Laborad

LABORATORUL DE ÎNCERCĂRI PENTRU CARACTERIZAREA COMBUSTIBILULUI NUCLEAR UZAT ŞI A DEŞEURILOR RADIOACTIVE

RAAN SCN PITESTI

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

M. MINCU, C. GENTEA, G. ANDRONE, L. DINU, C. LAZAR and M. TATARASCU

Institute for Nuclear Research, C.P.78 Pitesti, 0300 Arges, Romania
E-mail: marin.mincu@nuclear.ro

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OUTLINE

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Introduction

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

Laboratory accreditation

The laboratory (LABORAD):

- was notified as testing laboratory for waste characterization by the National Commission for Nuclear Activities Control (CNCAN) (Fig.1)

GUVERNUL ROMÂNIEI
COMISIA NAȚIONALĂ PENTRU CONTROLUL ACTIVITĂȚILOR NUCLEARE
Bd. Libertății nr. 14 București 5, CP 42-4
Telefon (021) 316 05 72
Fax (021) 317 38 87

NOTIFICARE Nr. LI-VP 02/2011

În temeiul art. 4 din Legea nr. 111/1996 republicată, privind desfășurarea, reglementarea, autorizarea și controlul activităților nucleare și al Ordinului președintelui C.N.C.A.N. nr. 274/2004 privind desemnarea organismelor notificate pentru domeniul nuclear,

ca urmare a analizării documentației înregistrate la C.N.C.A.N. cu nr. 6159 /VB/09.12.2010 și a completărilor ulterioare înregistrate la C.N.C.A.N. cu nr. 288/VB/21.01.2011, a evaluării competenței și a auditării capabilității solicitantului, care s-a efectuat în condițiile respectării criteriilor generale pentru evaluarea laboratoarelor de încercări prevăzute de SR EN ISO 9000 și SR EN ISO/CEI 17025,

COMISIA NAȚIONALĂ PENTRU CONTROLUL ACTIVITĂȚILOR NUCLEARE

DESEMNEAZĂ

Laboratorul de încercări pentru caracterizarea combustibilului nuclear uzat și a deșeurilor radioactive "LABORAD"

din cadrul : *Laboratorului Examinari Post-Iradiere (LEPI)*

al: *Sucursalei Cercetări Nucleare Pitești*

situată în *Mioveni , str. Câmpului nr. 1, tel: 0248 213400, fax: 0248 262449,* persoană juridică înregistrată la Oficiul Registrului Comerțului cu numărul J03/515/1998, Cod Unic de Înregistrare 11057002

din cadrul: *Regiei Autonome pentru Activități Nucleare*

din: *Drobeta Turnu – Severin, str. Nicolae Iorga nr.1, jud. Mehedinți,* persoană juridică, Cod Unic de Înregistrare R 10882752

ca

LABORATOR DE ÎNCERCĂRI NOTIFICAT

În conformitate cu documentația prezentată, Normele privind desemnarea organismelor notificate pentru domeniul nuclear și prevederile impuse în anexa nr. 01, care face parte integrantă din prezentul document.

Intră în vigoare la data de: 24.02.2011
Expiră la data de: 23.02.2014

PREȘEDINTE
VA /DK Bucșala

1/3

Fig. 1

The accreditation process is in accordance with international standard *ISO/CEI 17025:2005 "*General requirements for the competence of testing and calibration laboratories"

Sources of radioactive waste (RW)

Laboratory handles and characterizes row radioactive waste generated in following activities:

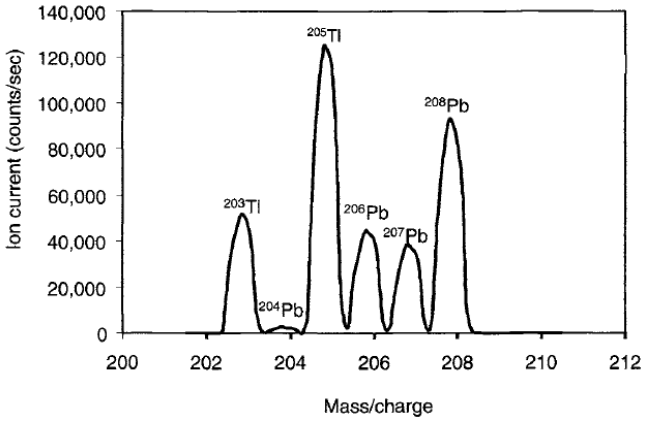
- Research activities;
- Current operation of research reactors, power plants and post-irradiation examination laboratory (PIEL);
- Production of radioactive sources for industrial and medical usage like iridium and molybdenum
- Decommissioning of spent radioactive sources from medical equipment.

Safety relevant radionuclides

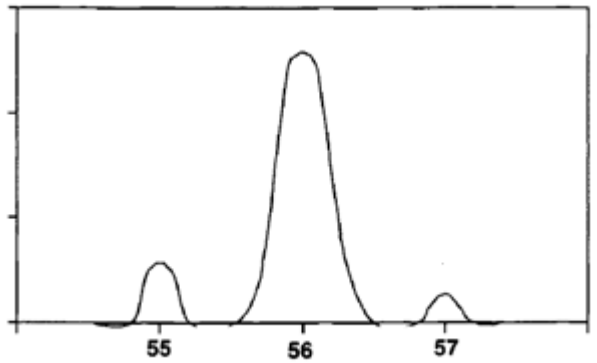
Radionuclides required to be quantified for radioactive waste caracterization:

- ^{3}H, ^{60}Co, ^{90}Sr, ^{137}Cs, ^{239}Pu, ^{241}Am, ^{14}C, ^{63}Ni, ^{94}Nb, ^{241}Pu, ^{237}Np, and ^{238}U,
- ^{59}Ni, ^{129}I, ^{99}Tc, ^{93}Zr, ^{93}Mo, ^{107}Pd, ^{151}Sm, ^{135}Cs, and ^{238}U,
- ^{36}Cl, ^{41}Ca, ^{79}Se, ^{108m}Ag, ^{238}Pu, ^{240}Pu, and ^{234}U.

Determination of isotopic composition



Mass spectrum obtained by quadrupole mass analyzer



Mass spectrum obtained by magnetic sector mass analyzer

ELAN DRC-e Quadrupole ICP-MS

Thermal Ionization Mass Spectrometer (TIMS)

Determination of isotopic composition

Isotopic ratios measured for three samples of uranium with different isotopic compositions

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

Relative standard deviation in function of isotopic concentration

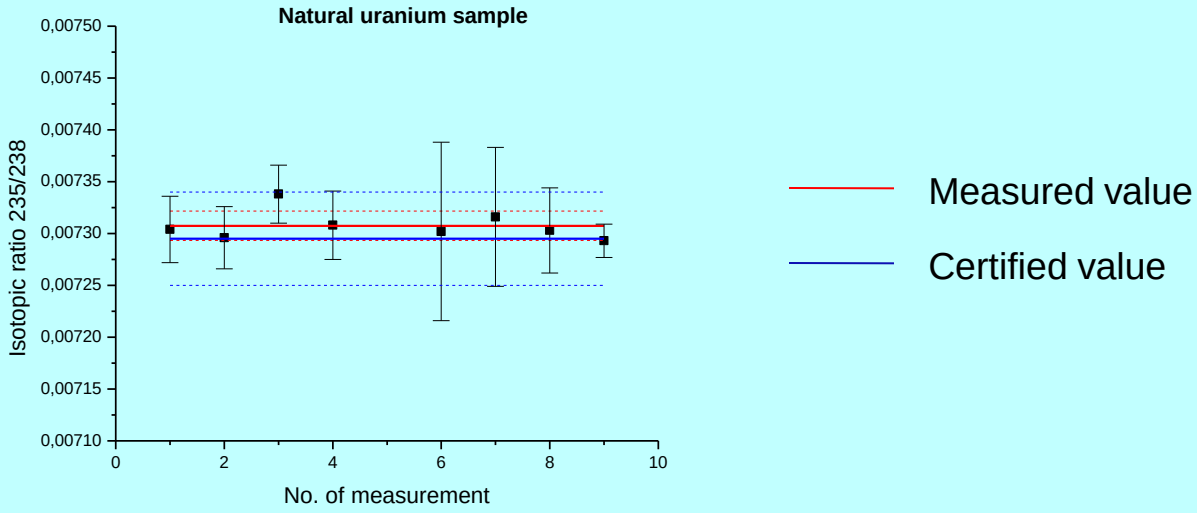
Isotopic concentration	Relative standard deviation
great then 1%	0.05%
between 0.1% and 1%	less than 0.1%
between 0.01% and 0.1%	less than 5%

Determination of isotopic composition

Comparison between measured and certified values for a natural uranium sample

Measured isotopic ratios	Certified isotopic ratio
$R_{235/238}$=0.007307±0.000014	$R_{235/238}$=0.007295
$R_{234/238}$=0.000059±0.000017	$R_{234/238}$=0.000055

The differences between certified and measured values are less than standard deviation of measured values



Determination of isotopic composition

Isotopic ratio for boron

	Isotopic ratio $^{10}B/^{11}B$	Standard deviation
1	0.250506	0.000477
2	0.250381	0.000795
3	0.250703	0.000397
4	0.250701	0.000537
5	0.250806	0.000597
6	0.250600	0.000149
7	0.250211	0.000323
8	0.250480	0.000194
9	0.250532	0.000216
10	0.250862	0.000227
	Mean value = 0.250582 ± 0.000084	

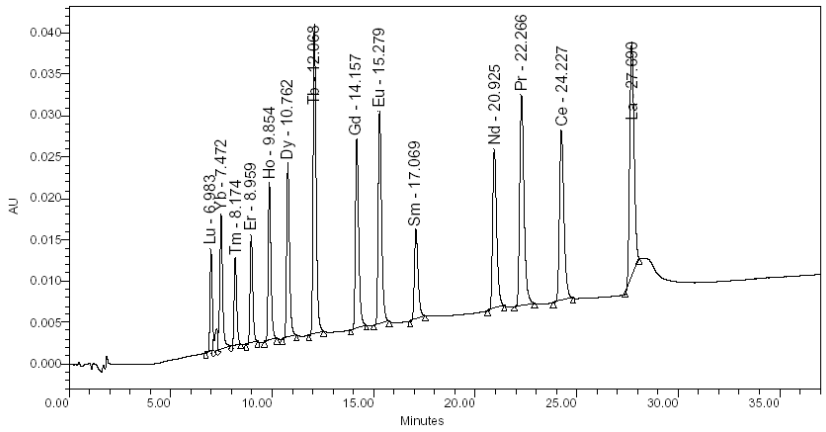
Measured ions were $Cs_2{}^{10}BO_2{}^+$ (308 a.m.u.) and $Cs_2{}^{11}BO_2{}^+$ (309 a.m.u.)

High Performance Liquid Chromatography (HPLC)

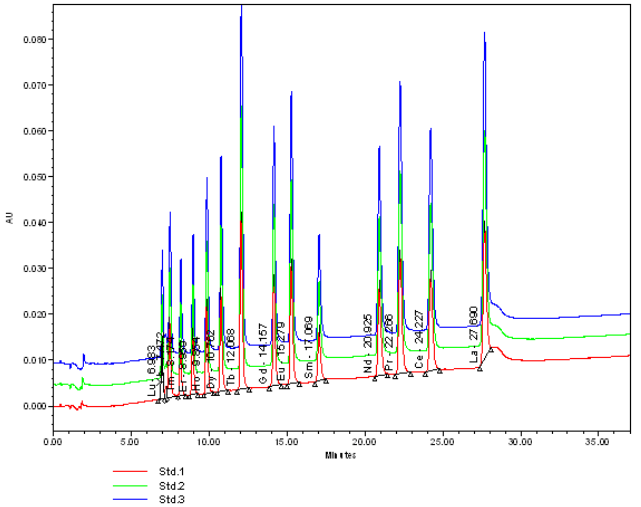
An Waters system for high performance liquid chromatography is available in the laboratory and contain following components:

- Pumping system with binary gradient;
- In-line degasser;
- Automatic injector;
- Waters Symmetry C_{18}(ΦxL:4,6x150mm; pore dimension 5µm) column;
- Post-column reagent pump;
- Dual λ absorbance detector and conductivity detector;
- Fraction collector.

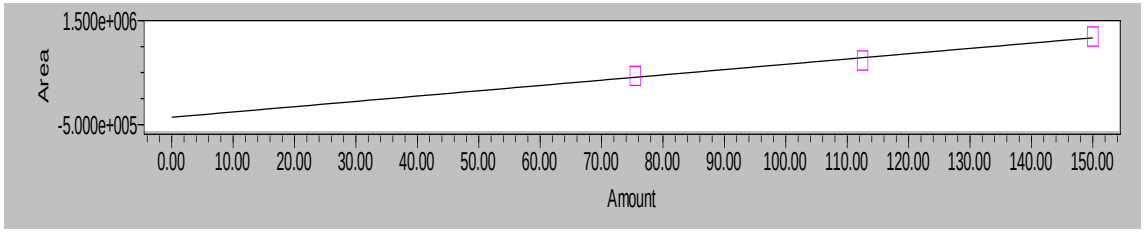
High Performance Liquid Chromatography (HPLC)



Chromatogram for a standard solution



Overlapped chromatograms for three standard solutions



Calibration curve for lanthanum (La)

Alpha spectrometry-Equipment

The equipment used for alpha spectrometry is composed of:

- ORTEC 576A dual channel alpha spectrometer,
- ORTEC Trump 8k multichannel analyzer
- ORTEC software.

The detector has an active area of 300 mm^2 and a specified resolution of 21KeV.

ORTEC 576A Alpha Spectrometer

One of the used performance techniques for the characterization of radioactive waste is alpha spectrometry 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.

Alpha spectrometry-Sample preparation

- **Preliminary treatment:**
  - sample dissolution;
  - adding of spike solutions;
  - Sample concentration by:
    - evaporation to dryness;
    - co precipitation of actinides on a filter;

Microwave digester

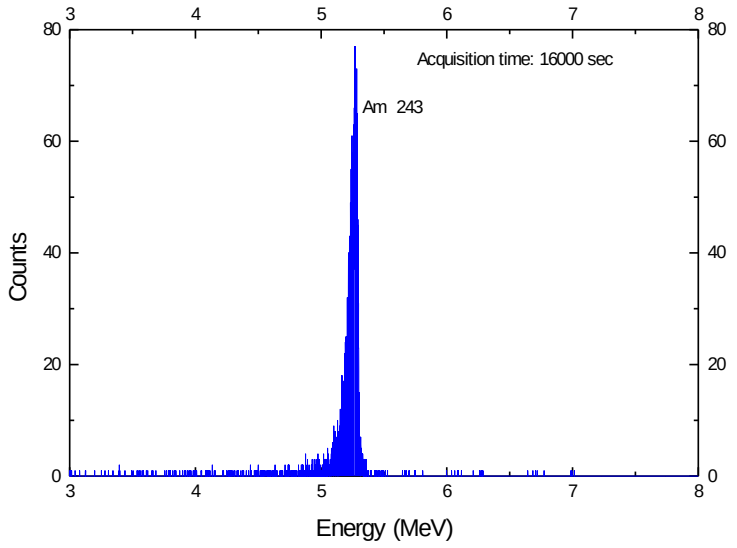
- **Chemical separation:**
  - The UTEVA and TRU Resin columns from Eichrom Technologies were employed for chemical separation.

Alpha spectrometry-Sample preparation

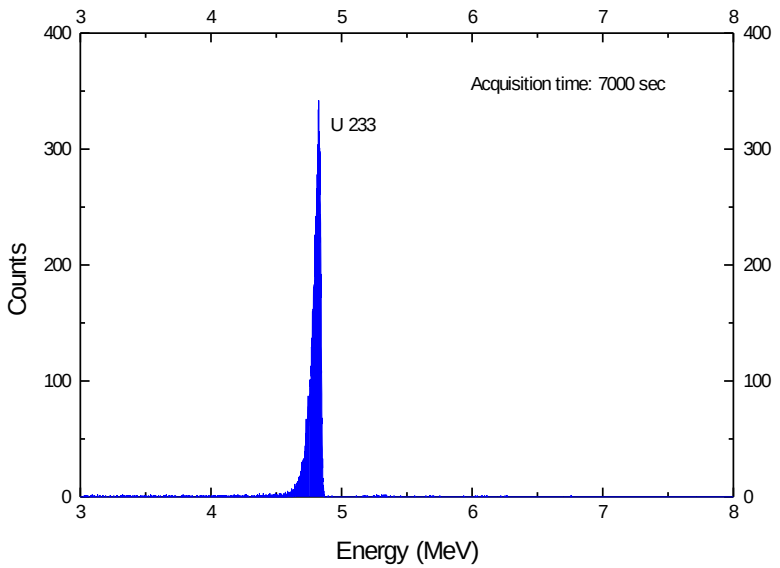
The main methods used for obtainment of thin alpha source:

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

Experimental results

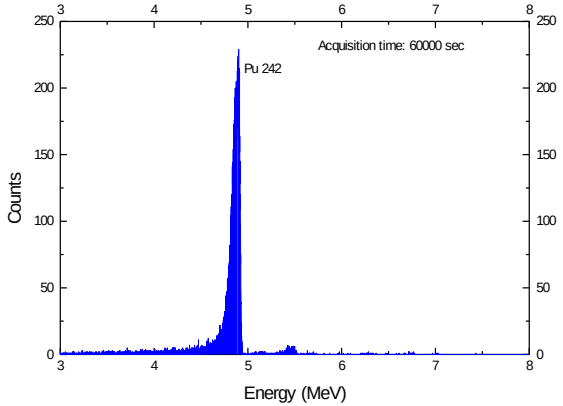


Alpha Spectrum of Am after separation



Alpha Spectrum of U after separation

Separation and determination of U, Pu and Am from radioactive waste



Alpha Spectrum of Am after separation

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

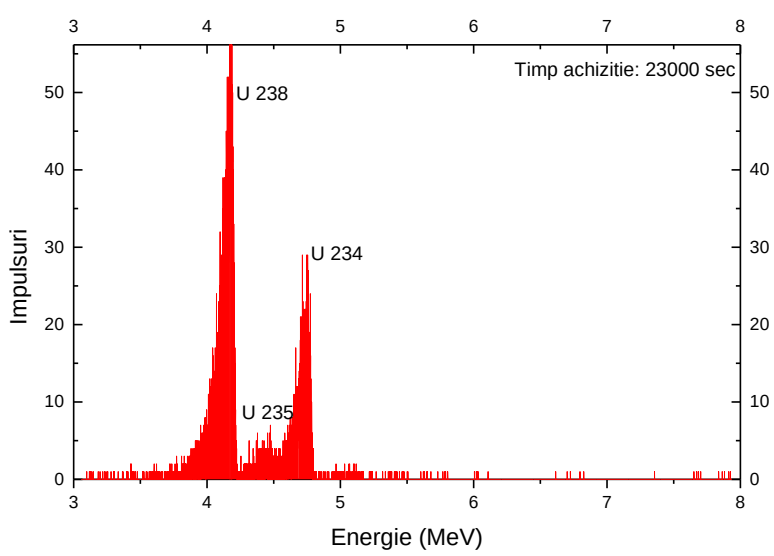
Separation and determination of U, Pu and Am from radioactive waste

Calculation of separation yield

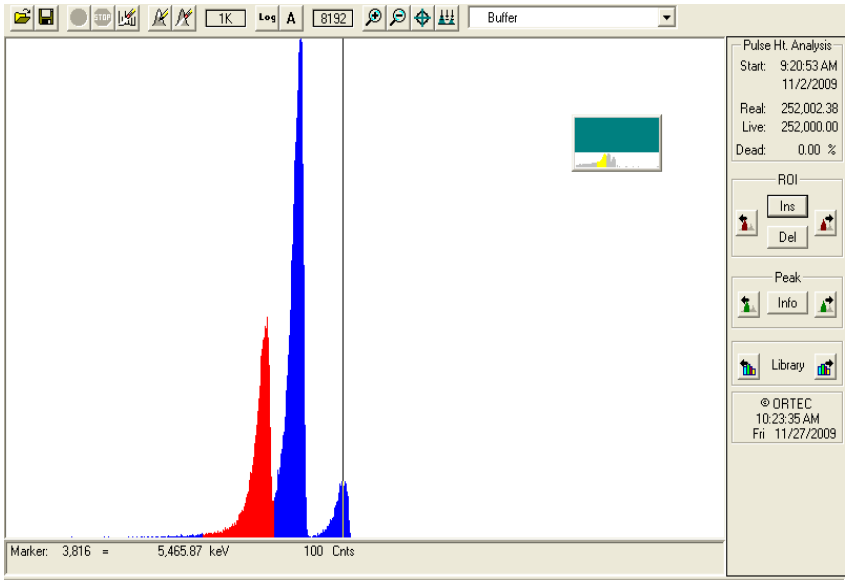
	Quantity of tracer added (µl)	Tracer specific activity (Bq/ml)	Tracer activity added (Bq)	Separation yield (%)
U-233	0.1	386.3	38.63	93.66
Am-243	0.2	37.307	7.461	52.81
Pu-242	0.2	28.2	5.648	74.02

The calibration in energy of the alpha spectrometric chain is performed using laboratory standard sources of ^{230}Th, ^{233}U and ^{244}Cm

Separation and determination of U, Pu and Am from spent fuel



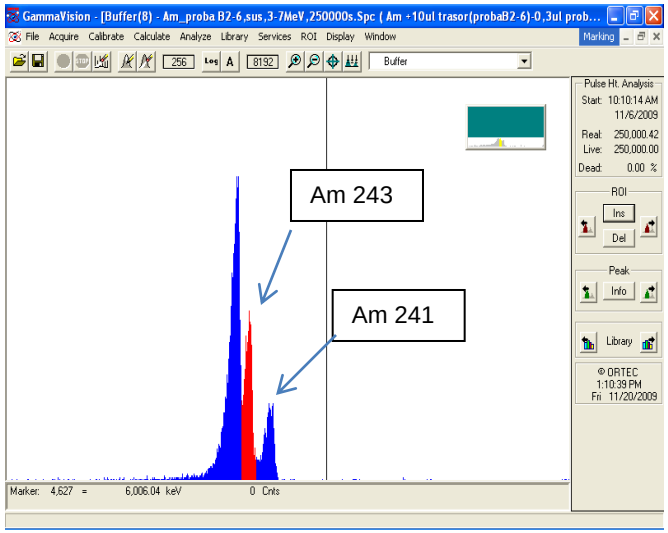
Alpha Spectrum of U after separation



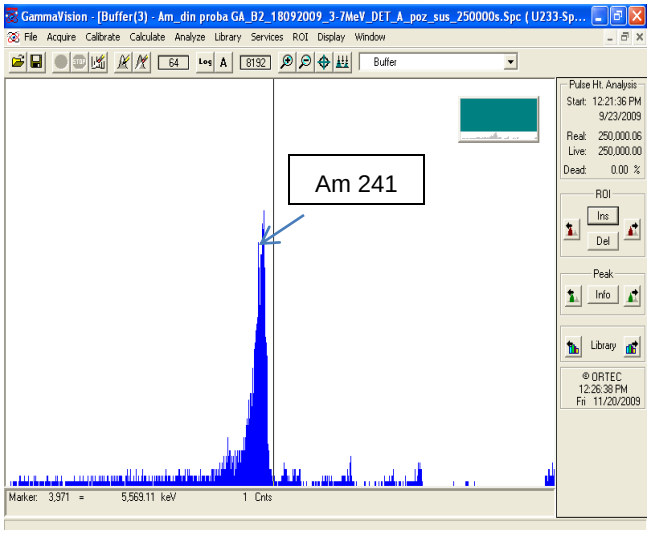
Alpha Spectrum of Pu after separation

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

Separation and determination of U, Pu and Am from spent fuel



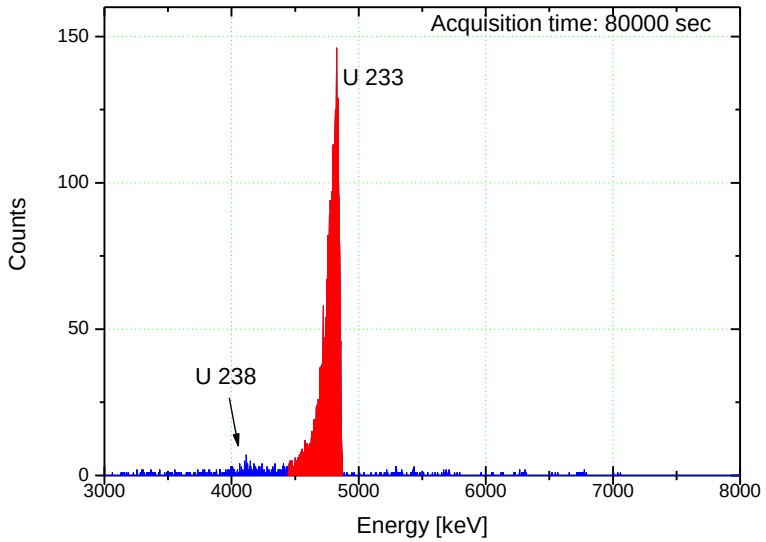
Alpha Spectrum of Am after separation



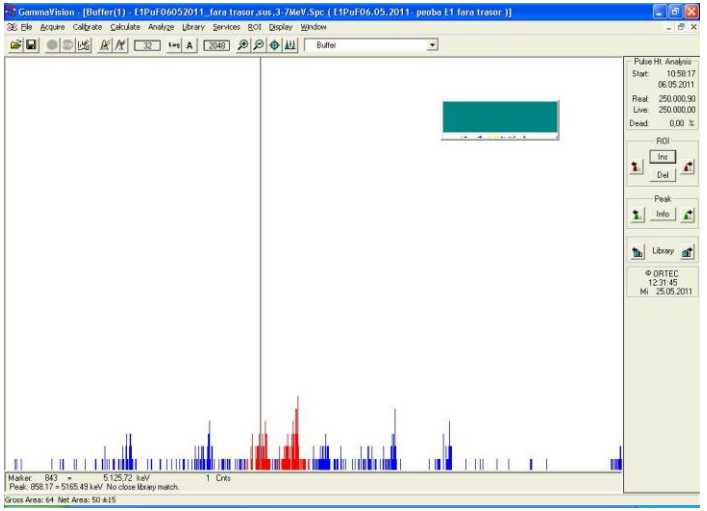
Alpha Spectrum of Am after separation without tracer

To separate Am from spent fuel, two steps of chemical separation were needed to remove Pu.

Sample E1 – effluent from Cernavoda NPP



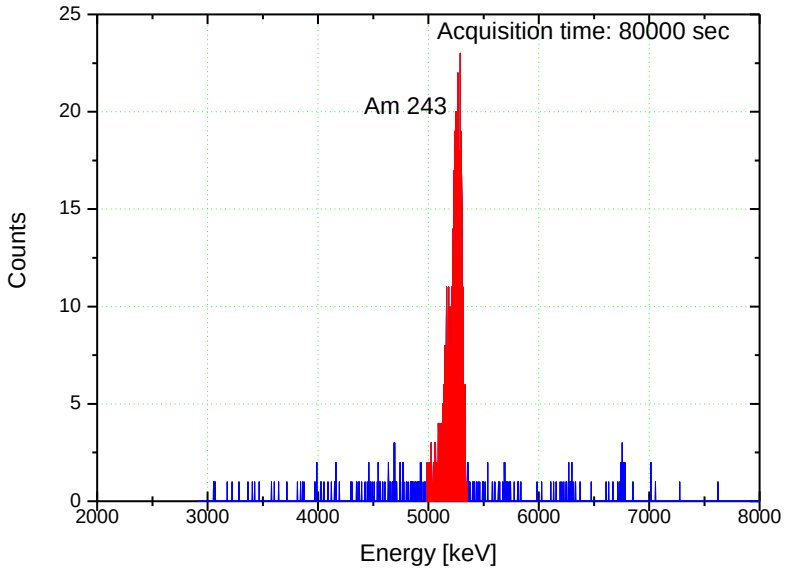
Alpha Spectrum of U for sample E1 after separation



Alpha Spectrum of Pu for sample E1 after separation

Trace of U and Pu was found in sample E1.

Sample E1 – effluent from Cernavoda NPP



Alpha Spectrum of Am for sample E1 after separation

Am was under limit of detection in sample E1.

Separation and determination of U, Pu and Am from spent fuel

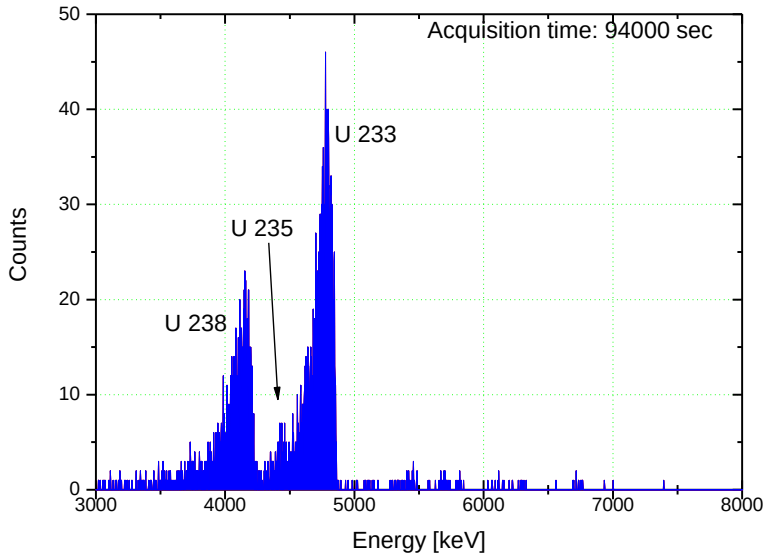
Calculation of separation yield for sample E1

	Counts	Acquisition time (s)	Count rate (imp/sec/2π)	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

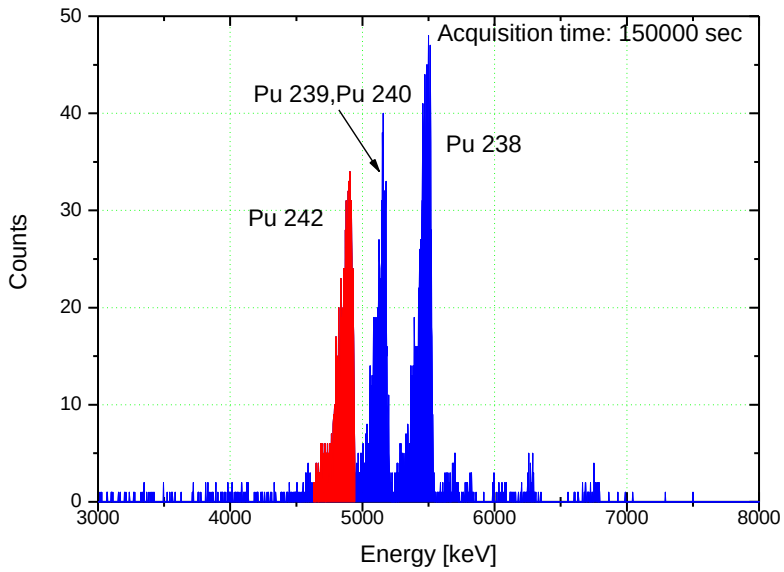
Measured alpha activity for sample E1

	Counts	Acquisition time (s)	Count rate (imp/sec/2π)	Activity (mBq)	Sample quantity (ml)	Specific activity (mBq/L)
Pu238	101	250000	0.000404	1.541	100	21.04
Pu239+240	64	250000	0.000256	0.977		13.33
U238	153	80000	0,00191	10,53		105,3

Sample B1 – decontamination solution from Cernavoda NPP

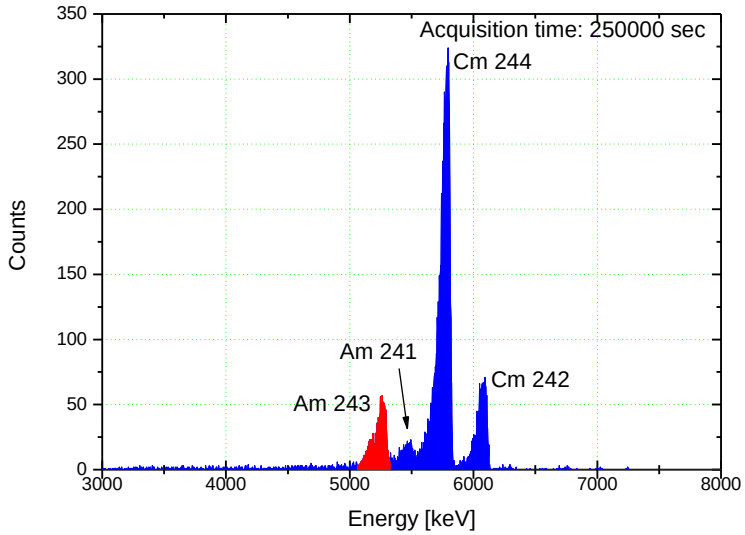


Alpha Spectrum of U for sample B1 after separation



Alpha Spectrum of Pu for sample B1 after separation

Sample B1 – decontamination solution from Cernavoda NPP



Alpha Spectrum of Am For sample B1 after separation

Cm go together with Am after chemical separation. An significant activity for Cm was found in sample B1.

Sample B1 – decontamination solution from Cernavoda NPP

In the phase of preliminary preparation, 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 for separation and thin alpha source preparation was the same.

Because of additional steps in case of sample B1, the separation yield decrease but only about 10%.

Sample B1 – decontamination solution from Cernavoda NPP

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			

Calculation of 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

Techniques for radioactive waste characterization available in our laboratory

- **Available and validated in the laboratory**
  - Determination of U, Pu and Am by alpha spectrometry;
  - Measurement of global alpha/beta activity
  - Determination of isotopic composition by thermo ionization mass spectrometry(TIMS);
  - Determination of lanthanides by high performance liquid chromatography (HPLC);
  - Measurement of gamma radio nuclides activity on laboratory samples in different geometries;
  - Measurement of gamma radio nuclides activity on shielded containers with radioactive waste.
- **In progress**
  - Determination of chemical composition and isotopic composition by QUADRUPOLE ICP-Mass Spectrometry.

Conclusions

- Reliable procedures for all methods presented were elaborated, tested and validated in the laboratory.
- The method 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 microwave digestion technique can be employed to dissolve complex matrix for small sample.

Conclusions

- An additional step consisting of co precipitation, filtering and microwave digestion lead to decrease of separation yield but only about 10%.
- For alpha source prepared as described above the resolution was usually 45-50keV.
- New methods for waste characterization will be implemented based on quadrupole ICP-MS

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