

# METHODS FOR CHARACTERIZATION OF RADIOACTIVE WASTE AND SPENT NUCLEAR FUEL. RESULTS OBTAINED DURING THE VALIDATION

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## ABSTRACT

In order to reduce radioactive risk on short term and long term for the environment and population, the radioactive waste has to be treated, conditioned and stored in appropriate conditions. In every country the regulatory body for nuclear activities establishes acceptance criteria for storage or disposal of radioactive waste package.

In order to satisfy requirements for radioactive waste characterization, in the frame of the National Program of Research and Development, the "Laboratory for characterization of spent nuclear fuel and high/medium level radioactive waste-LABORAD" was created. The purpose of the project was to accredit the analysis methods available in the laboratory, and also to develop new methods for the characterization of the radioactive waste.

Experimental results and performance obtained during validation of the methods will be presented in this paper.

Also new methods for radioactive waste characterization based on quadrupole ICP-MS are under validation in the laboratory.

**Key words: radioactive waste, alpha spectrometry, mass spectrometry,**

## 1. Introduction

The development of the nuclear energetics and progress of nuclear research activities have lead to the generation of radioactive waste of different types and activity levels. The necessity of processing, conditioning and storage of high and medium active radioactive waste has lead to the elaboration of national strategies for the management of radioactive waste and laws and regulations concerning the terms of their disposal.

During the phases of separation, treatment, conditioning and storage of radioactive waste, destructive and nondestructive methods for their characterization are needed. In order to satisfy this necessity, in the frame of National Program of Research and Development was created the "Laboratory for characterization of spent nuclear fuel and high/medium level radioactive waste- LABORAD". The purpose of the project was to increase the reliability of the results by accrediting the analysis methods available in the laboratory and also to develop new methods for the characterization of the radioactive waste. A special attention was paid to the high level radioactive waste and spent nuclear fuel characterization that require special facilities for handling. These facilities (e.g. hot cells, remote handlers, transport container) are already available in our institute.

Experimental results and performances obtained during validation of the methods will be presented in this paper. The laboratory (LABORAD) was notified as testing laboratory for waste characterization by the National Commission for Nuclear Activities Control (CNCAN). The accreditation process is in accordance with international standard *ISO/CEI 17025:2005* "General requirements for the competence of testing and calibration laboratories"

A special attention was paid to alpha spectrometry for which were elaborated and tested technics of chemical separation and samples preparation that lead to very good results. The laboratory will continue to develop testing methods based on inductively coupled plasma mass spectrometry.

The analysis techniques validated during the accreditation process are:

- Determination of isotopic composition by thermo ionization mass spectrometry (TIMS);
- Determination of lanthanides by high performance liquid chromatography (HPLC);
- Determination of U, Pu and Am by alpha spectrometry;
- Measurement of gamma radio nuclides activity on laboratory samples.
- Measurement of gamma radio nuclides activity on shielded containers with radioactive waste.

## 2. Experimental results

### 2.1. Thermal Ionization Mass Spectrometry (TIMS)

A Finnigan magnetic sector thermal ionization mass spectrometer equipped with a Faraday cup detector and a SEM detector is available in our laboratory.

Thermal Ionization Mass Spectrometry (TIMS) is a technique for isotopic characterization. This technique has a variety of characteristics that make it suitable for precise isotopic ratio determination and hence for precise nuclear fuel burnup determination.

The recently wide used quadrupole mass spectrometers are suitable to perform a multielement analysis and have a very low detection limit, but they are poor in isotopic ratio measurement. Usually the isotopic ratio measurements are one order of magnitude less than that measured by TIMS.

In figure 1 is presented the difference between spectra obtained with a quadrupole mass analyzer and a magnetic sector mass analyzer.

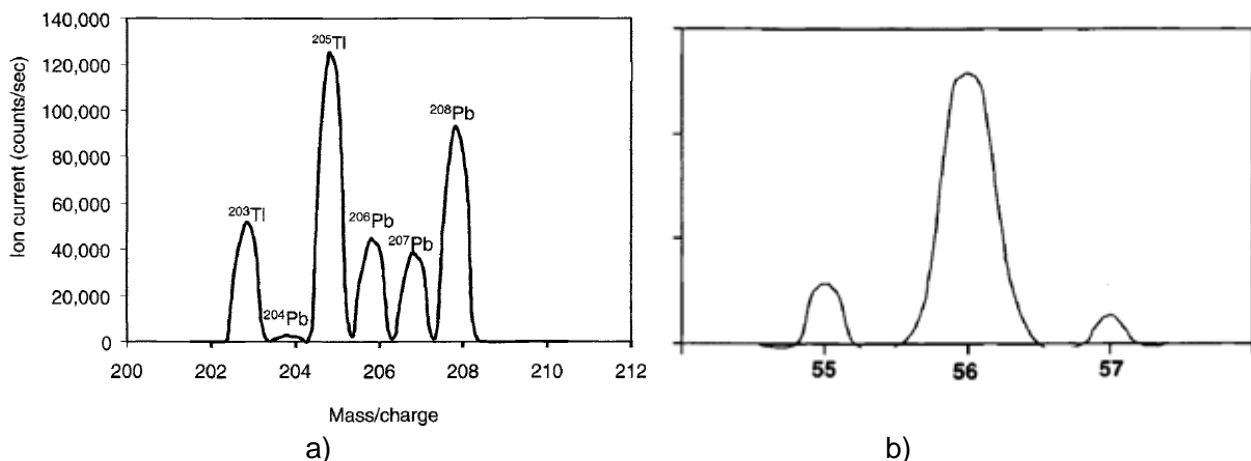


Fig. 1. Comparison between quadrupole mass analyzers  
 a) Mass spectrum obtained by quadrupole mass analyzer  
 b) Mass spectrum obtained by magnetic sector mass analyzer

In Table 2.1 are presented examples of isotopic ratio measured in our laboratory. We can see a relative standard deviation less than 0.05% for isotopic concentration above 1%, a relative standard deviation less than 0.1% for isotopic concentration between 0.1% and 1% and a relative standard deviation less than 5% for minor isotopes with concentration between 0.01% and 0.1%.

Table 1. – Isotopic ratio measured for uranium

Sample no.	Ratio	Mean value	Standard deviation	Relative deviation[%]
1.	234/238	0.000215	0.000006	2.69
	235/238	0.010464	0.000013	0.12
	236/238	0.005038	0.000016	0.32
2	234/238	0.000245	0.000014	5.9
	235/238	0.443469	0.000032	0.007
	236/238	0.005073	0.000023	0.45
3	234/238	0.007622	0.000004	0.31
	235/238	1.002621	0.000399	0.04
	236/238	0.009259	0.000040	0.43

Another example is given by a certified sample of natural uranium for which the isotopic ratios  $R_{235/238}=0.0073075\pm 0.000014$  and  $R_{234/238}=0.000059\pm 0.000017$  were measured. The certified values are  $R_{235/238}=0.007295$ ,  $R_{234/238}=0.000055$ . We can see that the differences between certified and measured values are less than standard deviation of measured values.

The precision mentioned above contribute to relative standard deviation of nuclear fuel burnup with less than 2%. Unfortunately, other not well known parameters lead to a burnup relative standard deviation that can exceed 4-5% in case of depletion method.

Using experimental data as input for nuclear fuel burn computation codes, we can obtain an inventory of spent fuel content useful for temporary storage or final disposal.

## 2.2. High Performance Liquid Chromatography (HPLC)

A Waters system for high performance liquid chromatography is available in the laboratory and contain the following components:

- Pumping system with binary gradient;
- In-line degasser;
- Automatic injector;
- Waters Symmetry  $C_{18}$ ( $\Phi \times L$ : 4,6x150mm; pore dimension 5 $\mu$ m) column;
- Post-column reagent pump;
- Dual  $\lambda$  absorbance detector and conductivity detector;
- Fraction collector.

The HPLC technique was employed for the determination of lanthanide content in spent nuclear fuel and other high radioactive waste. A procedure for this purpose was elaborated and tested experimentally.

Separation of lanthanides was made from a synthetic solution prepared from standard materials.

In fig. 2 is shown the chromatogram for a standard sample prepared in the laboratory by mixing elemental standard solutions.

In figure 3 are shown the chromatograms for three standard solutions prepared in the laboratory. We can see that the retention times are the same if the system parameters are not changed.

Also the calibration curves for each lanthanide are very good fitted by a line as we can see in figure 4.

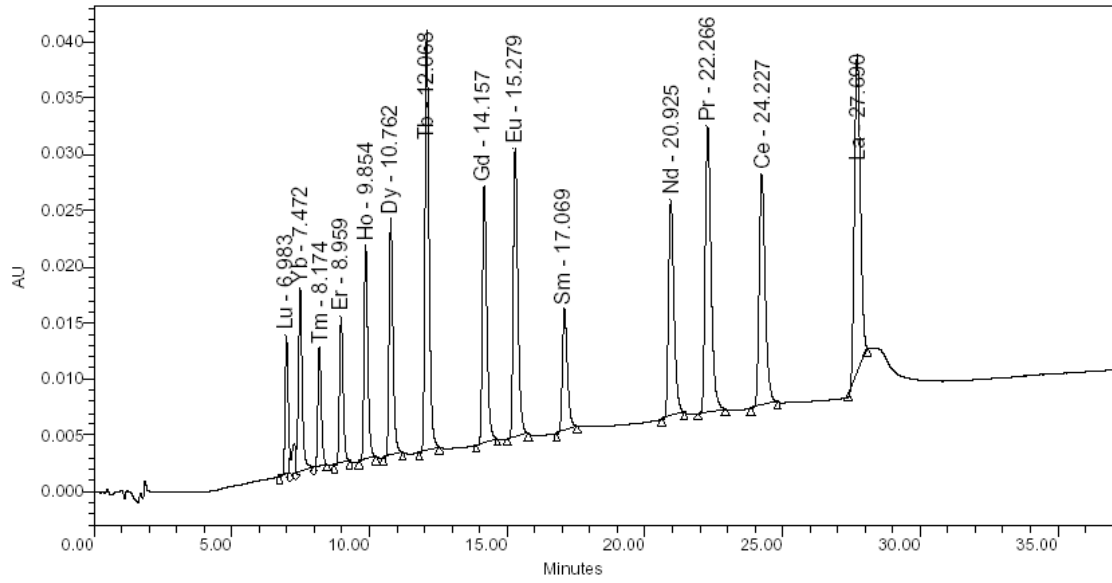


Fig. 2. Chromatogram for a standard solution prepared in laboratory

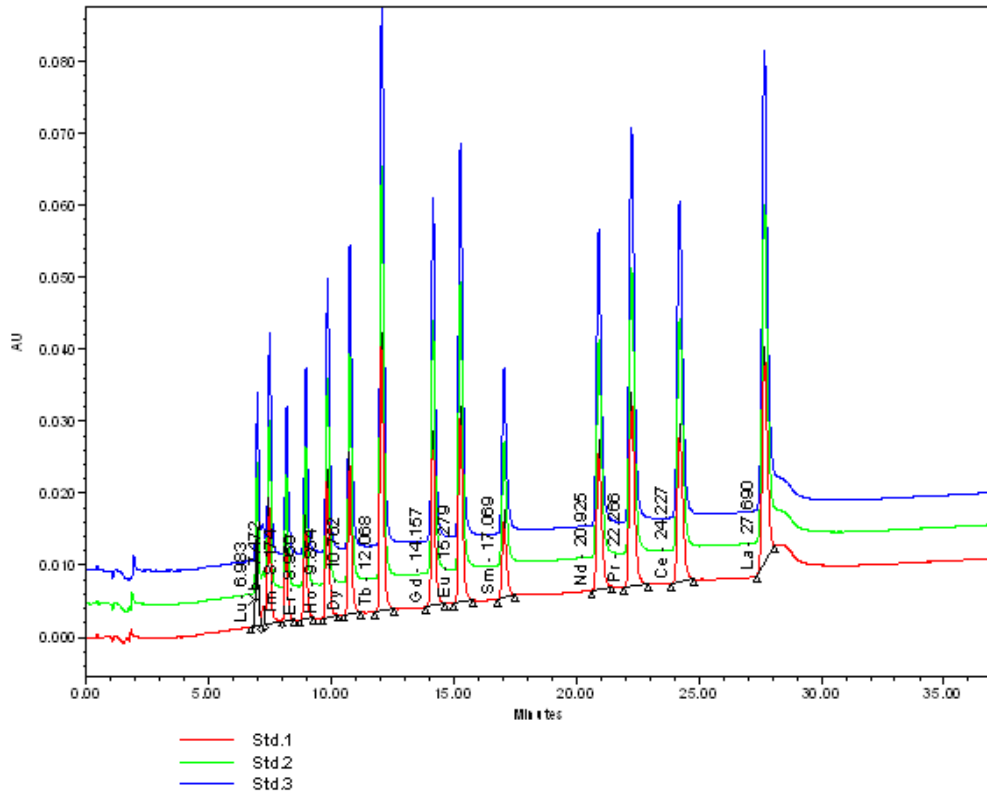


Fig. 3. Chromatograms overlapped for three standards solution prepared in laboratory

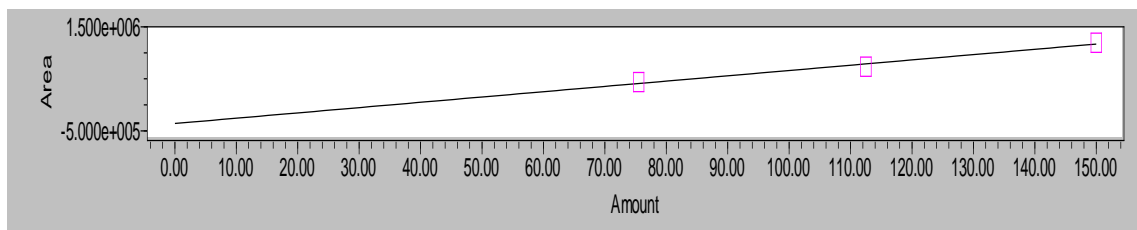


Fig. 4. Calibration curve for lanthanum (La)

Usually samples that have to be analysed contain uranium together with lanthanides. The ratio U/lanthanides is dependent on the nuclear fuel burnup. In order to determine the influence of uranium on retention times of lanthanides, samples with different ratios U/lanthanides up to 20000/1 were prepared and analysed. The results shows that the retention times are not affected by presence of uranium, but Lu, Yb and Tm are overlapped with uranium and they cannot be measured by this method.

### **2.3. Separation and determination of U, Pu and Am by alpha spectrometry**

The equipment used for alpha spectrometry is composed of an ORTEC dual channel 576A alpha spectrometer, an ORTEC Trump 8k multichannel analyzer and AlphaVision software. The detector has an active area of 300 mm<sup>2</sup> and a specified resolution of 21KeV.

The characterization of radioactive waste consists of the identification and the quantification of radioactive content, needed to evaluate and reduce the radioactive risk on short term and long term for the environment and population.

One of the used performance techniques for the characterization of radioactive waste is alpha spectrometry, with the help of which the alpha emitter content is measured, based on destructive analysis methods and going through many phases:

1. Preliminary treatment (sample dissolution, adding of spike solutions);
2. Chemical separation (ionic exchange, electro-deposition);
3. The obtainment of the source and the acquisition of the spectrum.

The preliminary treatment is applied for bringing the samples in a homogeneous form and the adjustment of these for the subsequent chemical processing, such as separation of every alpha emitting element. For the measurement of the radiochemical separation yields, tracers are added in the sample in the phase of preliminary treatment.

The general techniques used for separation and purification include co-precipitation, liquid-liquid extraction, ionic exchange etc. In some cases, two or more of these techniques are combined.

Co-precipitation is often used for the pre-concentration and the obliteration of the radio nuclides in the matrix which will be analyzed.

The liquid-liquid extraction (named extraction with organic solvents) is used for the extraction of U or of other actinides. For this, the following reagents are used: organic acids, cetones, ethers, esters, alcohols and organo-phosphoric derivatives. Methyl-isobutyl cetone has been intensively used in the nuclear industry for the extraction of U and Pu from spent nuclear fuel.

The ionic exchange is one of the most used techniques for chemical separation. With the sample in an aqueous acid environment, the ions (actinide compounds) replace the active groups from the resin, while other ions pass through and continue the process. The element retained on the resin is eluted using different elution agents.

The obtainment of the source has the goal of producing an ideal source for measurements by alpha spectrometry. A source like this must contain a uniform, thin and plane deposit of the element which has to be measured. The source has to be manipulable, chemically stable and all the solvent and acid traces have to be discarded to prevent the danger of destroying the counting and the detector chamber. To obtain these kinds of sources, three main methods are used:

- Direct evaporation from an aqueous or organic solvent;
- Electro-deposition;
- Precipitation as fluoride followed by filtration.

#### **2.3.1. Experimental results**

During the time, in our laboratory, different types of radioactive waste were characterized by alpha spectrometry. For developing and validate the method were elaborated and tested techniques of chemical separation and samples preparation that lead to very good results.

The characterized radioactive waste resulted mainly from the operation of Post Irradiation Examination Laboratory and TRIGA research reactor of Institute for Nuclear Research Pitesti and liquid radioactive waste from operation of Cernavoda Nuclear Power Plant.

In order to determine the selectivity of the method and the separation yield a quantity of fiber and paper waste was dissolved using a microwave digester and mixed with known quantities of  $^{243}\text{Am}$ ,  $^{233}\text{U}$  and  $^{242}\text{Pu}$ . The mixture was treated like an unknown sample.

The technique of chromatographic extraction on UTEVA and TRU resins was used for uranium, americium and plutonium separation.

The method of precipitation as fluorine followed by filtration was used for sample preparation. A Gelman filtration system with a polycarbonate filter of  $0.1\mu\text{m}$  coupled with a vacuum pump was used for precipitate filtration. After filtration of precipitate the filter are subsequently washed with ethanol and dried under infrared light. The dried filters are mounted on stainless steel disks to keep them plane and easy to manipulate in order to be introduced in the alpha spectrometer.

The alpha spectra measured for  $^{243}\text{Am}$ ,  $^{233}\text{U}$  and  $^{242}\text{Pu}$ , after chemical separation and sample preparation using the procedure briefly presented above, are shown in figures 5, 6 and 7. We can see that the radio nuclides were very good separated. Also the method of precipitation followed by filtration used for sample preparation conducted to good alpha spectra.

The calibration in energy of the alpha spectrometric chain is performed using laboratory standard sources of  $^{230}\text{Th}$ ,  $^{233}\text{U}$ ,  $^{244}\text{Cm}$ . In table 2 are presented the measured alpha activities for each sample and in table 3 the calculated separation yields.

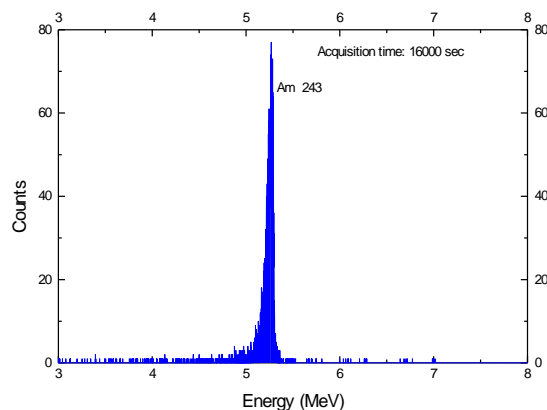


Fig. 5 Alpha Spectrum of Am after separation

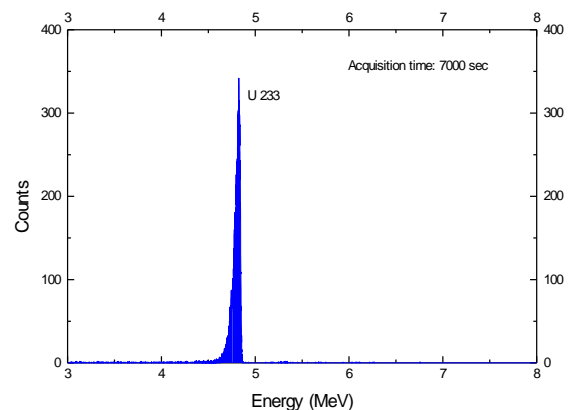


Fig. 6 Alpha Spectrum of U after separation

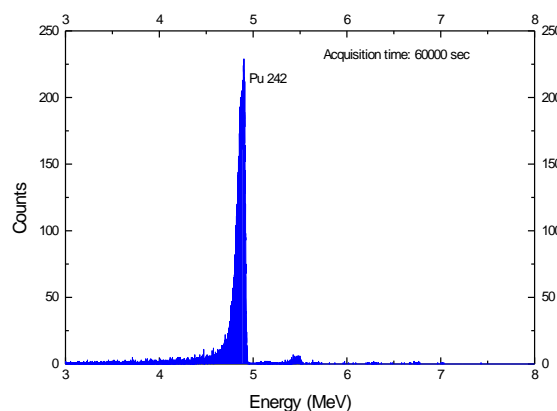


Fig. 7 Alpha Spectrum of Pu after separation

Table 2 Measured alpha activities

	Peak area	Acquisition time	Counts/sec/2π	Total activity (Bq)
Sample1 Am-243	8213	16000 s	1.970	3.940
Sample2 U-233	32894	7000 s	18.091	36.18
Sample3 Pu-242	32678	60000 s	2.090	4.180

Table 3 Calculated separation yield

	Quantity of tracer added (μl)	Tracer specific activity (Bq/ml)	Tracer activity added (Bq)	Separation yield (%)
U-233	0.1	386.3	38.63	93.66
Am-243	0.2	37.307	7.461	52.81
Pu-242	0.2	28.2	5.648	74.02

Determination of U, Pu and Am from spent nuclear fuel

One experiment was the separation of uranium and plutonium from nuclear spent fuel and their measurement by alpha spectrometry. In this case, the samples were prepared by direct evaporation and electro-deposition. The spectra obtained for U and Pu are shown in figures 8 and 9. This work is presented in detail in the reference [2].

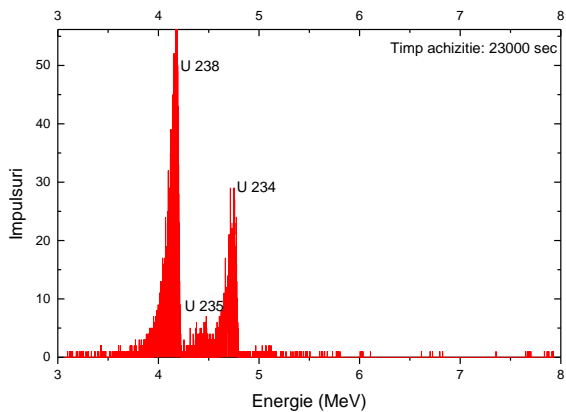


Fig. 8 Alpha Spectrum of U isotopes

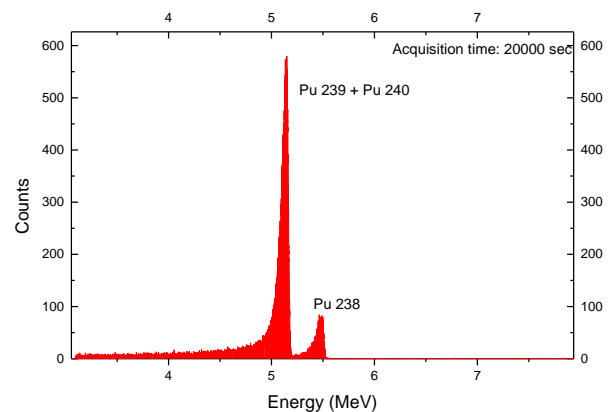


Fig. 9 Alpha Spectrum of Pu isotopes

Another experiment on spent nuclear fuel was done using co precipitation method for sample preparation. The spectra obtained are shown in figures 10,11 and 12.

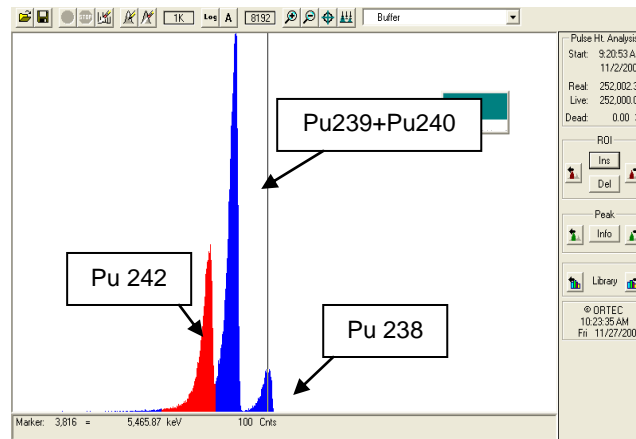


Fig. 10 Alpha Spectrum of Pu isotopes

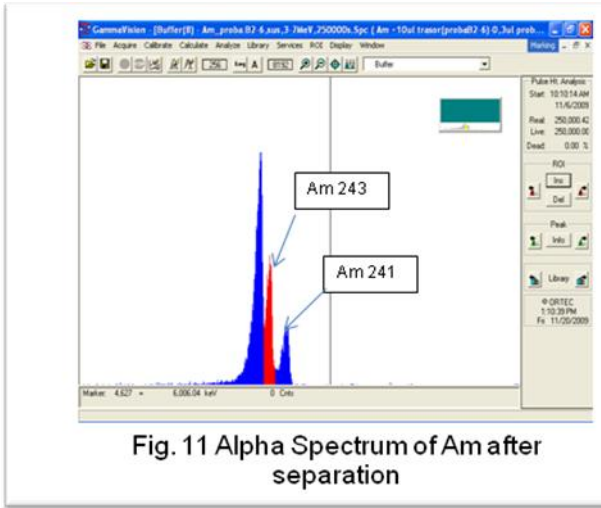


Fig. 11 Alpha Spectrum of Am after separation

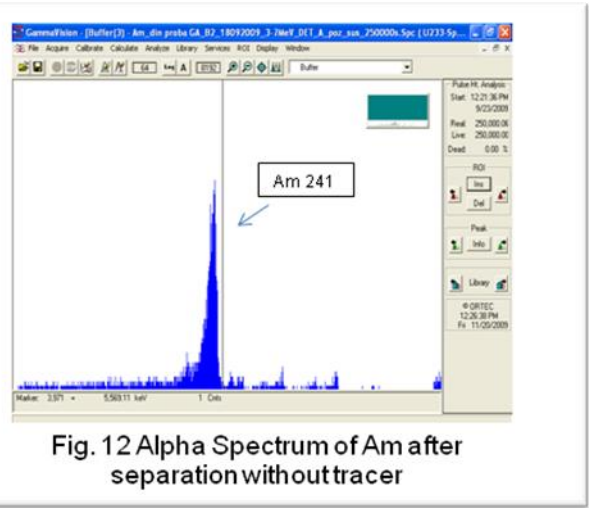


Fig. 12 Alpha Spectrum of Am after separation without tracer

As we can see in figure 11, because of his greater concentration the separation of the Pu was not completely. To separate Am from spent fuel, two steps of chemical separation were needed to remove Pu.

Determination of alpha radionuclides in liquid effluents from Cernavoda CANDU NPP

Two types of liquid radioactive wastes were analyzed in our laboratory.

First sample E1 was prepared following the same steps described above. A quantity of 100ml was taken for preparation. The alpha spectra obtained are presented in figures 13, 14 and 15.

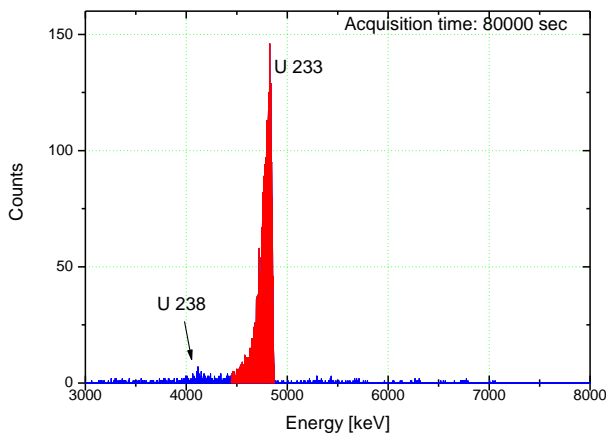


Fig. 13 Alpha Spectrum of U for sample E1 after separation

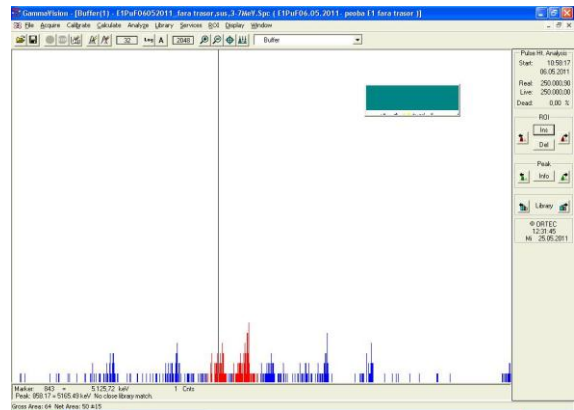


Fig. 14 Alpha Spectrum of Pu for sample E1 after separation

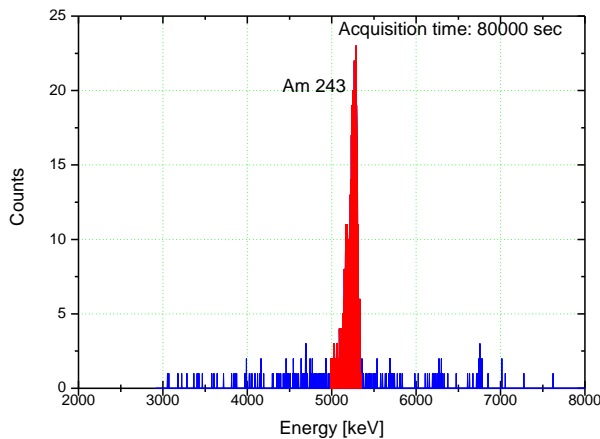


Fig. 15 Alpha Spectrum of Am for sample B1 after separation



In table 4 are presented the measured alpha activities for sample E1 for each sample and in table 5 the calculated separation yields. We can see sample E1 contain trace of uranium, americium is under detection limit but a significant activity for plutonium was found.

Table 4 Measured alpha activity for sample E1.

	Counts	Acquisition time (s)	Count rate (imp/sec/2)	Activity (mBq)	Sample quantity (ml)	Specific activity (mBq/L)
Pu238	1044	95000	0,01098	57,22	100	572,2
Pu239+240	457	95000	0,00481	25,05		250,5
U238	153	80000	0,00191	10,53		105,3

Table 5 Separation yield for sample E1

	Counts	Acquisition time (s)	Count rate (imp/sec/2)	Measured activity (Bq)	Added tracer activity (Bq)	Separation yield (%)
Pu242 (tracer)	1029	95000	0,01083	0,04134	0,0564	73,3
Am243(tracer)	853	80000	0,01066	0,04069	0,0747	54,5
U233 (tracer)	5612	80000	0,07015	0,26774	0,3863	69,3

Second sample B1 couldn't be evaporated to dryness due to a significant content of organics. In this case an additional step of co precipitation was added. Thus, the precipitate was filtered and the filter was dissolved by microwave digestion. Subsequently the procedure described above for the other samples was followed. Also a quantity of 100ml of B1 was sampled for preparation. The alpha spectra obtained are presented in figures 16, 17 and 18.

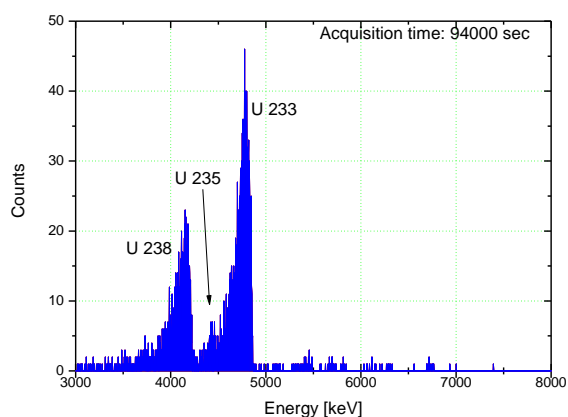


Fig. 16 Alpha Spectrum of U for sample B1 after separation

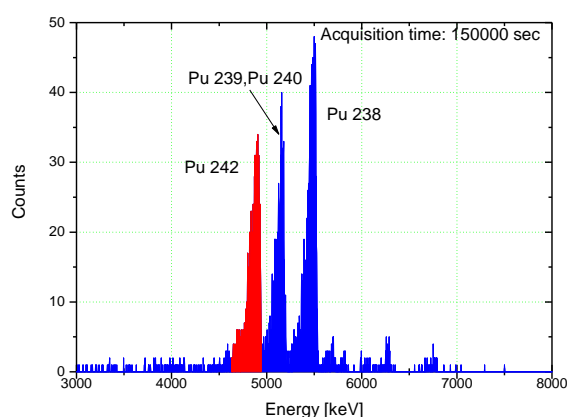


Fig. 17 Alpha Spectrum of Pu for sample B1 after separation

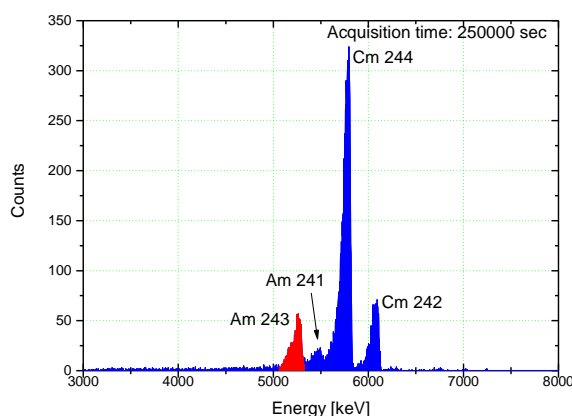


Fig. 18 Alpha Spectrum of Am for sample B1 after separation

In table 6 are presented the measured alpha activities for sample B1 for each sample and in table 7 the calculated separation yields.

Table 6 Measured alpha activity for sample B1

	Counts	Acquisition time (s)	Count rate (imp/sec/2)	Activity (mBq)	Sample quantity (ml)	Specific activity (mBq/L)
Pu238	1773	150000	0,01182	72,4	100	724,6
Pu239+240	1143	150000	0,00762	46,7		467,1
Am241	524	250000	0,00209	18,0		180,6
Cm244	11661	250000	0,04664	401,9		4019,9
Cm242	2454	250000	0,00981	84,5		845,9
U238	1210	94000	0,01287			
U235	172	94000	0,00183			

Table 7 Separation yield for sample B1

	Counts	Acquisition time (s)	Count rate (imp/sec/2)	Measured activity (Bq)	Added tracer activity (Bq)	Separation yield (%)
Pu242 (tracer)	1380	150000	0,0092	0,03511	0,0564	62,2
Am243(tracer)	2164	250000	0,008656	0,03303	0,0746	44,2
U233 (tracer)*	2138	94000	0,022745	0,08681	0,3863	22,4

\* A separation yield was estimated for uranium but it must be corrected because of peak overlapping of  $^{233}\text{U}$ ,  $^{234}\text{U}$  and  $^{236}\text{U}$ .

Sample B1 contain Am, U, Pu and Cm. The activity of curium was estimated supposing separation yield is similar to americium.

In our institute are in progress experiment of  $^{99}\text{Mo}$  separation from irradiated low enriched uranium. Alfa spectrometry was employed to determine the radionuclide purity of final solution of sodium molybdate.

In the last year a method for Th separation and determination was tested but it is not yet validated.

### 3. Conclusions

Reliable procedures for all methods presented were elaborated, tested and validated in the laboratory.

The laboratory (LABORAD) was notified as testing laboratory for waste characterization by the National Commission for Nuclear Activities Control (CNCAN) after ISO/IEC 17025:2005 „General requirements for the competence of testing and calibration laboratories”.

The method used in our laboratory for determination of alpha radionuclide from radioactive waste is rapid, reliable and proves a very good selectivity. The separation yield is reproducible in range of five percent. A complex matrix decreases the separation yield. A microwave digestion technique can be employed to dissolve complex matrix for small sample. For example, sample B1 was found containing organics. In this case additional steps consisting of co precipitation, filtering and microwave digestion were used. Because of additional steps in case of sample B1, the separation yield decrease but only about 10%.

If the sample contains curium, it goes together with americium and can affect the measurement precision (see fig. 18).

For alpha source prepared as described above the resolution was usually 45-50keV. This resolution is not very good but enough for applications in radioactive waste characterization. Other methods like gamma spectrometry on laboratory sample and shielded waste containers were validated and are available in the laboratory. Three gamma spectrometers are available in the laboratory, namely a portable ORTEC NOMAD Plus HPGe detector, a laboratory gamma spectrometry chain with a classic HPGe detector and a new gamma spectrometer based on an extended ORTEC GMX detector with beryllium window that have a very good efficiency at low energy, down to 5 keV.

Two methods for the determination of defects in nuclear fuel cladding and measuring of thickness of oxide on nonferrous materials by eddy currents technique are under validation. The methods are based on modern apparatus acquired last year.

Also new methods for radioactive waste characterization based on quadrupole ICP-MS are under validation in the laboratory.

#### 4. References

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