm}$	(IE + EC)	0.25

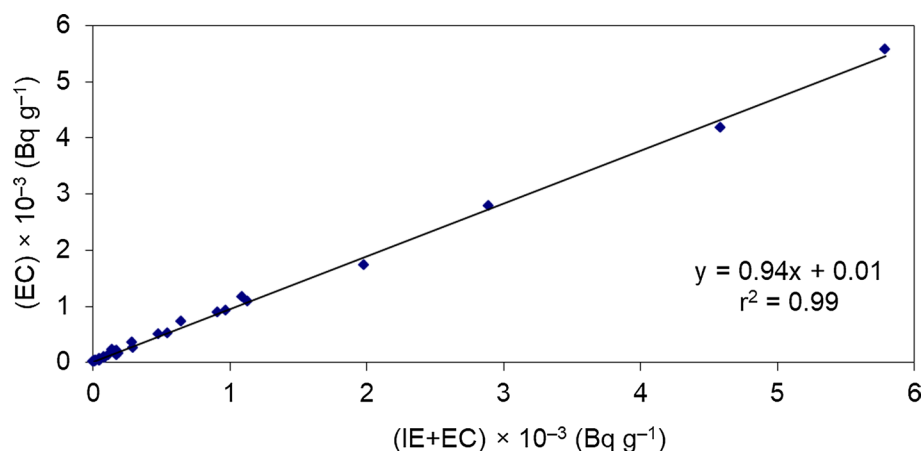
regression with clustered isotopes would better represent the data set. Figure 1 shows the graphical representation of the linear regression obtained by comparing the methods.

The result of linear regression indicates that the two methods present a high degree of correlation ($r^2 > 0.99$), indicating that they do not present significant differences.

As mentioned earlier in the *Reference Material* section, to validate the methodologies, the IAEA–368 (Radio-nuclides in the Pacific Ocean Sediment) was the reference material for the (IE + EC) method. Although it does not have the same matrix as the samples, it was adopted because it contained most of the radioisotopes of interest, namely ^{234}U , ^{235}U , ^{238}U , ^{238}Pu , $^{239+240}\text{Pu}$, and ^{241}Am .

The presence of silicon made it difficult to dissolve sediments, which was only possible with the addition of 5 mL

Fig. 1 Linear regression between EC and (IE + EC) methods



of 48% HF. Results obtained with the reference material are presented in Table 8.

Chemical yields were 100% (U), 90% (Pu) and 84% (Am) for (IE and EC); 87% (U), 35% (Pu) and 48% (Am), for EC. Comparing the (IE + EC) and EC methods, it is observed that, despite the differences between the chemical recoveries, the correction was performed and there was no significant difference in the activity concentrations of the elements. This is an indication that the application of the technique by EC is viable for the determination of U, Pu and Am isotopes as well as the technique by (IE + EC).

The final volume of radioactive waste from each analysis was measured and the mean values calculated were 613 and 320 mL for the (IE + EC) and EC methods, respectively. The EC method presented a lower waste volume than (IE + EC), which makes it a more economically and environmentally preferable method. As for the analysis time, no significant reduction was observed. In general, the EC method was more desirable because smaller reagent volumes with reduced concentrations were employed.

Cost analysis was evaluated as shown in Table 9. It is worth mentioning that the cost and maintenance of equipment, power consumption, and glassware were not taken into account. All values were obtained in Brazilian currency (R\$) and converted to US dollars by the 17th March, 2020 conversion rate (US\$/R\$ = 4.98), unless otherwise noted.

Note that the cost per analysis was higher when column regeneration was considered (Table 9). This is due to the

use of reactants in the regeneration method, but since it will be possible to reuse the columns, the cost is expected to decrease in subsequent radiochemical procedures. To calculate the volume of radioactive waste generated, we considered all steps from sample dissolution to electrodeposition, as shown in Table 10.

The analysis time was the same for the two methods, about seven working days. Five samples can be analyzed during this time interval using the calculated amounts of reactants. The radioactive waste volume generated by the (IE + EC) method was approximately 92% higher when compared to the volume generated by the EC. In terms of cost, they were 5% higher than the EC. The results suggest that the EC method is the most efficient for the determination of U, Np, Pu, Am, and Cm present in this type of radioactive waste.

Conclusions

Two separation techniques for the determination of U, Np, Pu, Am and Cm isotopes using Dowex[®] 1 × 2 produced by Sigma-Aldrich, TRU and UTEVA resins produced by Eichrom Technologies were tested and compared. From the results, it was concluded that the analysis time spent on the two methods was equal, approximately seven working days. (IE + EC) and (EC) methods provide statistically similar results. The (IE + EC) and (EC) methods have been validated

Table 8 Results of analyzes of ²³⁴U, ²³⁵U, ²³⁸U, ²³⁸Pu, ²³⁹⁺²⁴⁰Pu and ²⁴¹Am by (IE + EC) and EC methods and reference values (IAEA-368)

Method	Activity concentrations × 10 ⁻³ (Bq g ⁻¹)					
	²³⁴ U	²³⁵ U	²³⁸ U	²³⁸ Pu	²³⁹⁺²⁴⁰ Pu	²⁴¹ Am
(IE + EC)	44.00 ± 2.00	1.700 ± 0.100	34.00 ± 2.00	8.400 ± 0.400	36.00 ± 2.00	1.500 ± 0.200
(EC)	35.00 ± 1.00	1.600 ± 0.100	30.00 ± 1.00	7.900 ± 0.600	35.00 ± 2.00	1.700 ± 0.200
Reference values (IAEA-368)	36.00 21.00–45.00	1.900 1.600–2.600	31.00 25.00–33.00	8.500 7.600–8.900	31.00 29.00–34.00	1.300 1.200–1.500

Table 9 Cost per analysis for (IE + EC) and (EC) methods

Steps	Form of presentation	Price (unit)	(IE + EC)		(EC)	
			(\$)	(mL)	(\$)	(mL)
Dissolution of samples			35.49	214	34.63	214
Dowex 1 × 2 anionic 50–100 mesh	Powder (100 g)	102.41	17.31			
Preparation of the columns (I)			10.44	200		
Columns regeneration (I)			18.53	4480		
Am separation (TRU resin)	Cartridge	11.88	23.76		23.76	
Preparation of the columns (II)			0.39	20	0.78	40
Columns regeneration (II)			1.31	120	1.31	120
U separation (UTEVA resin)	Cartridge	10.08	20.16		20.16	
Preparation of the columns (III)			0.39	20	1.24	40
Columns regeneration (III)			1.14	80	1.14	80
Separation of Pu and Np			35.18	661.20	0.73	30
Chemical yield (²³⁶ Pu Tracer)	Ampoule	2,120.00	84.80	2	84.80	2
Chemical yield (²⁴² Pu Tracer)	Ampoule	2,120.00	84.80	2	84.80	2
Separation of U			1.16	80	3.68	160
Chemical yield (²³² U Tracer)	Ampoule	2,040.00	81.60	2	81.60	2
Separation of Am and Cm			12.56	180	9.68	207
Chemical yield (²⁴³ Am Tracer)	Ampoule	2,705.00	216.40	4	216.40	4
Electrodeposition			7.89	43	7.89	43
Total (with column regeneration)			(\$) 552.97		(\$) 524.42	
Total (without column regeneration)			(\$) 548.76		(\$) 523.93	

Table 10 Parameters used in the definition of the radioanalytical method

	(IE + EC)	(EC)
Chemical yield (%)	76–100	74–100
Analysis time (days)	6.9	6.5
Radioactive waste (mL)	613	320
Cost/sample (\$)	\$ 553	\$ 524

with reference material. It was not possible to apply a sequential determination method for all radionuclides in the same sample for several reasons, such as lack of chemical yield tracers without interferents, and resolution of the alpha spectrometer lower than the distance between the energy lines of one of the analytes (²³⁷Np) and that of the available tracer (²⁴²Pu). Therefore, two samples of the same waste had to be used for the determination of all radionuclides.

All radioactive waste generated during the work was properly disposed of. The (EC) method is the most suitable for determining the chosen analytes by the criterion of low volume of secondary radioactive waste. It is also the preferred method by the criterion of analysis cost because it is cheaper than the qualified competitor method.

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