Combined procedure using radiochemical separation of plutonium, americium and uranium radionuclides for alpha-spectrometry

4 **AUTHORS**, INCLUDING:

Aluísio Reis
Centro de Desenvolvimento da Tecnologia …
12 PUBLICATIONS   **18** CITATIONS

SEE PROFILE

Eliane S. C. Temba
Centro de Desenvolvimento da Tecnologia …
14 PUBLICATIONS   **16** CITATIONS

SEE PROFILE

COMBINED PROCEDURE USING RADIOCHEMICAL SEPARATION OF PLUTONIUM, AMERICIUM AND URANIUM RADIONUCLIDES FOR ALPHA-SPECTROMETRY

Aluísio S. Reis Jr, Eliane S. C. Temba, Geraldo F. Kastner and Roberto P. G. Monteiro

Centro de Desenvolvimento da Tecnologia Nuclear – (CDTN/CNEN – MG)
Serviço do Reator e Técnicas Analíticas - SERTA
Av. Presidente Antônio Carlos, 6627
Campus da UFMG -Pampulha
30123-970 Belo Horizonte, MG
reisas@cdtn.br

ABSTRACT

Radiochemical separation of Pu, Am and U was tested from synthetic solutions and evaporator concentrate samples for isolation of each of them for alpha-spectrometry analysis. A good chemical separation of radionuclides of interest from the matrix and interfering radionuclides is required, once the relatively small difference in α particle energy makes it difficult to spectrometrically separate the peaks. The separation was performed by anion-exchange chromatography, extraction chromatography, using TRU resin, and precipitation techniques. The aim of the study was to develop a sensitive analytical procedure for the sequential determination of $^{242, 238}$Pu, $^{239+240}$Pu, ^{241}Am and $^{235, 238}$U in radioactive wastes. ^{238}Pu, ^{242}Pu, ^{243}Am and ^{232}U were used as tracers. As the self-absorption of α particle in the source will not only reduce the counting efficiency, but also degenerate the energy resolution of alpha-spectrum, it is essential that a thin source is prepared in alpha-spectrometry. Then, after isolation of Pu, Am and U each of them was prepared as thin source by electrodeposition on stainless steel disks. The measurements of α emitting radionuclides were performed by semiconductor detector (PIPS) that is good for spectrometric information. Therefore, the isolation of radionuclides was confirmed by the spectra obtained and each of them was measured by the ratio of the alpha-spectral peak areas (analyte/tracer) that is taken to be equal to the ratio of the disintegrations rates. For synthetic solutions the recovery of iron was about 93 %.

1. INTRODUCTION

Simultaneous determinations, where several elements can be determined simultaneously in the same sample preventing that calcinations and separation procedure occur for each element, are the most desirable methods because they are not time consuming and they are low cost. There are several methods available for the determination of isotopes of Pu, Am and U in environmental and bioassay samples [1-3]. However few of them have considered nuclear wastes samples besides iron as potential interference in radiochemical separations [1,4-5].

Alpha-spectrometry is normally used for the determination of ^{238}Pu and $^{239+240}$Pu. Due to the interferences, the radionuclide of interest must be isolated of the matrix and other interfering radionuclides before measurement. The separation of Pu by ion exchange chromatography is based on the formation of anionic complexes of Pu(IV) with NO_3^- an Cl^- in concentrated HNO_3 or HCl. Alpha-spectrometry is a more sensitive method for determination of ^{241}Am. However, it must be separated from matrix and interfering radionuclides. The separation can be made by co-precipitation of hydroxides or oxalate, solvent extraction using TIOA(triisooctylamine)/xylene, anion exchange and extraction chromatography. Also, for

uranium isotopes alpha-spectrometry has been used for a long time, being the technique well established and very reliable as it presents only a few problems. Therefore each of the radionuclides has their peculiar behavior that allows isolation and sequential isotopic determination.

Standards solutions of Pu, Am, U, Sr, Fe and sample of evaporator concentrate were analyzed to study the separation factors and interferences in the measurement of Pu, Am and U isotopes.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

All reagents used were analytical grade. Certified radionuclides were obtained from the Instituto de Radioproteção e Dosimetria (IRD), Rio de Janeiro, Brasil and the certified activity level for each of them is: ^{238}Pu (0.56 KBq), ^{242}Pu (0.02 KBq), ^{243}Am (4.20 KBq), ^{232}U (4.26 KBq), ^{90}Sr (2.49 KBq) and ^{55}Fe (2.84 KBq). Working solutions were prepared by transferring a known weight of the tracer followed by volumetric dilution to an appropriate working concentration.

The alpha-spectrometry measurements were carried out with Canberra PIPS (passivated ion implanted planar silicon) detectors. The alpha-energy calibration and the measurement of counting efficiency of the detector were performed using a source from Analytics Inc. Analytics maintains traceability to the National Institute of Standards and Technology through Measurements Assurance Programs as described in USNRC Regulatory Guide 4.15, Rev. 1 [6]. The spectrometer used was a Canberra Model S509 Genie-2000 Alpha Analyst.

2.2. Sample Preparation

Synthetic solutions were prepared from working solutions of ^{238}Pu, ^{243}Am, ^{232}U and ^{55}Fe radionuclides and Fe(3 mg/L) as yield monitor. Mixture of forty grams of evaporator concentrate and ^{238}Pu or ^{242}Pu, ^{232}U and ^{243}Am as tracers were prepared in a Pt crucible and heated using a hot plate up to evaporation to dryness. After that, 20 mL of nitric acid and 15 mL of H_2O_2 were added into the crucible. The mixture was heated again up to evaporation to dryness. The solid obtained was calcined in an oven at 850 °C for 4 hours. The residue was dissolved and for each step after addition of acid the mixture was heated up to evaporation to dryness: first, with 30 mL of 3:2 nitric acid, after, with 15 mL of HF. Finally, the solid resultant was dissolved using a hot plate in 100 mL of 3:2 nitric acid.

2.3. Radionuclides Isolation

The radiochemical procedure [2] consists of a Pu isolation step by an anion exchange column (Dowex 1X8, Cl-form, 100-200 mesh, Sigma Chemical Co., USA). The solution, 100 mL in 3:2 nitric acid, is passed through the column and rinsed with 120 mL of 3:2 nitric acid. The effluent is retained for strontium, iron, americium and uranium isolation. Pu was removed from the column by reduction with a freshly prepared mixture of ammonium iodide [5%(w/v)] and concentrated hydrochloric acid (29:71 by volume). Iodide ions selectively reduce Pu(IV) to Pu(III), which is not adsorbed on the column under these conditions and elutes.

The effluent from the anion exchange column was used to separate Am and Sr by co-precipitation with oxalic acid when the pH of the solution was adjusted to 5.5-6.0 with 25% ammonia solution [3]. Iron is an interfering radionuclide for americium isolation and under these conditions in many cases, most of the Fe remains in solution in the form of oxalate complexes. After filtration, the precipitate was used for americium isolation by using a TRU resin extraction chromatography column (EiChroM industries Inc. USA). If iron is present before elution of the solution ascorbic acid is added to reduce Fe(III) to Fe(II).

The filtrate retaining uranium and iron fractions was heated to dryness and the solid was dissolved in 30 mL of concentrate nitric acid and heated to dryness to destroy the excess of oxalic acid. The solid obtained was hot dissolved in 30 mL of 3:2 nitric acid and was diluted to 200 mL with deionized water. The pH of the solution was corrected to 9.0 with ammonia hydroxide for co-precipitation of iron hydroxide and uranium. The precipitate was filtered and the filtrate was dissolved in 20 mL 9M HCl. They were separated by anion exchange column (Dowex 1X8, Cl-form, 100-200 mesh, Sigma Chemical Co., USA) that was loaded with the solution and either was stripped iron with 50 mL of 8M nitric acid and uranium with 100 mL of 0.1M HCl.

2.4. Determination of Pu, Am and U

Determination of Pu, Am and U was carried out by using alpha-spectrometry. Solutions of the isolated radionuclides were evaporated to dryness and dissolved in a mixture of nitric acid, 10 mL, and perchloric acid, 5 mL. The samples were evaporated to dryness and retaken in a solution of 3M H_2SO_4 and 0.8M $(NH_4)_2SO_4$ with the pH adjusted in a range of 1.2-2.8 (Thymol blue indicator) with concentrate NH_4OH. Electrodepositions disks were prepared from 0.90 mm thick sheets of stainless steel, by machining sections to 24.8 mm diameter planchets. The electroplating was done at an applied current of 1.0 A for U and Am and 1.2 A for Pu for 1 hour.

3.   RESULTS AND DISCUSSION

Among nuclear techniques, alpha-spectrometry offers a high-energy resolution. The use of low background semiconductor detectors makes this technique particularly sensitive for the measurement of very low activities of actinides. Although the resolution of detectors for alpha-spectrometry is good, the relatively small difference in α particle energy between some α emitters makes it difficult to spectrometrically separate the peaks [7].The simultaneous availability of new resins improves the element separation selectivity, particularly the development of sequential steps to extract and purify Pu isotopes, [241]Am and U isotopes [8]. The combined high-resolution with the good chemical separation of radionuclides of interest makes the technique very attractive to be used for the measurement of α emitting radionuclides.

The method used here combines the well established procedure for Pu analysis based on anion exchange, the application of the TRU-Spec column for separation and purification of the Am fraction and the anion exchange for U isolation. In order to determine chemical recovery of Pu, the evaporator concentrate was spiked with a known activity of [242]Pu and [238]Pu.The chemical recoveries [9] for Pu are usually higher than 80 % and show narrow dispersion. In the analysis for Am a crucial point lies in the influence of Fe(III) on the Am

uptake on TRU-Spec column. For synthetic solutions, the recovery of Fe(III) were about 93%. That is, following the separation procedure part of the iron co-precipitate with calcium oxalate. In this case ascorbic acid was used to reduce Fe(III) in nitric solutions. The reduction of Fe(III) allows the maximum retention of americium on the stationary phase [3].

The experiences with synthetic solutions provided a way to compare alpha-spectra obtained for radionuclides with the aim of their isolation and characterization, due the high resolution of the PIPS detector. For the radionuclides tested in synthetic solutions using ^{238}Pu, ^{242}Pu, ^{243}Am and ^{232}U, the separation process produces high-quality spectra in terms of good energy resolution and without interference lines. Typical spectrum obtained by alpha-spectrometry after isolation of Pu isotopes, for a sample of evaporator concentrate spiked with Pu isotopes, ^{243}Am and ^{232}U is shown in the Fig 1.
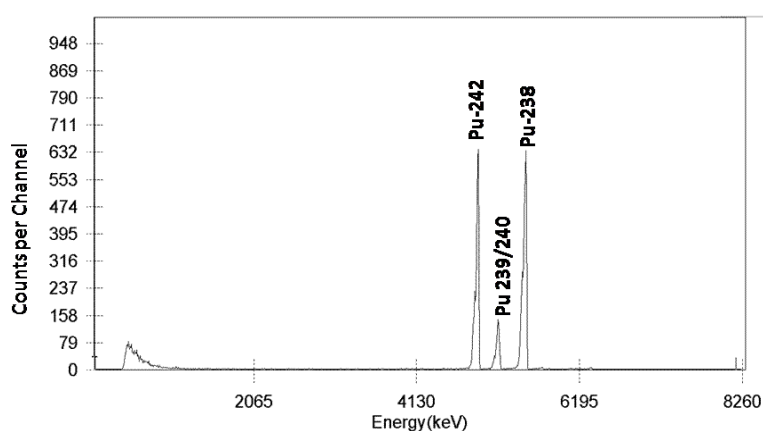
Figure 1: Alpha-spectrum of plutonium isotopes in evaporator concentrate spiked with ^{242,238}Pu, ^{243}Am and ^{232}U.

There is a good separation of the radionuclides present in the initial sample. The resolution of alpha-spectra is 25.63 keV at 4.908 MeV for the ^{242}Pu peak, 26.41 keV at 5.512 MeV for the ^{238}Pu peak and 38.29 keV for the $^{239+240}$Pu peak in terms of the full width at half maximum (FWHM). These resolutions were obtained without oxidation state adjustment [10]. Besides, it is noticed that there are no peaks that can be marked to Am or U, the others α emitting radionuclides presents in the initial sample.

4. CONCLUSIONS

In this study, Pu, Am and U were analyzed by radiochemical separation followed by alpha-spectrometry spectra with good resolution. The method of sequential analysis provided an excellent purification of each radionuclide. Therefore, further improvements of the method are foreseen as it is necessary to develop accurate and reliable methods for the determination of actinides in the low and medium radioactive wastes that arise from nuclear power plants.

.

ACKNOWLEDGMENTS

REFERENCES

1. P. Tavcar, B. Smodik, L. Benedik, "Radiological characterization of low- and intermediate-level radioactive wastes," *Journal of Radioanalytical and Nuclear Chemistry*, **273(3),** pp. 593-596 (2007).
2. Jeng-jong Wang, Ing-Jane Chen, Jih-Hung Chiu, "Sequential isotopic determination of plutonium, thorium, americium, strontium and uranium in environmental and bioassay samples," *Applied Radiation and Isotopes*, **61,** pp. 299-305 (2004).
3. J. Moreno, N. Vajda, P. R. Danesi, J. J. Larosa, F. Zeiller, M. Sinojmeri, "Combined procedure for the determination of ^{90}Sr, ^{241}Am and Pu radionuclides in soil samples," *Journal of Radioanalytical and Nuclear Chemistry*, **226**, 1-2, pp. 279-284 (1997).
4. Tagami, K., Uchida, S., "Use of TEVA resin for the determination of U isotopes in water samples by Q-ICP-MS," *Applied Radiation and Isotopes*, **61**, pp. 255-259 (2004).
5. R. K. Singhal, Usha Narayanan, Rupali Karpe, Ajay Kumar, A. Ranade, V. Ramachandran, "Selective separation of iron from uranium in quantitative determination of traces of uranium by alpha spectrometry in soil/sediment sample," *Applied Radiation and Isotopes*, **67**, pp. 501-105 (2009).
6. Analytics, Certificate of Calibration 75551-121, 2007.
7. Xiaolin Hou, Per Roos, "Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples," *Analytica Chimica Acta*, **608**, pp. 105-139 (2008).
8. Florence Goutelard, Marcel Morello, Dominique Calmet, "Alpha-spectrometry measurement of Am and Cm at trace levels in environmental samples using extraction chromatography," Journal *of Alloys and Compounds* **271-273**, pp. 25-30 (1998).
9. International Atomic Energy Agency, International Labour Office, Assessment of Occupational Exposure due to Intakes of Radionuclides, Laboratory Practices Module VI.2/2, IAEA, Vienna (1999).
10. M. H.T. Taddei, N. C. Silva, "Radiochemical procedure for the determination of plutonium isotopes in powdered milk," *Journal of Radioanalytical and Nuclear Chemistry*, **269(2)**, pp.457-461 (2006).