Determination of plutonium isotopes in spent nuclear fuel using thermal ionization mass spectrometry (TI-MS) and alpha spectrometry

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Introduction

Determination of actinides and fission products produced during irradiation in a nuclear reactor is important for the radio-chemical characterization of spent nuclear fuel.

One of the techniques used for destructive characterization of spent nuclear fuel is alpha spectrometry. Alpha emitters such as uranium, plutonium, and americium can be measured only by destructive methods after their separation.

Alpha spectrometry is used to determine the actinides from different types of samples because it is a simple method, with good detection limits, which allows using spike solutions during the radio-chemical separation and also has relative low costs. Alpha spectrometers typically require 200 KeV peak to peak separations for baseline resolution between successive alpha emissions of different isotopes. Therefore it is difficult to determine the abundance of ^{239}Pu and ^{240}Pu isotopes in samples by alpha spectrometry because the five primary alpha emissions for the two isotopes lie within a range of 65 keV. (Table 1) [1]

Table 1. *Alpha energies and intensities for ^{239}Pu and ^{240}Pu*

Isotopes		α Energies (keV)	Probabilities
^{239}Pu	α_1	5155,5	0,732±0,007
	α_2	5142,8	0,151±0,002
	α_3	5104,7	0,106±0,013
^{240}Pu	α_1	5168,2	0,735±0,004
	α_2	5123,7	0,263±0,0021

Alpha spectrometry cannot resolve the individual isotopes and the results are reported as ^{239}Pu+^{240}Pu. For these reasons is difficult to separate these two isotopes using an alpha spectrometer, but using thermal ionization mass spectrometry (TI-MS) the amounts of ^{239}Pu and ^{240}Pu can be determined separately.

1. The key stages of the process

a. Spent nuclear fuel dissolution and dilution of the concentrate solution - The fragment of the spent nuclear fuel element was cut according to a sampling plan. Fuel dissolution is performed into a hot cell with lead walls in order to ensure operator's biological protection. The hot cell is fitted with telemanipulators and an observation window. The cut section of the fuel rod was dissolved in a stainless steel vessel with lid (Figure 1) which ensures the sealing during the process, with a mixture of nitric acid and hydrofluoric acid under boiling conditions. During the process of chemical dissolution and dilution (c_U=1mg/ml), we obtained a *final solution* of uranyl nitrate in the majority, and also nitrates of actinides and fission products resulting from irradiation. [2]

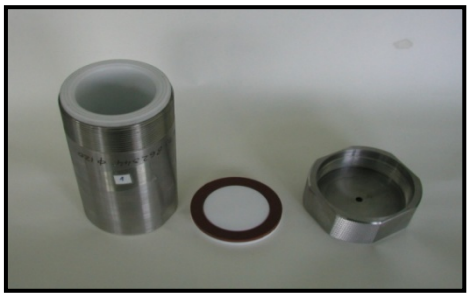

Fig. 1. *Dissolution device*

b. Radiochemical processing of the samples - Several radiochemical procedures must be performed before alpha spectrometry and TI-MS measurements. We processed two samples, first for alpha spectrometry and second for TI-MS measurements as follows:

1. the first aliquot was sampled from the *final solution* and 5 ml of ^{242}Pu spike solution were added (^{242}Pu spike solution was prepared in 3M HNO_3 at approximately 22,6 mBq/ml). This sample was named "*Plutonium+^{242}Pu spike"*.

2. the second aliquot was sampled from the *final solution* and named just "*Plutonium*". The two samples were then subjected to repeated chemical purifications consisting of:

a) evaporation to dryness on a hotplate;

b) bringing back to the liquid phase of the precipitate obtained during the previous evaporation step;

c) sample purification onto UTEVA resin from uranium (the UTEVA resin is able to retain uranium (VI) and tetravalent actinides from nitric acid solutions, while trivalent actinides such as plutonium are not retained). [3]

d) loading the fraction obtained in previous step onto TRU resin in order to retain the different traces of americium and fission products that could be present in the analyzed sample. The TRU resin provides a simple and effective method for separation of trivalent actinides from aqueous solution. TRU Resin is an extraction chromatographic material in which the extractant system is octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (abbreviated CMPO) dissolved in tri-n-butyl phosphate (TBP). [4]

e) the elution of plutonium fraction from TRU column with acid ammonium oxalate.

The procedure of sample preparation for plutonium analysis in spent nuclear fuel solution is shown in Figure 2.

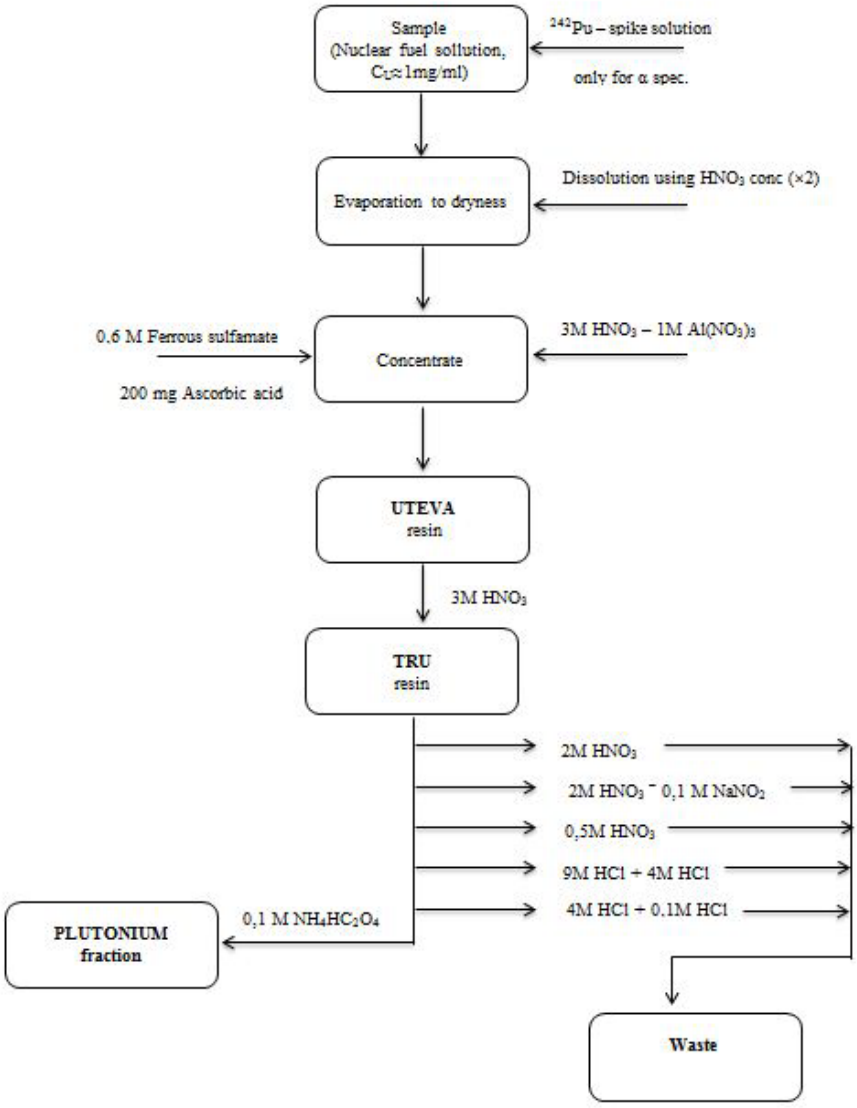

Fig. 2. *Sample preparation procedure for plutonium analysis in spent nuclear fuel solution*

The two collected plutonium fractions in the previous steps were subjected to successive evaporations with concentrated nitric acid.

c. Sample preparation for alpha spectrometry measurements - To get the best resolution for alpha spectrometry measurements are necessary sources of infinite thickness of thin, weightless on a perfectly flat substrate. In the present work the alpha source was prepared using the technique of co-precipitation using cerium nitrate. After evaporations, the plutonium fraction (named *Plutonium+^{242}Pu spike*) was converted with 4M HCl to the chloride form. The precipitate was then allowed to form for about 30 minutes before it was removed by filtration and washed using a Gelman system equipped with vacuum pump (Figure 3). The filter with the precipitate was then dried under an UV lamp (Figure 4) and fastened on a stainless steel disks to facilitate better handling for the source. (Figure 5)

d. Sample preparation for thermal ionization mass spectrometry measurements - After evaporation, the plutonium fraction (named *Plutonium*) was dissolved in 50 µL nitric acid 0,1M. To determine the isotopic ratio ^{240} / ^{239}Pu by TI-MS, 1µL from plutonium sample was deposited on the rhenium filament. The role of this filament is to heat the sample to evaporation, at a constant time rate. (Figure 6)

Fig. 3. *Gelman filtration system equipped with vacuum pump*

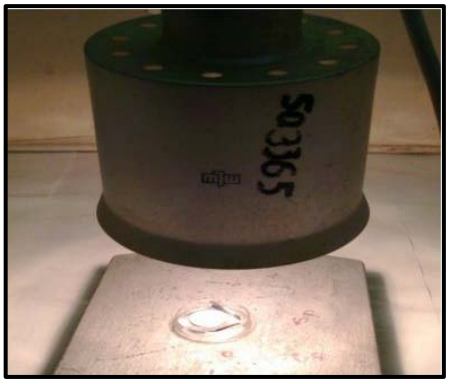

Fig. 4. *Filter's dry under the UV lamp*

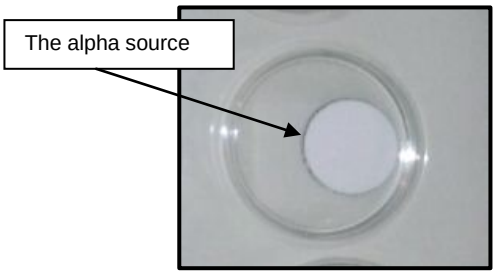

Fig. 5. *The filter fastened on a stainless steel disk*

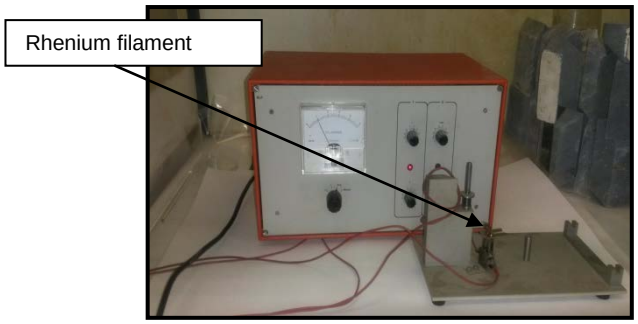

Fig. 6. *Device for heating the filament*

2. Results

a. Alpha spectrometry measurements – The obtained alpha source is measured using the ORTEC 576 alpha spectrometry system, with two individual measurement chambers (Figure 7) which allows to know in detail the inventory of alpha radio nuclides present inside the sample and the associated activities for each radionuclide separately.

Fig. 7*. ORTEC 576 alpha spectrometry system*

The obtained alpha spectrum is shown in Figure 8. The identified isotopes of plutonium in nuclear fuel solution are ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{242}Pu (spike). As shown in Figure 8 we cannot precise delimitate using alpha spectrometry ^{239}Pu isotope by ^{240}Pu isotope because alpha emissions for the two isotopes are overlapped (the five primary alpha emissions for the two isotopes lie within a range of 65KeV), and for these reasons we decided to determine the isotope ratio ^{240}Pu/^{239}Pu using TI-MS.

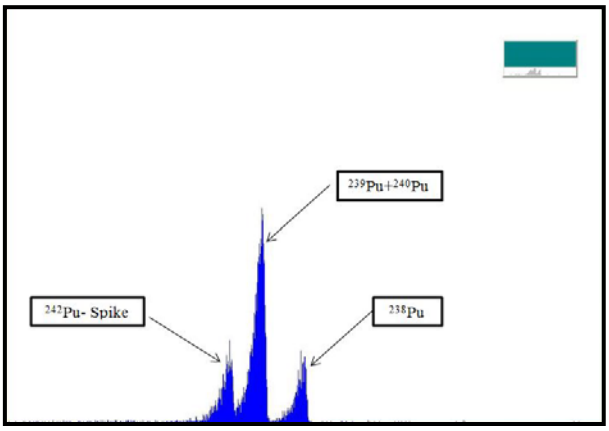

Fig. 8. *Alpha spectrum of the Plutonium+^{242}Pu spike source*

Next table shows the activity of plutonium source measured using alpha spectrometry. As can be seen the chemical recovery for the ^{242}Pu spike was about 80%.

Table 2. *Activity of plutonium source measured using alpha spectrometry*

Isotope	**Net aria (Counts)**	**Time (s)**	Measured source activity [mBq]	Activity of the added spike [mBq]	Yield [%]
^{242}Pu	1 804	80 000	89,8	113	**79,5**
^{239}Pu + ^{240}Pu	5 554		277,7		
^{238}Pu	1 504		75,3		

b. Thermal ionization mass spectrometry measurements – the rhenium filament which contains the evaporated plutonium sample is measured using the FINNIGAN MAT 261 mass spectrometer. The obtained spectrum is shown in Figure 9 and the results are shown in Table 3. The identified plutonium isotopes are: ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu.

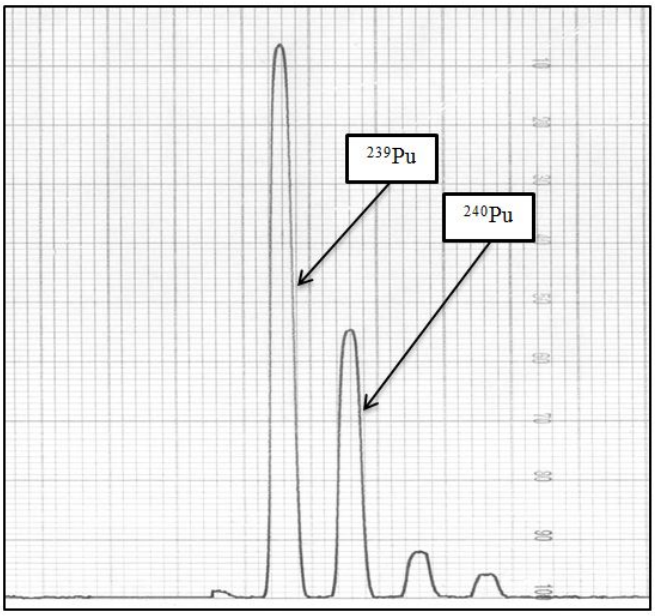

Fig. 9. *The spectrum of Plutonium sample analyzed by TI-MS*

Table 3. *The results using TI-MS measurements*

Isotope ratio				
$R_{238/239}$	**$R_{240/239}$**	$R_{241/239}$	$R_{242/239}$	
0.021518	**0.481854**	0.081469	0.038647	
Concentrations – mass percent				
C-238	C-239	C-240	C-241	C-242
1.317347%	61.47853%	29.74773%	5.050569%	2.405827%

The ^{240} / ^{239}Pu isotopic ratio determined using TI-MS in spent nuclear fuel is **0.481854**. To calculate the ^{240}Pu and ^{239}Pu amounts we used the equation no. 1.

$$N = \frac{m}{A} \times N_A \leftrightarrow m = \frac{N \times A}{N_A} \qquad \text{(equation no. 1)}$$

Where:
N – number of ^{239}Pu nuclei or ^{240}Pu nuclei (The number of ^{240}Pu nuclei or ^{239}Pu nuclei was calculated taking into account the value of $^{240/239}$Pu isotopic ratio determined by TI-MS, the results obtained by alpha spectrometry and the radioactive decay law).
m - ^{239}Pu amount or ^{240}Pu amount (g)
A - ^{239}Pu atomic weight, or ^{240}Pu atomic weight (g/mol)
N_A - Avogadro number – $6{,}023 \times 10^{23}$(particles/mol)

The results are shown in next table, and as can be seen the $^{240/239}$Pu mass ratio determined by TI-MS is the same with the calculated one.

Table 4. *$^{240/239}$Pu mass ratio*

Isotope	Amount (g)	$^{240/239}$Pu mass ratio – calculated	$^{240/239}$Pu mass ratio – by TI-MS measurements
^{239}Pu	$4{,}3432 \times 10^{-11}$	0,48387	0,48387
^{240}Pu	$2{,}1015 \times 10^{-11}$		

3. The dependence between $^{240/239}$Pu mass ratio and the fuel burn up using ORIGEN code

Using ORIGEN code we estimated the dependence between $^{240/239}$Pu mass ratio and the fuel burn up. The results are illustrated in next figure. As can be seen mass ratio determined by us corresponds to a fuel burn up at about 8,000 MWd/tU (this being the burn up of the fuel studied in present paper).

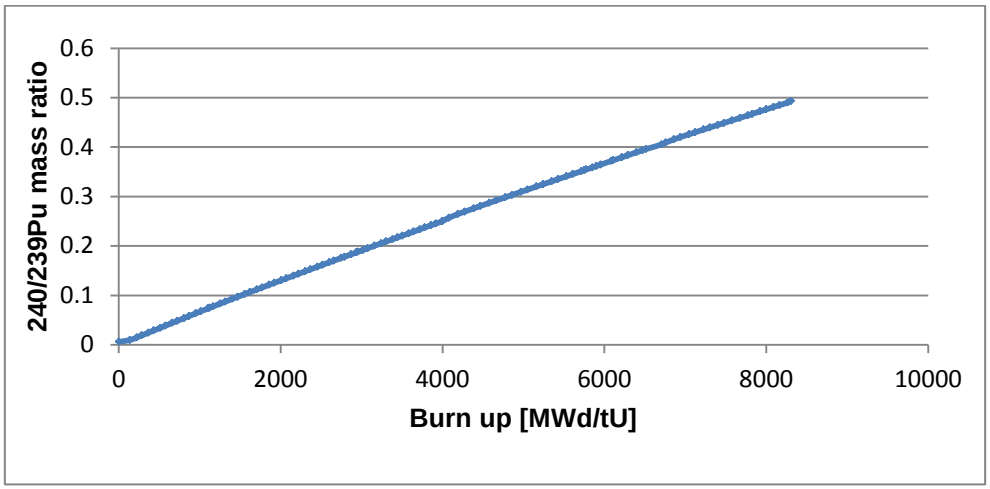

Fig. 10. *The dependence between $^{240/239}$Pu mass ratio and fuel burn up*

4. Conclusions

Fuel dissolution was performed into a hot cell with lead walls to ensure operator's biological protection. The cut section of the fuel rod was dissolved in a stainless steel vessel with lid which ensures the sealing during the process, with a mixture of nitric acid and hydrofluoric acid under boiling conditions.

We processed two samples, first for alpha spectrometry and second for TI-MS measurements. In the present work the alpha source was prepared using the technique of co-precipitation as CeF_3. The chemical recovery for the ^{242}Pu spike was about 80%. The determination of the ^{239}Pu/^{240}Pu ratio was not possible using alpha spectrometry because of the overlapping of the ^{239}Pu and ^{240}Pu peaks in the spectrum, but TI-MS offers the ability to individually identify ^{239}Pu and ^{240}Pu along with very low detection limits.

The $^{240/239}$Pu isotopic ratio determined using TI-MS in spent nuclear fuel is **0.481854**, and the $^{240/239}$Pu mass ratio is **0,483870**.

Using ORIGEN code we estimated the dependence between $^{240/239}$Pu mass ratio and burn up fuel. The $^{240/239}$Pu mass ratio determined by us corresponds to a fuel burn up at about 8,000 MWd/tU (this being the burn up of the fuel studied in present paper).

5. References

[1] S.P. LaMont, S.E. Glover, R.H. Filby Determination of plutonium-240/239 ratios in low activity samples using high resolution alpha-spectrometry, Journal of Radioanalitycal and Nuclear Chemistry, vol. 234, No. 1-2 (1998), p. 195-199;

[2] M. Tatarascu, C. Lazar, D. Ilinca, M. Mincu, O. Ichim, R. Negrea, Separation and determination of plutonium out of liquid waste from post-irradiation examination of nuclear fuel, Proceedings of the 5th NUCLEAR Conference on Sustainable Development through Nuclear Research and Education, Pitesti, May 16-18, 2012;

[3] http://www.eichrom.com/products/info/uteva_resin.cfm (July 2012);

[4] http://www.eichrom.com/products/info/tru_resin.cfm (July 2012);