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Report on Long-Lived Nuclides Characterisation Methods

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Report on Long-Lived Nuclides Characterisation Methods

Executive summary

Little concentrations of long-lived alpha and beta emitters' in irradiated reactor graphite and other irradiated carbonaceous waste are important for the radioactive waste management. Before determination of activity of such difficult-to-measure radionuclides their separation from other radionuclides in the waste is necessary. Efficient methods for determination of ^{63}Ni activity and activity of ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{242}Cm, and ^{243,244}Cm isotopes in irradiated reactor graphite and other carbonaceous waste are developed. The methods are based on preliminary incineration in a muffle or microwave mineralization of graphite samples and subsequent separation of radionuclides using anion-exchange chromatography.

The results that come out from this task are necessary for implementation of tasks 3.4, 3.5 as well as for Work Packages 4, 5, and 6.

Revisions

Rev.	Date	Short description	Author	Review	Task Leader	WP Leader
01	16/05/2011	Final report	R. Druteikienė FTMC	G. Duškesas FTMC	D. Vulpius FZJ	G. Pina Lukas CIEMAT

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Glossary

AAS	Atom Absorption Spectrometer
LSC	Liquid Scintillation Counting

1. Introduction

Determination of little concentrations of long-lived alpha and beta emitters' in irradiated reactor graphite and other irradiated carbonaceous waste is one of the most difficult tasks in the radioactive waste characterisation. Before determination of activity of such difficult-to-measure radionuclides their separation from other radionuclides in the waste is necessary. In this task efficient methods for determination of ^{63}Ni activity and activity of actinides in carbonaceous waste are developed.

The method for determination ^{63}Ni activity is based on recommendations [1-6] and one for determination of activity of actinides follows recommendations [1, 7-11]. The results that come out from this task are necessary for implementation of tasks 3.4, 3.5 as well as for Work Packages 4, 5, and 6.

2. Method for Determination of ^{63}Ni Activity in Irradiated Graphite

2.1 Introduction

This method can be applied to determinate radionuclide ^{63}Ni activity in irradiated graphite samples including other irradiated carbonaceous waste like structural material made of graphite or non-graphitised carbon bricks and fuel coatings (pyrocarbon, silicon carbide) samples.

Necessary volume or mass of the sample is computed prior the radiochemical analysis according to the ^{137}Cs and ^{60}Co activity after gamma spectrometry. The sample pre-treatment includes transfer of solid samples to liquid phase and concentration of radionuclides by evaporation or co-precipitation.

Solid samples of mass 0.0005-0.002 kg are mineralized in a microwave system. Samples of larger mass are mineralized at corresponding temperature in a muffle oven or by extraction, by heating with acids.

The developed radioanalytical method is based on a group co-precipitation of iron and nickel radioisotopes and their stable elements on inert carrier and subsequent their separation using anion-exchange chromatography. Selective ^{63}Ni separation is performed by extraction chromatography.

Following the initial sample treatment (nickel co-precipitation with iron hydroxide in aqueous samples or leaching with acids from ashed and fresh solid samples) separation of iron from nickel is achieved by anion-exchange chromatography. Application of extraction chromatography using special nickel columns (Eichrom Technologies, Inc., Darien, IL 60561) provides nickel decontamination from interfering traces. Nickel columns allow get the following decontamination factors: ^{51}Cr>37,000; ^{54}Mn-270,000; ^{58}Co – 110,000; ^{60}Co – 113,000; ^{95}Nb– 13,700; ^{134}Cs>9,000; ^{137}Cs– 58,000.

Chemical yield is evaluated according to stable nickel added to the sample or according to the amount of this element in the sample. Control of stable nickel amount (before and after radiochemical analysis) is available due to the Atom Absorption Spectrometer (AAS, PERKIN ELMER Zeeman 3030). Purified ^{63}Ni fraction is measured for its activity using Liquid Scintillation Counting (LSC). Referring to the results of measurements on the AAS and LSC, the activity concentration of ^{63}Ni in the sample is calculated.

2.2 Pre-treatment of Samples

2.2.1 Pre-treatment of samples of mass bigger than $2•10^{-3}$kg

Sample of mass 0.5-1.5 g is transferred to porcelain crucible and incinerated in a muffle at 600º C (1mg /1hour). If some carbon amount occurs after incineration ashing is repeated. After that, leaching of samples is performed using mineral acids (H_2SO_4, $HClO_4$, HNO_3, H_2O_2).

2.2.2 Pre-treatment of samples of mass in the range of $5•10^{-4}$ - $2•10^{-3}$ kg

Mineralization of graphite samples which mass $5•10^{-4}$ - $2•10^{-3}$ kg is carried out using microwave mineralization system. Following steps are necessary:

1. Weighting out of $5·10^{-4}$ - $2·10^{-3}$ kg of the sample into a high pressure test-tube,
2. Addition of 3 mL 12 mol/L hydrochloric acid and 1 mL of 14 mol/L nitric acid,
3. Sample digestion at maximum temperature 255º C and pressure 71.6 bar following regimes provided in Table 1.

Table 1 Sample Digestion Regimes

Phase	Power, W	Time, min:s	Cooling regime
1	400	6:00	1
2	900	30:00	1
3	0	15:00	3

The volume of solubilised sample is determined using pipetor and necessary volume of the sample is taken for AAS with graphite atomisator. The basic elements of matrix and stable elements of studied radionuclides are determined by this method with an error of 5-10 %. If stable iron and nickel are known to be absent, the carriers 2 mg Ni^{2+} and 3 mg Fe^{3+}must be added.

1. Pour solution into 0.150L beaker,
2. Wash the test tube with 2x10 mL of demineralised water and combine the washings to the sample,
3. Heat solution to 70-80º C,
4. Add 6 mol/L NaOH to pH 9 (continue with 1 mol/L NaOH),
5. Filter the hydroxide precipitate,
6. Discard the filtrate,
7. Dissolve the hydroxides in 12 mol/L HCL.

2.3 Radiochemical Analysis of Samples

Radiochemical analysis includes following steps:

1. Prepare an anion-exchange column containing 14 mL of AG 1x4, Cl^- form,
2. Add 30 mL of concentrated HCl for conditioning the column, flow rate 1-1.5 ml/min,
3. Load sample solution (12 mol/l HCL) into column with flow rate 1 mL/min,
4. Collect effluent in a labelled 50 mL beaker,
5. Rinse the column with 20 mL 9 mol/L HCL and combine it to eluate (step 4),
6. Evaporate the combined in beaker effluents (step 4,5) to dryness,
7. Dissolve residue in 1-2 mL 1 mol/L HCL,
8. Add 1-2 mL ammonium citrate solution pH 8-9,
9. For each sample, place a Ni Resin column in the column rack,
10. Remove the bottom plug from each column and allow each column to drain,
11. Pipette sample solution (step 8) into conditioned column,

12. Rinse the column with 20-25 mL 0.2 mol/L ammonium citrate, pH 8-9. Rinse solution discard,
13. Pipette 10-15 mL 3 mol/L HNO_3 into column and allow to drain to strip the nickel,
14. Evaporate the effluent to dryness,
15. Dissolve residue in 2 mL demineralised water,
16. Measure volume of redissolved residue by pipettor and transfer 1 mL of solution to LSC vial,
17. Transfer 1 mL ^{63}Ni standard solution to other LSC vial,
18. Transfer remaining 1 mL of redissolved residue into plastic vial for stable nickel measurement.

2.4 ^{63}Ni Activity Calculation

Data obtained by LSC and AAS measurements are used to calculate ^{63}Ni activity concentration (Bq/kg) or volume activity (Bq/L) in the sample according to the formula:

$$C = \frac{Av}{m(v_t)E_t}, \tag{2.1}$$

where: A – activity concentration for ^{63}Ni, Bq/mL after LSC;

v – total sample volume, mL;

m – mass of analyzed probe, kg;

v_t – volume of sample aliquot analyzed, L;

E_f – efficiency of radiochemical analysis, parts of one.

3. Method for Determination of Activity of Actinides in Irradiated Graphite

3.1 Introduction

This method can be applied to determinate radionuclide ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{242}Cm, and ^{243,244}Cm activity in irradiated graphite samples including other irradiated carbonaceous waste like structural material made of graphite or non-graphitised carbon bricks and fuel coatings (pyrocarbon, silicon carbide) samples.

The method is based on the ashing and dissolution of matrix by aqua regia and radiochemical separation using of extraction chromatography method for sample of resins. ^{242}Pu and ^{243}Am isotopes are used for chemical yield determination. ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{242}Cm, and ^{243,244}Cm are deposited on stain steel disks prior to measurement by alpha spectrometry.

3.2 Pre-treatment of Samples

Sample of mass 0.5-1.5 g is transferred to porcelain crucible and incinerated in a muffle at 600º C (1mg /1hour). If some carbon amount occurs after incineration ashing is repeated. After that, leaching of samples is performed using mineral acids (H_2SO_4, $HClO_4$, HNO_3, H_2O_2).

3.3 Radiochemical Analysis of Samples

Plutonium is separated by Eichrom resins (UTEVA, TRU) prior to measurement by alpha spectrometry. ^{242}Pu are used to monitor chemical recoveries.

The separation of Pu and Am is continued using UTEVA and TRU Resin columns of 2 ml (commercially available from Eichrom Industries, USA). The UTEVA Resin column is connected onto the top of the TRU Resin and both columns were preconditioned with 3 M HNO_3. The sample after digestion is dissolved in 5M HNO_3, and the final solution contained 2.5 M HNO_3 – 0.6 M $Al(NO_3)_3$, iron sulfamate and ascorbic acid. Then the solution is transferred into preconditioned UTEVA–TRU columns. Th is extracted onto the UTEVA resin, while the trivalent actinides, Pu and Am eluted with 3M HNO_3 and are extracted onto the TRU resin. The UTEVA and TRU columns are disconnected and the procedure is continued with the TRU column. The TRU resin is washed with 2M HNO_3 and 2M HNO_3 – 0.1M $NaNO_2$ to oxidise Pu(III) to Pu(IV). The TRU resin is converted to the chloride form by means 9M HCl, and Am is eluted with 4M HCl and both HCl eluates are combined for the preparation of Am sources. Pu is eluted with 0.1M $NH_4HC_2O_4$. The samples are evaporated to dryness and oxalates in the Pu fraction and some organic in Am fraction are destroyed by heating with HNO_3/H_2O_2, $HNO_3/HClO_4$ and HNO_3. Scheme of actinide separation is shown in figure 3.1

Pu and Am are deposited on the stainless steel disk. The activities of samples are measured using the Alphaquattro (Silena) spectrometer and passivated implanted silicon barrier detectors with the diameter of 300 mm and resolution of 16 keV.

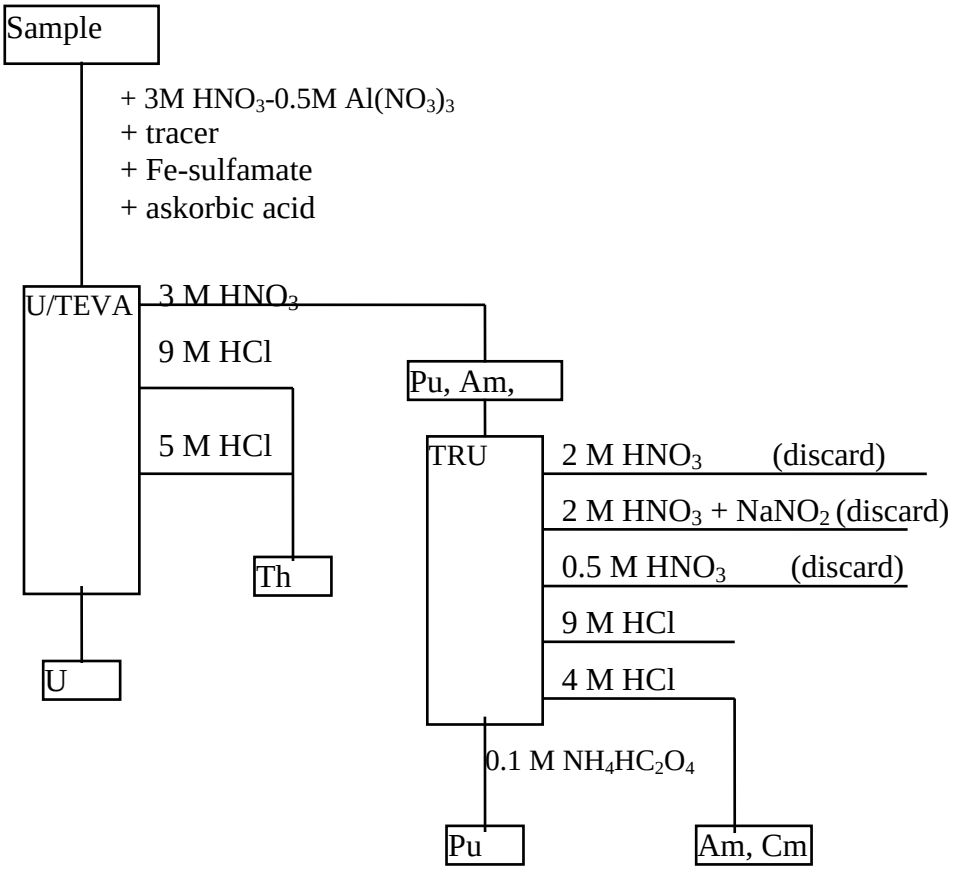


Figure 3.1 Scheme of Actinide Separation

3.3 Actinide Spectra

In figures 3.1-3.5 typical actinide alpha spectra in different samples of irradiated RBMK-1500 sleeve graphite after actinide separation and calibration spectrum (see figure 3.6) are provided.

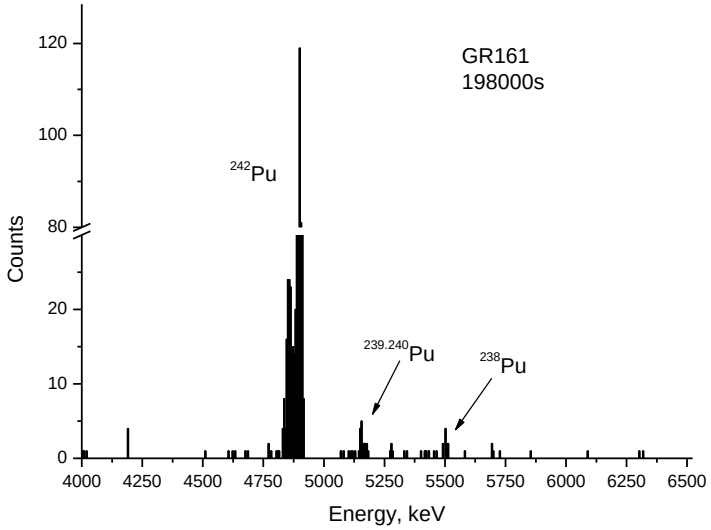


Figure 3.2 Alpha Spectrum of Plutonium Isotopes

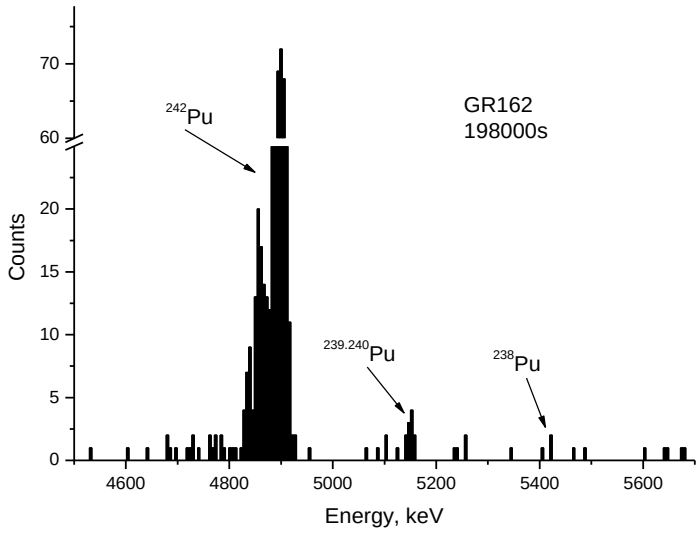


Figure 3.3 Alpha Spectrum of Plutonium Isotopes

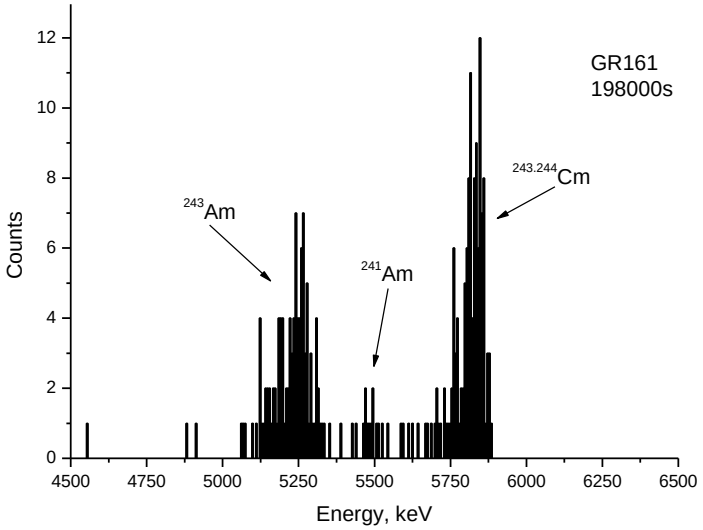


Figure 3.4 Alpha Spectrum of Americium and Curium Isotopes

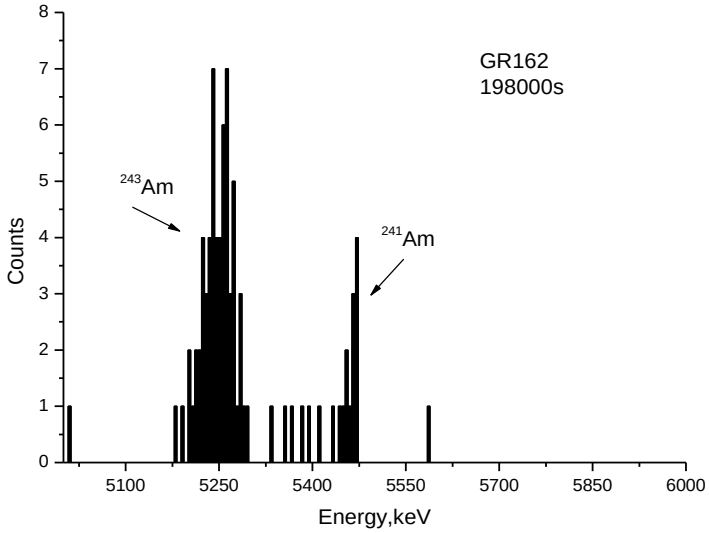


Figure 3.5 Alpha Spectrum of Americium Isotopes

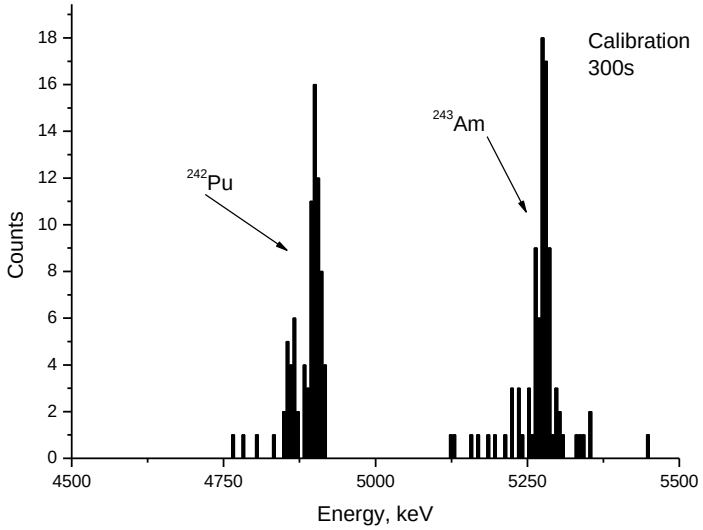


Figure 3.6 Alpha Spectrum of ^{242}Pu and ^{243}Am Isotopes Used for Calibration

3.4 Actinide Activity Calculation

Actinide tracer yield can be calculated by formula:

$$I = \frac{(N - B)}{E \cdot A}, \tag{3.1}$$

where: I – yield;

N – measured actinide tracer, cps;

B – background, cps;

A – tracer activity, Bq;

E – counting efficiency for tracer.

Actinide isotope activity is calculated by expression:

$$A_i = \frac{S - B}{E \cdot I \cdot V}, \tag{3.2}$$

where: A_i – sample activity Bq/g or Bq/L

I – yield;

S – measured sample activity, cps;

B – background, cps;

V – sample weight, g or volume, L;

E – counting efficiency of isotopic standard.

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