SEPARATION AND DETERMINATION OF ACTINIDES FROM NUCLER SPENT FUEL SOLUTION BY ALPHA SPECTROMETRY

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I.GENERAL CONSIDERATIONS

Spent nuclear fuel represents an important category of radioactive waste produced in nuclear domain. 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.

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

1. 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.

2. Chemical separation. The general techniques used for separation and purification include co precipitation, liquid-liquid extraction, ionic exchange etc. In some cases, two ore 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. For example, the precipitation of calcium oxalate will eliminate the majority of the actinides from complex mixtures, leaving the majority of the organics and inorganic separated. The mechanism of co precipitation for the majority of the components is inclusion. More compounds, such as iron hydroxide are amorphous in nature and usually contain more water molecules. When radionuclide tracks are in a complex mixture, a procedure of co precipitation for the preliminary

separation is used. For example, iron or aluminium hydroxide can be used for the separation of U from aqueous solutions by adding carbonate free of ammonium hydroxide. U can be co precipitated, also with Al, Ti, Zr or La, as fluorine or phosphate.

- The liquid-liquid extraction (named extraction with organic solvents) is used for the extraction of U or of other actinides. For this the following 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. In some cases, solvent extraction can concentrate the nuclide 10 times or even more and can be selective for a specific nuclide. Extraction means that the nuclide is found in an ionic form in aqueous solutions. Nuclides cannot be extracted from this kind of colloidal solutions, suspensions or if the aqueous solution contains complex organic materials. Depending on the distribution coefficient, K_D, for a liquid extraction system, it is necessary that a few extractions from the sample are made, to obtain high retrievals for the radionuclide.
- 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 followed element is eluted from the resin, using different elution agents. Carefully selecting the parameters, the ionic exchange procedures can achieve very good performances.

3. 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. Ideally, the source must have a mono atomic layer of alpha emitters, without foreign material which wears off the alpha radiation. 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:
   - Evaporation from a aqueous or organic solvent;
   - Electro deposition;
   - Precipitation as fluorine followed by filtration. The obtainment of a source as similar to the ideal one is the result of this precipitation followed by filtration.

Direct evaporation from aqueous solution can be utilized to obtain acceptable alpha sources, but these tend to be less uniform than the one produced by other methods. In the solution, pulverizing agents can be added, but these generate organic deposits that have to be burned before the measurement of the sample.

Direct evaporation from organic solutions can offer deposits of alpha emitters, separated from solids. Tenoil-trifluoride-acetone (TTA) in benzene can be used for the U and Th complexation, and TTA in toluene is often used for Pu. The typical way is that of separation of the sample with solvent extraction and ionic exchange, dry evaporation, then treating with perchloric acid and nitric to oxidize the residual and organic materials. The purified ion in the aqueous solution is then extracted in TTA, deposited on a stainless steel evaporated disk

Electro deposition is the most used method for the preparation of the alpha sources. This is applicable for more elements and deposits can be realized on disks made out of stainless steel, copper, nickel and other materials. An electro deposition cell is used, in which the cathode is a metal disk, which only has one face exposed to the electrolyte. The anode is made out of platinum. Two processes are used: electro deposition from an electrolyte which consist of a salt in an organic solution, known as molecular plating and the electro deposition from an aqueous solution. The electro deposition from an aqueous solution is the most used technique of electro deposition. For the electro deposition of the actinides from solutions of weak acid or aqueous alkaline solutions, different electrolytes can be used. Adding the compound acids such as hydrofluoric acid, sodium bisulphate or penta-acetic tetra-amino diethyl acid offers the electrolytes a higher tolerance to the impurities that can be present in the solution. The most used electrolytes are the ones containing the ammonium ion; sulphate, oxalates or ammonium chlorine

can be used alone or in different combinations. Electro deposition is made at a low tension, about 10-12 V, with the intensity of 300mA/cm^2 enough to cover the deposition surface.

II. THE METHODOLOGY OF WORK FOR THE SEPARATION AND IDENTIFICATION OF ACTINIDES FROM SPENT NUCLEAR FUEL SOLUTION.

1. Dissolution of the sample

The operations of dissolution of the fuel are made in a hot cell with concrete walls to ensure the biological protection of the operator.

For dissolution, it is used a device (fig. 1) composed of a Teflon glass with a lid, in which the dissolution in HNO_3 8 M +HF 0.1 N at a temperature of 92-100 ^oC. The glass with the sample and the acid solution is introduced in a stainless steel vessel with a lid. In the hole of this glass, the tightening during the dissolution process is ensured. The dissolution takes place according to the following equation:

$$UO_2 + 8/3H^+ + 2/3NO_3^- = UO^{2+} + 4/3\ H_2O + 2/3NO$$

After the process of chemical dissolution and dilution (C_U=1mg/ml), a solution of uranyl nitrate is obtained (in majority), and as traces, the nitrates of the fission and actinides products resulted following the irradiation..

2. The separation of the U and Pu fraction by ionic exchange chromatography

The separation takes place in the presence of ionic exchangers, based on an interphasal equilibrium of ionic exchange, which takes place between a stationary phase, composed of the ionic exchanger and a mobile phase, which is liquid. The ionic exchanger is a polymer with a big molecular mass, insoluble, but permeable for the diluted solution of fuel with which it has contact. The polymeric skeleton or the matrix has immobile functional groups, whose electrostatical load is neutralized by the mobile ions. These can exchange with similar load ions, present in the solution. The reactions that characterize the behavior in the solution and on the resin are presented in the following lines:

The reaction of obtaining the U compound in the solution is:

$$UO_2(NO_3)_2 + 2NO_3^- \longrightarrow UO_2(NO_3)_4^{2-}$$

The reaction of conditioning of the resin to adsorb U is:

$$2RCl_r + 2HNO_{3\ aq} \longrightarrow 2R(NO_3)_{®} + 2HCl$$

The reaction of adsorption of U is:

$$2R(NO_3)_{®} + UO_2(NO_3)_4^{2-} \longrightarrow R_2UO_2(NO_3)_{4®} + 2NO_3^-$$

The reaction of eluting U on the ionic exchanging resin is:

$$R_2UO_2(NO_3)_{4®} + 4\ HNO_{3\ (aq)} \longrightarrow 2\ R(NO_3)_{®} + UO_2(NO_3)_{2\ (aq)} + 4NO_3^-,$$ where

r-represents the ionic exchanging resin with the functional group $CH_2N^+(CH_3)_3NO_3^-$.
aq-represents the aqueous phase.

Pu is present in aqueous solutions in five oxidation statuses: II,IV,V,VI and VII. The inferior oxidation statuses coexist in aqueous diluted solution, in substantial quantities. The chemical treatments that are performed are tied to obtaining Pu in the oxidation status IV, which in the form of $(Pu(NO_3)_2)^{2-}$ is retained on the resin as U and can be separated by the rest of the components in the solution.

The separation of U and Pu by ionic exchange is presented schematically in fig. (2):

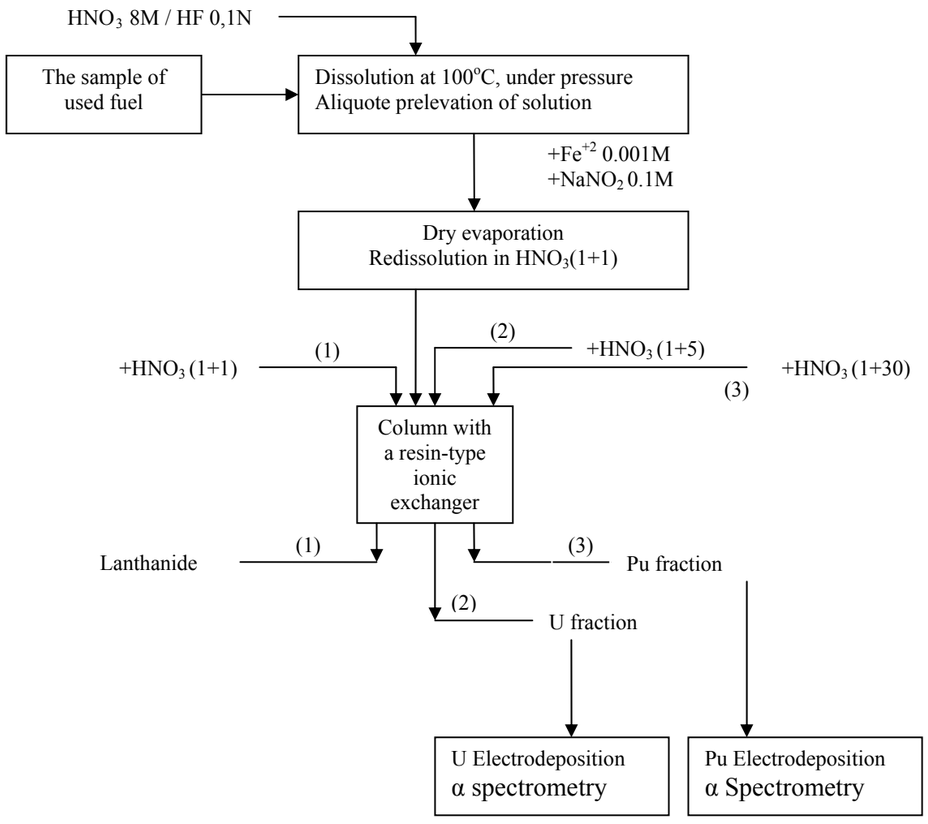
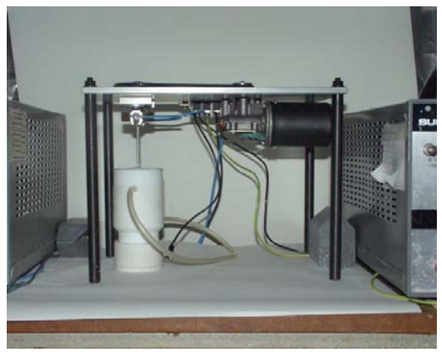
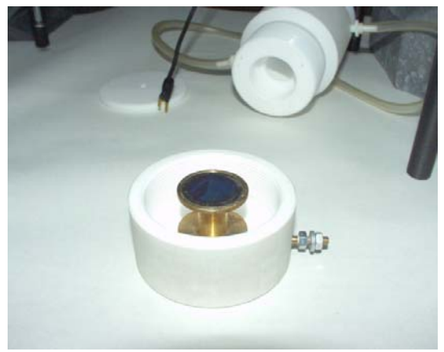


Fig. 2 Diagram of separation of U and Pu from solutions of spent nuclear fuel.

3.The preparation of the samples for alpha spectrometry is made using an electro deposition cell made out of Teflon, provided with a water mantle, to ensure a constant work temperature. The cathode is a stainless steel disk, with an exposed electro deposition surface of about 3.14 cm^2(fig.3). For the confection of the anode a platinum wire with a diameter of 1 mm with was used, reshaped as a spiral with the diameter of 8 mm. This wire is installed above the cathode with the possibility of modifying the distance to the cathode and is rotated during the process of electro deposition, with about 12 rotations/minute. The rotation of the anode is necessary to obtain a layer that is as uniform as possible. For electrodeposition, an adjustable tension source of 0-40 V is used, in domain 0-2A.



a)



b)

Fig. 3

a) Ensemble body cell electro deposition

b) Platinum anode;stainless steel cathode and the cooling circuit

4. **The acquisition of the spectrums is made with an alpha spectrometry system** with two independent canals, composed of a vacuum pump, a vacuum chamber, 2 ORTEC TR – 021 – 300 -100 detectors, with ionic implant, positioned under the silicon surface, with an active surface of 300 mm^2, guaranteed alpha resolution of 19 KeV(FWHM), multichannel analyzer made of a PC with a TRUMP 8 K(ORTEC) interface.

For the electro deposition of the U ,$(NH_4)_2SO_4$ 1M is used as an electrolyte and is adjusted at pH 3.5 with NH_4OH conc. The deposition current is 1.2 A, for 1 hour. For the electro deposition of Pu , Na_2SO_4 0,3M, at pH=2 is used as an electrolyte. The deposition current is 1A, for 1 hour.

III. EXPERIMENTAL RESULTS.

The calibration in energy of the alpha spectrometric chain is performed using laboratory standard sources of ^{230}Th, , ^{233}U, ^{244}Cm. The alpha spectrums of the ^{230}Th , ^{233}U, ^{244}Cm sources are presented in fig. 4-6. In table I the nuclear characteristics of the radio nuclides used for the calibration of the alpha system in energy and of the alpha emitting radio nuclides which can be found in the spent fuel, are presented.

Table I. The list of alpha emitting radio nuclides and their nuclear characteristics

Radionuclide	$T_{1/2}$ (years)	E_α (MeV)	Intensity (%)
Th-230	7.7 E+4	4.621 4.6875	23.40 76.30
U-233	1.592 E+5	4.7835 4.8242	13.20 84.40
Cm-244	18,11	5.7628 5.805	23.60 76.40
U-238	4,47E+09	4.147 4.196	23.00 77.00
U-234	2,445E+5	4.7237 4.7758	27.40 72.40
U-235	7,038E+08	4.3640 4.3960	11.00 55.00
Pu-239	2.4131E+4	5.1429 5.1554	15.10 73.30
Pu-240	6.569E+3	5.1234 5.1683	26.39 73.50
Pu-238	8.775E+1	5.4565 5.4992	28.30 71.60

Fig.4. The alpha spectrum of ^{230}Th and the diagram of disintegration

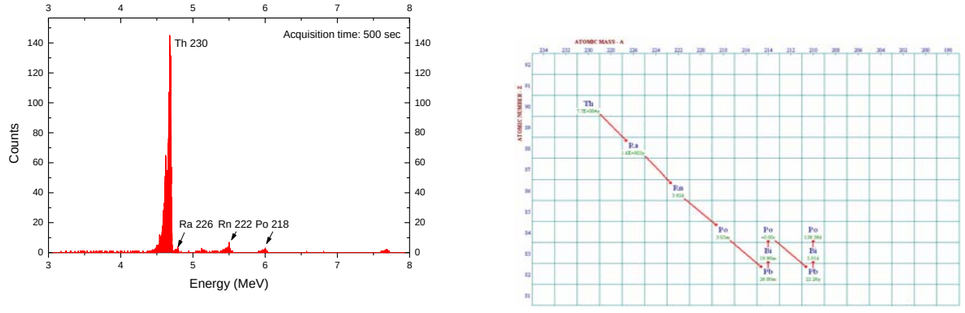


Fig.5. The alpha spectrum of ^{233}U and the diagram of desintegration

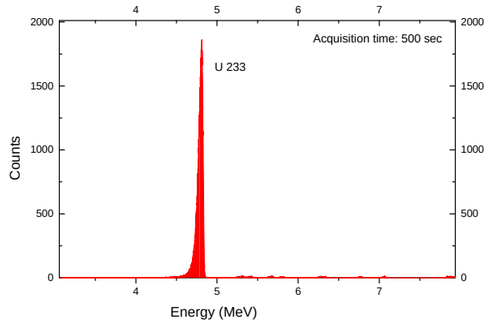
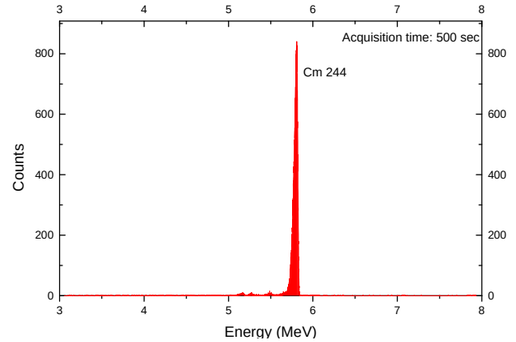
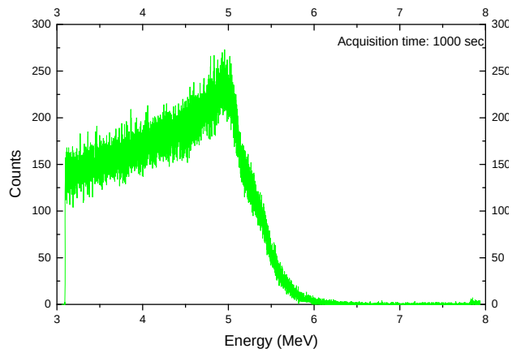


Fig.6. The alpha spectrum of ^{244} Cm and the disintegration diagram



To mark out the necessity of the separation of the elements so that they can be measured by alpha spectrometry, in fig. 7 the spectrum of the solution sample of spent fuel that contains the alpha emitting elements in the mixture.

Fig. 7. The alpha spectrum of the solution of spent fuel, without the chemical separation



For the preparation of the measurement source, from the spent fuel, a volume of solution of 100 µl that contains approx. 100 µg fuel is deposited on an alpha spectrometry disk by direct evaporation. As it results from the acquisitioned spectrum, a specific alpha emitter cannot be identified, but only the fact that in the source there are alpha emitters in the mixture.

In fig.8 and fig. 9 the alpha spectrums of U and Pu are presented, after the applying of the methodology of separation described above, applied on nuclear spent fuel samples.

Fig. 8 Alpha Spectrum of U isotopes

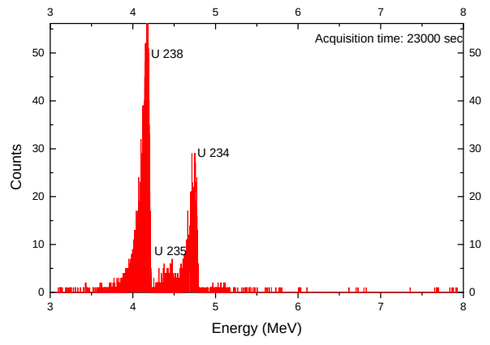
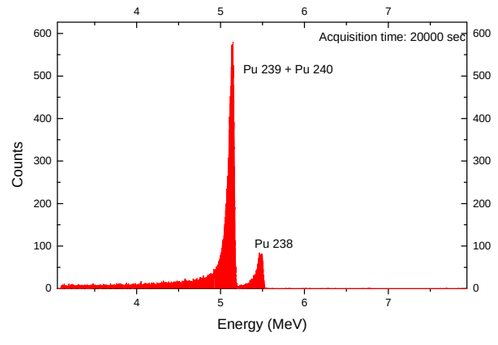


Fig. 9 Alpha Spectrum of Pu isotopes



IV. CONCLUSIONS

By applying the separation methodology of alpha emitters and with the help of the measurement technique by alpha spectrometry, the alpha emitting components of the spent nuclear fuel solution(like U, Pu, etc.) can be identified

The method can also be used for the determination of the alpha emitters concentration, if tracers(^{232}U, for the determination of U isotopes and ^{242}Pu, for the determination of Pu isotopes) are added at the samples that have to be analyzed. These are added in known amounts(activities), before the phase in which the elements are separated between them and they are measured in the final phase, to measure the chemical yields of separation of the elements which have to be analyzed, yields that will apply to each alpha emitter.

V.BIBLIOGRAPHY

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