SEQUENTIAL DETERMINATION OF AMERICIUM, PLUTONIUM AND URANIUM IN LIQUID EFFLUENTS FROM NUCLEAR POWER PLANTS

Ruxandra TOMA[1], Cristian DULAMA[2], Ilie PRISECARU[3]

The characterization of the liquid effluents means identifying the source, the physical and chemical properties and the radionuclide inventory. In general, the determination of actinides involve complex chemical analysis to separate them from the matrix, as they are mainly alpha emitters and the samples for the alpha spectrometer must be thick and without other impurities or interfering nuclides. This paper presents the tests performed in the Laboratory for Radioprotection, Environmental Protection and Civil Protection, RAAN-SCN, Piteşti, Romania, for the implementation of the Eichrom® procedure for sequential determination of actinides in liquid effluents. The validation of the results was performed by determining the activities using two different methods, alpha spectrometry and liquid scintillation counting.

Keywords: liquid effluents, actinides, sequential separation, nuclear power plants

1. Introduction

Liquid effluents represent a very important aspect in radioactive waste management mainly due to the fact that they are released in the environment and very special attention must be paid. In a nuclear power plant the liquid effluents originate from sanitary facilities, leakage, laboratories, radioactive waste treatment facilities, and other activities which use radioactive sources. After a proper characterization, the liquid effluents are disposed in the environment according to the radiological safety norms emitted by the regulatory body.

In Romania, liquid effluents from nuclear power plants are released in the environment according to the Norms for the limitation of radioactive effluents emission in the environment, approved by Order CNCAN no. 221/2005 [1]. CNCAN (National Commission for Nuclear Activities Control) is the national authority, having responsibilities of regulation authorization and control in nuclear field in Romania.

[1] Eng. Faculty of Power Engineering, Department of Nuclear Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: rux.toma@gmail.com

[2] Phys. Laboratory for Radioprotection, Protection and Civil Protection, RAAN-SCN, Piteşti, Romania

[3] Prof., Faculty of Power Engineering, Department of Nuclear Engineering, University POLITEHNICA of Bucharest, Romania

The norms' objective is the limitation and optimization of radioactive effluents emission in the environment for public health protection and environment protection in the present and in the future. These norms give the dose constraints, the derived emission limits, the minimum documentation for environmental release of the effluents and the responsibilities of the operator.

In order to meet the CNCAN requirements, the operator should collect as many data on the effluents such as physical and chemical properties and radionuclide inventory.

Regarding the radionuclide inventory, among high energy gamma emitters, which are easy to measure nuclides by non destructive methods (gamma spectrometry), the liquid effluents also contain beta and alpha emitters, and their determination requires laborious radiochemical separation from other interfering nuclides and sample preparation for beta or alpha spectrometry. Among these radionuclides, Tritium, Carbon 14, Strontium 90, Iodine isotopes and Actinides are very important.

Due to their long half-lives and high radiotoxicity, Actinides represent an important hazard to the environment, especially when they are emitted in soluble form through the effluent pathway from nuclear installations. Measurement of actinides concentration is usually based on detection of their alpha particles emission which is a very sensitive process requiring preconcentration and separation from the excess inactive matrix and other radioactive isotopes (fission products, other actinides or naturally occurring radionuclides) [2].

Actinides determination in the liquid effluents is still in early stages in laboratories in Romania. This paper presents the tests performed in the Laboratory for Radioprotection, Environmental Protection and Civil Protection, RAAN-SCN, Piteşti, Romania for the implementation of a sequential separation procedure for actinides in liquid effluents, based on the Eichrom procedure. The Eichrom procedure can be downloaded from the Eichrom website by registered users.

The procedure was adapted to the laboratory's equipments and apparatus in reference [3].

2. Method description

For the determination of actinides in liquid effluents it was decided to implement the Eichrom® procedure for sequential separation of actinides using the Eichrom® resins, UTEVA® for Uranium isotopes and TRU® for Plutonium and Americium isotopes, and determination of the concentration by alpha spectrometry. These resins are chromatographic resins which can be purchased from Eichrom® in preconditioned columns or the resin directly. The validation of the results was performed by determining the activities using two different methods, alpha spectrometry and liquid scintillation counting.

The procedure indicates the sample preparation such as filtration, in case there are impurities and evaporation in case their activity is low. Besides the separation procedure on the chromatographic resins, the procedure gives indications on the alpha sources preparation by electrodeposition using a sulfate system or by Cerium Fluoride micro-coprecipitation. The tests presented in this paper were performed using the micro-coprecipitation option. Moreover, the procedure indicates how to calculate the chemical recovery of the separation processes and the actinide isotope activity.

Due to the complexity of the procedure the tests for the validation of the method in the laboratory were performed gradually, in reverse order and all the steps were verified using two detection methods for the isotopes activity, alpha spectrometry and liquid scintillation counting in the alpha region (alpha-LSC).

The first step was to test the micro-coprecipitation process. An Americium 241 solution and a natural uranium solution were prepared and their activity concentration was determined by gamma spectrometry. The initial concentrations of stock solutions were checked by using gamma-ray spectrometry and further dilutions were validated by using alpha-LSC [2].

After determination of the radionuclide inventory in the initial solutions, two aliquots are prepared and their weight is noted. The aliquots are converted to the same media in which the actinides result in the Eichrom's separation procedure, 1M HCl for Uranium and 9M HCl for Americium. Each solution is transferred to a filtration funnel with a 0.1 micron 25 mm filter. After the filtration is complete, the filters are removed, placed on a watch glass and dried under IR lamps for a few minutes.

Next, the filters are transferred on stainless planchets and analyzed by both alpha spectrometry and alpha-LSC. With the results obtained by analysis before and after micro-coprecipitation the detection efficiency of the alpha spectrometer for this geometry and the chemical yield of this process could be determined. Fig. 1 presents the diagram of this process.

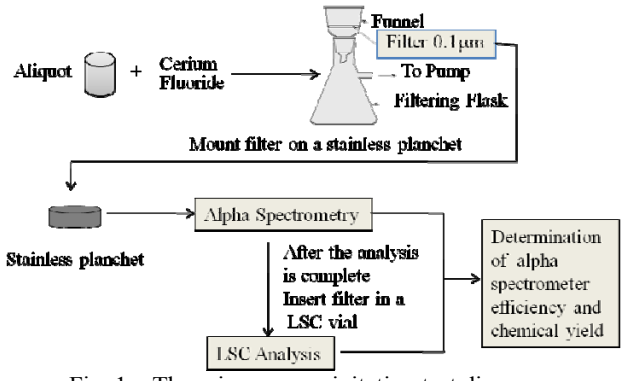

Fig. 1 – The micro-coprecipitation test diagram

Next step is the testing of Americium separation with TRU Resin and alpha sources preparation. The same Americium 241 solution prepared at the first step is used next. An aliquot from this solution is prepared and is converted to 3M HNO3 before transferring to TRU resin, by evaporation to dryness and dissolve in 3M HNO3.

The solution is then transferred into the TRU resin column and allowed to drain. The next steps are according to the Eichrom® procedure for Plutonium and Americium separation using TRU Resin. The chemical recovery yield is also determined for this step. Fig. 2 presents the diagram of this process.

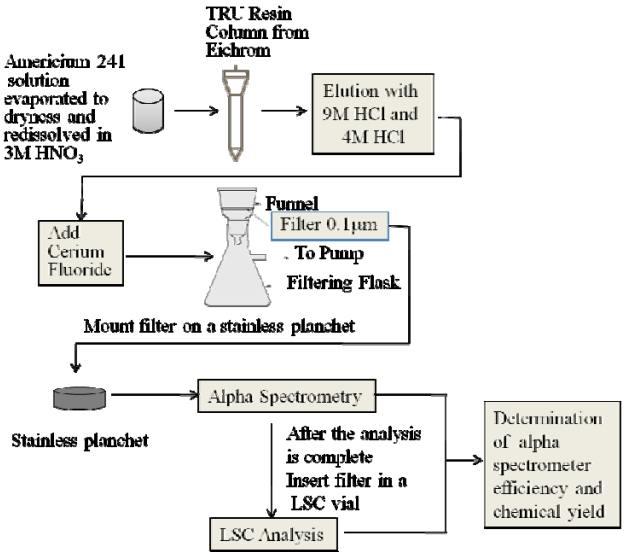

Fig. 2 – The americium separation test diagram

Last step is to test the Eichrom® procedure by using a simulated solution with known concentration of Americium, Uranium and Plutonium. Radioactive tracer solutions are prepared from certified U-233, Am-243 and Pu-242 solutions and their masic concentration is calculated based on initial solutions calibration certificates. The calculated data is verified by gross alpha counting using a liquid scintillation counter.

A simulated liquid effluent is prepared by mixing known quantities from the natural Uranium and Americium 241 solutions prepared at step one. The Eichrom procedure is applied and the concentration of U-238, U-235, U-234 and Am-241 is determined, as well as chemical separation yield for Uranium, Americium and Plutonium.

The results obtained were used to determine the optimum counting intervals (regions of interest – ROI) and the minimum detection limits for the alpha emitters analyzed in this paper.

The equipments used was a TRICARB Liquid Scintillation Counter and an ORTEC Alpha Spectrometer for the determination of the concentration activity of the radionuclides in the analyzed samples.

3. Tests and results

Preparation of the initial solutions and tracer solutions

A known quantity of Am-241 solution in 2M HNO_3 media was transferred to a 100 ml volumetric flask. The solution was diluted with 2M HNO_3 to 100 ml and analyzed by gamma spectrometry and liquid scintillation counting in the alpha region. The results are presented in table 1.

Table 1

Americium 241 initial solution concentration determined by gamma spectrometry and LSC [3]

Method of Analysis	Concentration (Bq/g)	Discrepancy
Alpha LSC	562 ± 2	3,5%
Gamma	543 ± 18	

Through successive dilutions a 5.4 ± 0.5 Bq/g Am-241 solution was prepared (this solution will be referred in this paper as am_1).The concentration activity was verified by gross alpha counting using a liquid scintillation counter.

For the natural uranium solution preparation, a quantity of U_3O_8 anhydrous was dissolved in concentrated nitric acid so that the concentration in the solution was approximately 10 g/l. The solution was characterized by gamma spectrometry and the results are presented in table 2. The values obtained were confirmed by determining the gross alpha activity of the sample by liquid scintillation counting.

Table 2

Natural Uranium initial solution concentration determined by gamma spectrometry

Uranium Isotope	Gamma emitter radionuclide	Concentration (kBq/l)
U-238	Pa-234m	108.056 ± 2.796
	Th-234	103.933 ± 1.491
U-235	U-235	5.012 ± 0.060

The tracer solutions were prepared from NIST certified solutions. Their activity was determined gravimetrically and confirmed by gross alpha counting using a liquid scintillation counter. The results are presented in table 3.

Table 3

Radioactive tracer solutions concentration

Tracer	C_g[a](Bq/g)	C_{LSC}[b](Bq)	Discrepancy
U-233	3,77	3,85	-2%
Pu-242	0,54	0,57	-5%
Am-243	0,76	0,72	5%

a. Concentration activity determined gravimetrically

b. Concentration activity determined by liquid scintillation counting

Results for the micro- coprecipitation step

From the am_1 solution two 0.5 ml aliquots were prepared. The two aliquots were tested in parallel for the micro-coprecipitation step. The results are presented in table 4. Fig. 3 presents the alpha-LSC spectra of the filters obtained in the micro-coprecipitaton step and Fig. 4 presents the alpha spectra of the filter prepared in the second run of the test.

Table 4

Results for the micro-coprecipitation test [4]

Test	η	ε
#1	0.97	0.23
#2	0.99	0.21

where:

ε - the alpha detector efficiency;
η - the chemical recovery yield.

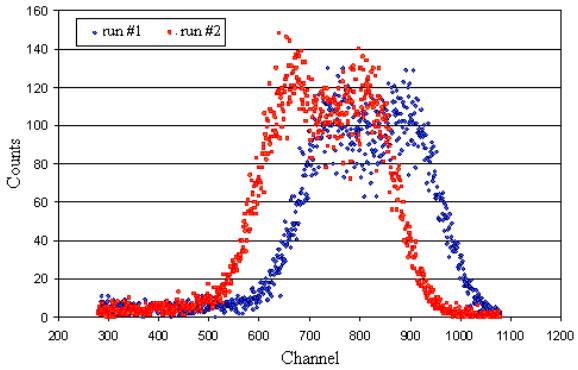

Fig. 3 – Alpha- LSC spectra of the filters obtained in the micro-coprecipitation step

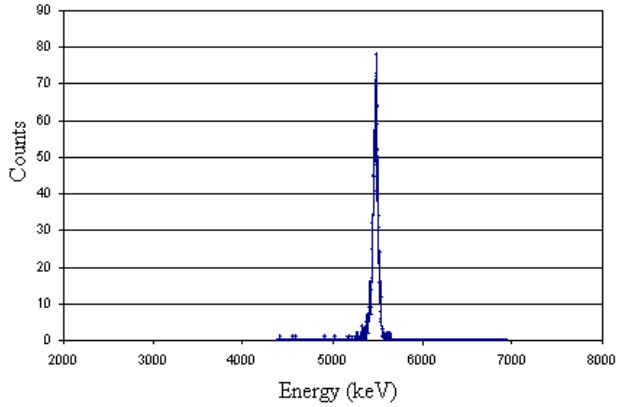

Fig. 4 – Alpha spectra of the filter obtained in the second run of the micro-coprecipitation step

Results for the Americium separation on TRU resin step

From the am_1 solution two 0.5 ml aliquots were prepared. The two aliquots were tested in parallel for the Americium separation on TRU Resin step. The results are presented in table 5.

Table 5

Results for the Americium separation on tru resin test [4]

Test	η	ε
#1	0.98	0.22
#2	0.98	0.20

where:

ε - the alpha detector efficiency;

η - the chemical recovery yield.

Results for the sequential separation of actinides step

For testing the sequential separation of actinides on UTEVA and TRU resins, followed by micro-coprecipitation, a simulated solution has been prepared, with known concentrations of U-233, U-235,U-238, Am-241, Am-243 and Pu-242. The solution was prepared from 0.1 ml uranil nitrate solution (see table 2) and 1 ml am_1 solution. The Eichrom procedure was applied. The results are presented in table 6, where A_e is the estimated activity and A_{mas} is the measured activity and η is the chemical recovery yield for the separation of the radioisotope.

Table 6

Results for the sequential separation of actinides on uteva and tru [4]

Radionuclide	A_e *[Bq]*	A_{mas} *[Bq]*	η
U-233	3.96	3.69	0.86
U-235	0.06	0.05	0.94
U-238	1.05	0.95	0.91
Am-241	5.34	4.10	0.77
Am-243	0.76	0.64	0.84
Pu-242	0.59	0.36	0.61

Fig. 5 presents the alpha spectra of the americium isotopes and Fig. 6 presents the alpha spectra of Plutonium 242.

The minimum detection limits were calculated with the results obtained for the regions of interest and the results obtained from alpha spectrometry analysis of the filters for an aquisition time of 100000 s. The results are presented in table 7.

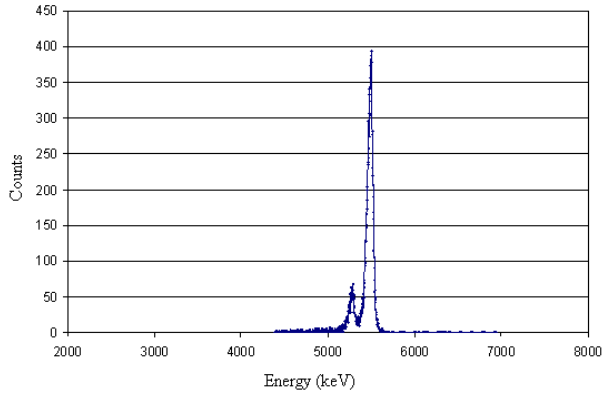

Fig. 5 – Alpha spectra of Americium 241 and Americium 243

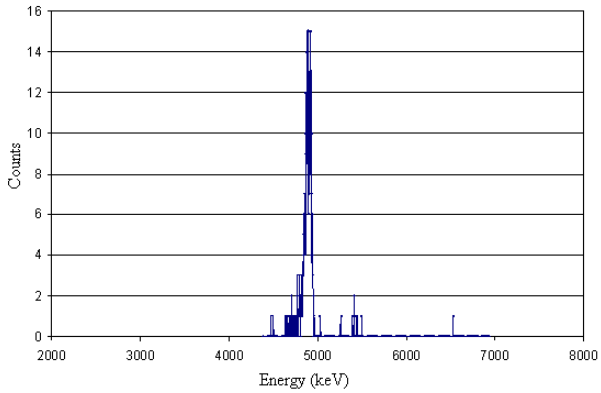

Fig. 6 – Alpha spectra of Plutonium 242

Table 7

Results for the minimum detection limit [2]

Radionuclide	MDL (mBq)
U-238	0.47
U-235	0.20
U-234,233	0.43
Pu-242	0.29
Am-243	0.25
Am-241	0.57

4. Conclusions

The work performed at the Radiation Protection and Environmental Protection Laboratory of the Institute for Nuclear Research, had the objective to validate the Eichrom procedure for sequential separation of actinides on UTEVA and TRU resins with micro-coprecipitation, for radiological characterization of waste in Romania.

The tests were performed on solutions with known activities and concentration of radionuclides and the sources were measured by both alpha spectrometry and LSC.

The resulting filters for each radionuclide, after micro-coprecipitation were measured by alpha spectrometry and liquid scintillation counting (LSC). The results obtained through these two methods, while knowing the initial activity of the solutions, conducted to the determination of the alpha spectrometer efficiency for the source geometry and the recovery yield used during this experiment.

The results showed that the procedure was well implemented at the Radiation Protection and Environmental Protection Laboratory.

R E F E R E N C E S

[1] *CNCAN*, Norme privind limitarea eliberarilor de efluenti radioactivi in mediu (NDR-04), aprobate prin Ordin al Presedintelui CNCAN nr. 221/25.08.2005 si publicate in Monitorul Oficial al Romaniei Partea I nr. 820/09.09.2005.

[2] *C. Dulama, R. Dobrin, A. Toma, R. Toma, S. Stoica*, "Experimental tests for separation of actinides from aqueous samples", Procedings of The 5th Annual International Conference on Sustainable Development through Nuclear Research and Education, NUCLEAR 2012, May 16-18 2012, Piteşti, Romania, ISSN 2066-2955.

[3] *C. Dulama*, "Optimizarea metodei radiochimice pentru separarea actinidelor din probe apoase şi elaborarea procedurii tehnice pentru determinarea activităţii actinidelor în efluenţii lichizi de la CNE Cernavodă", SCN Internal report no. 9218/2011.

[4] *R. Toma, C. Dulama, I. Prisecaru,* "Experimental Tests Using a Sequential Separation Procedure for Actinide Determination in Liquid Samples", International Youth Nuclear Congress 2012, Charlotte, United States of America, 5-11 August 2012, unpublished.