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PLUTONIUM EMPLOYING RESIN BEAD TECHNIQUE

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PLUTONIUM 240

PLUTONIUM 241

URANIUM 234

URANIUM 235

URANIUM 236 °.

URANIUM 238

ON-LINE SYSTEMS

SPENT FUELS

SOLUTIONS

PLUTONIUM 242

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ABSTRACT

Sequential mass spectrometric analysis of uranium and plutonium employing anion exchange resin bead technique is reported using a high sensitive single stage magnetic analyser instrument, the routinely employed rhenium double filament assembly and 0.5M HNO₃ as a wetting agent for loading the resin beads. A precision of better than 0.3% (2σ) is obtained on the isotopic ratio measurements. However, extreme care has to be exercised to carry the resin bead experiments under ultra clean conditions so as to avoid pick up of contamination.

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1. INTRODUCTION

The determination of isotopic composition of uranium and plutonium in the dissolver solution of spent fuel is normally carried out by chemically separating them from fission products. Further uranium and plutonium are separated from each other using anion exchange procedure before the mass spectrometric analysis. In view of high radioactivity, very small amounts of dissolver solution samples containing plutonium only at microgram levels, are handled. The need to have a sequential analysis of very small amounts of uranium and plutonium (in sub ppm amounts) from a single loading of dissolver solution of the spent fuel has been recognized by the nuclear community as it does away with the tedious separation procedures. Mass spectrometric analysis of uranium and plutonium from a direct loading of the dissolver solution was reported in literature⁽¹⁾, but in that case isobaric interference at mass number ^{241}Pu due to ^{241}Am cannot be ruled out. Further, direct loading of the dissolver solution is troublesome due to the concentration of the salts and fission products loaded with uranium and plutonium. Of late, sequential

determination of these elements from a single anion exchange resin bead has attracted investigators. An interlaboratory analysis program conducted by NBS⁽²⁾ for isotopic ratio measurements of nanogram quantities of uranium and plutonium on resin beads brought out the potential of this technique for determining U and Pu in the dissolver solution. The advantages of this technique are:

(i) Small sample size (nanogram amounts of U and Pu) may be handled and large number of samples can be shipped without heavy shielding and also minimising the radiation exposure to the personnel.

(ii) Ion exchange procedure can be avoided.

(iii) Contamination of the instrument with fission products is eliminated.

(iv) Americium and curium are not absorbed. Isobaric interferences at Pu mass numbers do not exist.

The work reported so far in the literature⁽³⁾ has been carried out using single filament assembly, collodion and other gluing agents for loading and fixing the resin bead and ion counting systems in specially designed mass spectrometers⁽³⁻⁶⁾ with two stage tandem magnetic analysers to enhance the abundance sensitivity. The present work was undertaken with a view to investigating the feasibility of utilising a high sensitive single stage magnetic analyser mass spectrometer and secondary electron multiplier detection system for analysing U and Pu from the resin bead. Routinely employed rhenium double filament assembly was used in the present investigations. This has a definite advantage over the single filament assembly as the

sample filament temperature as well as ionisation filament temperature can be independently controlled.

A summary of the work carried out was presented at the second National Symposium on Mass Spectrometry⁽⁷⁾. This report gives the details of the work carried out and puts forth the present status of the resin bead technique.

2. EXPERIMENTAL

2.1 Instrument

A thermal ionisation mass spectrometer model MAT-261(1980) was employed. It is a single focusing, magnetic sector analyser mass spectrometer. The mass spectrometer uses a 90° magnetic sector field with a mean radius of 23 cm. and 26.5° ion entrance and exit angle. This ion optical system has a mass dispersion which corresponds to a 46 cm. radius for a conventional magnetic sector field and it produces stigmating focusing. With this type of focusing, the ion beam coming out of the analyser is focused in the Z-direction (in the direction of the magnetic field). The resolution (10% valley definition) of the instrument measured between mass numbers 235 and 238 and with main and collector slit widths at 0.2mm and 0.6mm respectively is 450. The abundance sensitivity is about $2 \cdot 10^{-6}$ measured at mass 237. Thirteen samples loaded on a turret can be introduced at a time into the ion source. There is a provision in the ion source to preheat two samples while the third one is being analysed. Preheating is required to control the sample on the filament so as to get controlled evaporation during the analysis. Both faraday cup and

electron multiplier detectors are provided for ion detection and measurement. Both the detectors are connected to extremely linear voltage to frequency converters leading to high sensitivity in ion detection.

The instrument is completely automated and an on-line HP-9835A desk top computer is provided for this purpose. Manual intervention is required only upto the stage of inserting the loaded samples into the ion source. The computer does all the operations starting from bringing the desired sample into the ion source position, heating the ionisation and sample filaments at a predefined rate, focusing of the desired ion signals for maximum intensity, correction for the drift in the ion beam intensities, computation of the isotopic ratios and printing of the results. The on-line computer increases the sample throughput, relieves the operator from the manual labour of accounting the mass spectra for the isotopic ratios and gives the results with a better precision and accuracy.

It may be mentioned that the factors responsible for the accuracy in the isotopic ratio measurements are taken care of in the following way:

The results obtained from the on-line computer, which carries out all the steps in the measurement of isotopic ratios according to a predefined experiment under reproducible conditions, are free from any operator bias.

The electromagnet is driven by an extremely stable, hall probe controlled power supply and is under computer control. The magnetic field is stable to better than 0.1% at uranium mass numbers. The detectors are highly sensitive and are connected to

linear voltage to frequency converters .Hence low abundant isotopes can also be measured with high sensitivity and reproducibility.

Considering these factors and the high sensitivity of the instrument, it is possible to get a precision of better than 0.05% and accuracy better than 0.1% at 1% abundance in the mass spectrometric measurements compared to about 1% obtained with the instruments available in 70's. Before proceeding with the experiments, the overall linearity of the ion current measuring system was checked by measuring the isotopic ratios over a wide range of intensities in the various isotopic reference materials of uranium and plutonium.

2.2 Selection of Ion Exchange Resin

Strong adsorption behaviour of Pu on anion exchange resins in 8M HNO₃ ⁽⁸⁾ makes the anion exchange resin DOWEX 1 an ideal choice for the resin bead experiment. In this acid concentration, Pu and U have distribution coefficients of 10⁴ and 10 respectively. This large difference in distribution coefficients coupled with the fact that the U/Pu ratios in the dissolver solution are normally about 200 leads to a desirable loading of Pu and U on the resin for their sequential analysis. Accordingly DOWEX 1x8 100-200 mesh resin was converted to nitrate form and equilibrated with 8M HNO₃. The 100-200 mesh beads were found suitable for picking up and subsequent loading on the sample filament of the rhenium double filament assembly.

2.3 Samples and Resin Bead Loading

Three types of samples were taken for the resin bead experiment

(a) A mixture of isotopic reference materials of plutonium SRM-947 and uranium SRM U-010

(b) A mixture of isotopic reference materials of plutonium SRM-947 and uranium SRM U-500

(c) Dissolver solution of spent fuel having a burn-up of about 10,000 MWD/TU

An U/Pu ratio of about 200 was maintained. About 5-10 preequilibrated resin beads, after viewing through a microscope to ensure same size, were added to 0.2 ml of samples taken in centrifuge tubes. The synthetic samples of uranium and plutonium were prepared so as to have 40-60 ng of Pu and 8-10 μg of U per 0.2 ml of the solution. The resin beads were allowed to equilibrate for about 48 hours which was enough time for the beads to adsorb both U and Pu in sufficient amounts. A single resin bead was placed over a planchette and was counted for the determination of α -activity. It was found that about 10 ng of plutonium were present on a single resin bead.

A single resin bead was picked up with the help of a needle and transferred on to the filament. (The resin bead is held at the tip of the needle by surface tension). In the absence of any fixing/gluing agent, the bead was observed to fly off during the heating of the filament. In order to retain the bead on the filament a drop of 0.5 M HNO_3 as wetting agent was placed on the filament. As the purpose of using the organic reagent such as collodion is only to glue the resin bead on the filament during

the mass spectrometric analysis so that the bead does not fly away, it was thought worthwhile to use 0.5 M HNO₃ instead of the organic reagent because in that case Pu and U are desorbed from the resin bead on to the filament and mass spectrometric analysis can be carried out even if the bead is not on the filament during the course of the analysis. Further avoiding the organic reagents helps in attaining and maintaining the ion source vacuum during the mass spectrometric analysis. Subsequently the resin bead was placed on the drop of nitric acid. The filament was then heated using the programmable heating unit. All the resin beads were loaded under exactly similar loading conditions.

2.4 Mass Spectrometric Determination

The experiments for uranium and plutonium isotopic analysis were separately defined and stored in the memory of the computer. Before carrying out the mass spectrometric analysis of U and Pu on the resin beads, the instrument was calibrated with respect to uranium and plutonium mass numbers and the corresponding magnetic fields by analysing directly isotopic reference materials of uranium(U-010) and plutonium(SRM-947).

During the analysis of the sample from the resin bead, the temperature of the ionisation filament was slowly raised to 5.6 A continuously monitoring the ¹⁸⁷Re⁺ signal. When the strength of the signal was about 0.3V the temperature of the sample filament was raised slowly. Measurement of isotopic ratios of uranium were carried out by raising the sample filament temperature to 1 A. At this temperature plutonium peaks were not observed during the entire course of analysis of uranium as monitored by program. The

sample filament temperature was then again slowly raised to about 2 A for the isotopic analysis of plutonium. Uranium peaks were found decreasing fast at this temperature. Secondary electron multiplier was used as detector for isotopic ratio measurements carried out in peak switching mode. After collection and processing of the data the isotopic ratios were directly obtained on the printer.

Each sequential analysis consisted of 2-3 blocks of 10 scans each for uranium and plutonium. Six individual loadings of the resin beads from each of the synthetic mixtures as well as from the dissolver solution were carried out.

3. RESULTS AND DISCUSSION

Table 1 gives the atom ratios of the synthetic mixtures analysed using resin bead technique. The precision quoted is at 95% confidence level (2 σ). Also shown in the table are the certified atom ratios of uranium and plutonium of the isotopic reference materials used in the present investigations. The plutonium isotopic composition was corrected for the ^{241}Pu decay upto the time of analysis. A half life of 14.4 y was used for ^{241}Pu to correct for its decay. It is seen from the table that all the isotopic ratios are within the 95% confidence limits of the measurements.

The sequential analysis of uranium and plutonium from the single resin bead has been extended to the dissolver solution of the spent fuel with a burn-up of 10,000 MWD/TU. Table 2 gives the results of this exercise. The RSD quoted here is at 95% (2 σ) confidence level. For comparison purpose, the table also gives the

results obtained after chemically separating uranium and plutonium using anion exchange separation procedure. The agreement in the isotopic ratios of U and Pu obtained using the resin bead technique as well as the conventional procedure is very good and the isotopic ratio of $^{241}\text{Pu}/^{239}\text{Pu}$ clearly shows the complete decontamination from ^{241}Am .

4. CONCLUSIONS

Results from the foregoing experiments indicate that reliable isotopic analysis of sub microgram amounts of uranium and plutonium in the dissolver solution of spent fuel can be carried out with minimal chemistry and sample handling. The simplicity of the method in utilising a high sensitive single stage magnetic analyser instruments and employing the routinely used rhenium double filament assembly for loading the resin bead samples with a drop of 0.5 M HNO_3 as wetting agent and its easy adaptability in the case of dissolver solutions, makes it an attractive alternative to the conventional methods of ion exchange separation and purification prior to the mass spectrometric analysis particularly when large number of dissolver solution samples are to be transported for mass spectrometric determination. However extreme care has to be exercised to carry out the resin bead experiments under ultra clean conditions so as to avoid the pick up of contamination.

5. CURRENT STATUS

National Bureau of Standards, USA conducted an interlaboratory analysis program (round robin)⁽²⁾ for evaluating the resin bead technique. Nanogram amounts of isotopic reference materials (SRM's) and unknown samples were loaded onto the anion exchange resin beads and transported to eleven participating laboratories for measurements. Typical accuracies and precisions achieved in the measurement of major isotopic ratios were 0.3%. It is concluded that the isotopic fractionation is a major source of imprecision while the degree to which isotopic fractionation can be calibrated limits the measurement accuracy particularly when nanogram amounts are analysed. Internal normalization technique employed to evaluate isotopic fractionation demonstrated the improvements in both precision and accuracy. But this could be done only in the case of uranium as certified isotopic reference materials are available on an absolute basis. The necessity of having Pu isotopic reference materials on an absolute basis for the calibration of fractionation for Pu was pointed out.

6. ACKNOWLEDGEMENTS

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Table 1 Isotopic ratios determined by using resin bead technique

Sample	Uranium			Plutonium		
	234/238	235/238	236/238	240/239	241/239	242/239
Synthetic mixture	0.000058 ±0.000006	0.01013 ±0.000010	0.000080 ±0.000014	0.2416 ±0.0020	0.0370 ±0.0002	0.0155 ±0.0004
SRM Pu-947+ SRM U-010	{0.000055}	{0.01014}	{0.000070}	{0.24159}	{0.0370} [*]	{0.0156}
Synthetic mixture	0.01055 ±0.00002	0.9997 ±0.0030	0.00152 ±0.00002	0.2405 ±0.0008	0.0372 ±0.00004	0.0155 ±0.0002
SRM Pu-947+ SRM U-500	{0.01042}	{0.9997}	{0.00152}	{0.24159}	{0.0370} [*]	{0.0156}

Table 2 Isotopic ratios determined in the dissolver solution by using resin bead technique

Sample	Uranium			Plutonium		
	234/238	235/238	236/238	240/239	241/239	242/239
Dissolver solution (burn-up=10,000 MWD/TU)	0.000060 ±0.000006	0.00558 ±0.00004	0.00157 ±0.00006	0.4140 ±0.0016	0.0886 ±0.0008	0.0411 ±0.0006
	{0.000061} {±0.000006}	{0.00560} {±0.00004}	{0.00156} {±0.00004}	{0.4145} {±0.0010}	{0.0888} {±0.0004}	{0.0411} {±0.0002}

{ } = Certified values { } = Determined by routine procedures

* ²⁴¹Pu corrected for β decay
the value is as on 16.11.1981

12

