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I. Thermal Emission Resin Bead Mass Spectrometric Two-Filament Arrangement Evaluation-A.82

II. The Rapid Bulk Resin Bead Method of Sample Preparation for Mass Analysis of Plutonium and Uranium in Spent Reactor Fuel-A.56

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Analytical Chemistry Division

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Introduction

Safeguards has a need for better precision in mass spectrometric measurements of isotopic ratios on nanogram-sized samples. ISPO Task A.82 was initiated to seek means of improving precision through investigation of a two-filament arrangement fitted to an existing mass spectrometer; other possibilities were also investigated.

Results and Discussion

After substantial initial literature work and discussion, we decided that the multi-filament design most easily duplicated in our laboratory was that used by Varian on its MAT 260 instrument. This arrangement consists of two parallel Re filaments about 1 mm apart. One serves as the ionizer and is operated at about 2100°C; the second is the sample filament for evaporation.

We mounted a fixed Re ionizer on the case plate of our source and positioned on the optical axis. Sample filaments were made of flat Re ribbon; these were mounted on a sample wheel and positioned to provide the desired spacing with respect to the ionizer. These filaments were 0.0025 x 0.75 cm. A series of NBS 500 samples was run; these were loaded as solutions whose area of contact with the filament was confined to the cross-sectional area of a microliter drop. For mass spectrometric analysis, we followed procedures developed at Varian, WAK, and elsewhere.

Of 17 measurements, the precision of the 235/238 ratio (NBS-500) was $\pm$0.37%. It required a minimum of 100 ng of sample to obtain an ion beam of the requisite stability.

A number of resin-bead-loaded samples were analyzed. Fully loaded beads (300 ng U) gave long-lived, stable ion beams at evaporation temperatures substantially higher than those required for solution loadings. Beads prepared in our conventional manner (3 ng U) gave ample signal for analysis, but were plagued by excessive fractionation. In neither case were the results better than those obtained from solution loadings.

The external precision of all these analyses is somewhat worse than those obtained routinely on normal resin-bead loaded samples mounted on single filaments. There was therefore no reason to pursue the investigation further.

Concurrent investigation of other aspects of this kind of mass spectrometry led to more promising results. Improved beam stability and reduction in fractionation were obtained by adding a layer of a mixture of rhenium and sucrose to the filament after loading the sample (on a resin bead). Work has not yet progressed far enough to allow definition of a protocol applicable to routine laboratory analyses; this is the goal of the project, which is continuing.

The enhanced beam stability achieved through this technique aided in designing an improved voltage divider and ion source with circular symmetry. This source provides a stabler beam and somewhat better precision than the old one.

Conclusions and Recommendations

Although our two-filament assembly is admittedly somewhat crude in comparison to Varian's, it is good enough to establish that designing or fabricating a multi-filament source at ORNL would require a major investment in time and money. Our conclusion is that acquisition of a "turret" source from a commercial vendor is a more cost-effective solution to the problem. Such a unit is available from VG-Micromass for about $60,000. We would have to modify it so it would mount on our instrument; this would involve, at the minimum, fabrication of several adaptors for making the required high vacuum connections. Depending on the details of the configuration of the unit, it might be necessary to build a new flight tube, pump-out port, and other components.

The new source and high-voltage divider panel that ORNL has developed offer advantages over the previous designs. The IAEA may wish to consider acquisition of one or both of these. The combination of these instrument modifications and the introduction of a rhenium-carbon layer over the resin bead on the filament has led to improvement in precision by about a factor of two. The Re-C overcoating is still somewhat cumbersome to implement, and more work needs to be done before it is ready for routine laboratory use. Approaches such as these, rather than development of a multi-filament source, offer an attractive alternative to the IAEA for improving precision.

II. The Rapid Bulk Resin Bead Method of Sample Preparation for Mass Analysis of Plutonium and Uranium in Spent Reactor Fuels - A.56

1.0 SCOPE

1.1 This method outlines a procedure for the separation of plutonium and uranium from fission products and other actinides created in the fuel cycle, followed by mass spectrometric analysis. Basic anion beads in the nitrate form are used to adsorb plutonium and uranium from solutions of spent reactor fuel adjusted to 7-8 M in HNO_3. After adsorption of these actinides on a small amount of resin beads, a single bead is loaded onto a rhenium filament and the elements isotopically analyzed in a mass spectrometer. A pulse counting detection system is required because of the small amount of sample present (1-3 ng). Concentrations of the two elements are measured through the isotope dilution technique using an isotopically enriched spike: ^{233}U or ^{236}U and ^{242}Pu or ^{244}Pu.

2.0 SIGNIFICANCE AND USE

2.1 Irradiated power reactor fuel is analyzed by this method.[1,2] A typical burnup of 30,000 to 35,000 MWd/ton will produce a plutonium concentration about 1% that of uranium. Input solutions typically contain about 230 mg U/g and 2.3 mg Pu/g of solution. The method is applicable to solutions from any source whose U/Pu ratio is in the range of 10 to 500.

3.0 SAMPLING

3.1 The amount of original input solution taken for isotopic dilution analysis must be chosen through consideration of three primary factors: 1) the permissible level of radioactivity which can be handled; 2) the cost and availability of the isotopic spikes; and 3) the desired accuracy and precision of the isotopic dilution measurements. For this type of analysis, the optimum ratio of the spike isotope to the most abundant sample isotope is 1. This ratio should be the goal for the isotope dilution analysis of samples not specified in this procedure.

For input solutions with uranium concentrations of about 230 mg/g, a dilution of about 400 times is the maximum that can be made and yield results of the desired precision. A dilution factor of 400 will yield a solution whose uranium concentration is about 0.6 mg/g; thus, a spike containing this amount of the spike isotope is required. Since the plutonium concentration will usually be about 1% of the uranium, the plutonium spike should be about 1% of the uranium spike multiplied by the atom fraction of the most abundant plutonium isotope in the sample.

3.2 The quantity of uranium in contact with the resin beads must be carefully adjusted to ensure the adsorption of appropriate amounts of uranium and plutonium and thus allow isotopic analysis of the two elements from a single bead. This is achieved by adjusting the uranium concentration in the solution so that there is 1-2 μg of this element for each bead to be exposed. If 1000 beads are to be loaded with the uranium and plutonium, a solution containing 1-2 mg U should be put in contact with them. The amount of plutonium in solution will then be about 1% of the uranium or 10-20 μg.

3.3 For isotopic dilution measurements to be accurate, equilibrium between sample and spike must be established. This presents little problem for uranium, but plutonium requires careful adjustment of the valence state and destruction of polymers and/or complexes on aged solutions. Several methods have been developed to accomplish sample-spike equilibration, and the ones described herein are not the only valid procedures that can be used in this application.

3.3.1 For fresh dissolver solutions, equilibration is obtained on spiked aliquants by reduction with Fe(II) and sulfamic acid followed by oxidation with $NaNO_2$. This method has been found to be >99.9% effective.[3].

3.3.2 A second method is used when analyzing aged dissolver solutions or other sample types containing molecular species. Destruction of polymers and complexes is achieved by evaporating the spiked aliquants to near dryness with $HClO_4$ and HF. Repeat Step 3.3.1.

4.0 CRITICAL FACTORS IN SAMPLE PREPARATION

4.1 Extreme care must be taken to avoid contamination of the sample with uranium either from the environment or from other samples. This involves using triple distilled water and redistilled HNO_3; distillations are carried out in a quartz still. Containers must be leached in 1:1 HNO_3:H_2O before use. A clean, preferably isolated, laboratory hood should be set aside for resin bead manipulations.

4.2 Sampling and aliquanting of input solutions and spikes should be done on a weight basis.

4.3 Calibration of the spikes must be done accurately; spikes are calibrated using certified reference materials of the approximate isotopic compositions expected in the samples.

4.4 Sample and spike isotopes must be in isotopic equilibrium before introducing resin beads to the solutions.

4.5 Unspiked and spiked aliquants must be prepared to obtain both isotopic composition and concentration unless pure ^{233}U and ^{244}Pu spikes are used and are absent in the samples.

5.0 APPARATUS

5.1 Glassware and polyethylene bottles. All glassware should be boiled in 1:1 HNO_3, rinsed with triple-distilled H_2O, and stored until used. Polyethylene bottles and other plastic apparatus should be rinsed well in 1:1 HNO_3 and distilled H_2O before use.

5.2 Analytical balances: for cell, Torbal Model EA-1ER,* 160 g capacity and <0.1 mg sensitivity; for laboratory, Ainsworth Right-A-Weigh single-pan,* 199.9 g capacity and 0.1 mg sensitivity or equivalent.

5.3 Microscopes: 2 low-powered are required.

5.4 Vortex mixer, 2-tube: Cat. No. S8230-1, Scientific Products Catalog.*

*These items have been found to be satisfactory.

5.5 Polypropylene Econo-Columns, 0.7 x 4.0 cm, Cat. No. 731-1110,* Bio-Rad Laboratories, 32nd and Griffin Aves., Richmond, CA 94804.

5.6 15 ml plastic bottles with caps.

5.7 30 ml plastic bottles, without caps.

5.8 #7 cork stoppers.

5.9 Plastic funnels, 11 cm, Scientific Products Catalog.*

5.10 Polyethylene disposable pipets, Cat. No. 6220, Preiser Scientific Catalog.*

5.11 Polyethylene bottles, 100 ml capacity, with polyethylene caps.

6.0 REAGENTS

6.1 Nitric acid, conc. ACS reagent grade, triple distilled.

6.1.1 Nitric acid, ~8 M. Dilute conc. acid with equal amount of dist. H_2O.

6.1.2 Nitric acid, ~5 M. Dilute 1 part conc. acid with 2 parts dist. H_2O.

6.2 Anion resin, Dowex 1 x 2, 50-100 mesh, nitrate form.

6.3 Mixed spike solutions; these must be well calibrated, and the aliquots for analysis should contain ~0.8 mg ^{233}U and 0.005 mg ^{242}Pu on weight basis.

6.4 0.25 M Fe(II) - 1 M NH_2SO_3H (sulfamic acid) mixture; in a 100 ml volumetric flask, dissolve 7 g of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in about 50 ml of distilled water containing 1 ml of conc. H_2SO_4, and to the same flask add 9.7 g sulfamic acid. Dilute to volume with distilled water.

*These items have been found to be satisfactory.

6.5 3 M $NaNO_2$ - dissolve 2.07 g in 10 ml distilled water; make fresh daily before using.

7.0 SPIKED SAMPLE PREPARATION PROCEDURE

7.1 Operations performed outside the analytical hot cell.

7.1.1 Label two (2) 15 ml polyethylene bottles for each sample. One is used first to obtain the weights of the mixed spike and then the weight of the sample aliquant; the second bottle is used for subsequent containment of the equilibrated sample solution and resin beads.

7.1.2 Obtain a tare weight on the bottle intended to contain sample plus spike; include the cap in the weighing.

7.1.3 Add mixed ^{233}U and ^{242}Pu spikes. Reweigh and record spike weight to nearest 0.1 mg.

7.1.4 Label another bottle Fe(II) - NH_3SO_3; add about 1 ml of this solution.

7.1.5 Label another bottle $NaNO_2$; add about 1 ml of this solution.

7.1.6 Add approximately 1000 beads to the second bottle intended to contain the equilibrated spike-sample mixture plus beads (Step 7.1.1). Section 9 outlines a procedure for delivering approximately 1000 beads to the bottle.

7.1.7 One funnel for each sample, to be used to transfer the sample to the bottle containing the resin beads.

7.1.8 One plastic pipet for each sample, to be used to add the sample aliquant to the bottle containing the mixed spike.

7.1.9 One bottle containing approximately 10 ml of 8 M HNO_3 per sample.

7.1.10 For each sample preparation, spiked and unspiked, take a polypropylene Econo-Column and break off the tip. Place the column in one of the two 30-ml plastic bottles needed for this operation. Very gently insert a #7 cork stopper into the top of the column. This permits its later removal with the manipulator in the cell (Step 7.2.11). Two bottles are needed--one to hold the column and catch the filtered waste and the second to hold the column after preparation (Steps 7.2.15 - 7.2.18).

7.1.11 All the above items are entered into the analytical hot cell.

7.2 Operations performed in the analytical hot cell with manipulators.

7.2.1 Prepare a 150-200 fold dilution of the input solution. First obtain a tare weight for a 100 ml polyethylene bottle, add by pipet or medicine dropper ~0.5 ml of input solution to the bottle and reweigh, then dilute to ~100 ml with 5 M HNO_3 and reweigh to determine weight of diluted sample. Record weights of the input solution and the diluted sample to ±0.1 mg. Mix well by shaking.

7.2.2 Reweigh the bottle containing the spikes to ±0.1 mg. This will be the tare weight for the sample aliquant and should be the same as the recorded weight after spike addition (Step 7.1.3).

7.2.3 Add an aliquant of the diluted sample containing 1 mg of U using a plastic pipet, cap and weight to ±0.1 mg. Net weight equals the weight of sample aliquant added.

7.2.4 Dilute the spike and sample mixture to about 3 ml with distilled H_2O.

7.2.5 Add three (3) drops of Fe(II)-sulfamic solution and heat at 60°C for 20 minutes using a heat lamp.

7.2.6 Add six (6) drops of 3 M $NaNO_2$ and shake by hand with manipulator for about 2 minutes.

7.2.7 Add enough concentrated HNO_3 and distilled H_2O to bring the sample to approximately 8 M HNO_3 in a volume about 10 ml. (About 2 ml distilled H_2O + about 4.5 ml concentrated HNO_3).

7.2.8 With the aid of a plastic funnel, pour the equilibrated sample into the bottle containing approximately 1000 anion beads and cap tightly.

7.2.9 Place on the Vortex mixer and agitate for 10 minutes at low setting. The beads are now ready to be separated from the solution.

7.2.10 Remove the cap from the bottle containing the beads and the 8 M HNO_3.

7.2.11 With one of the manipulators, gently remove the cork stopper and hold until ready to replace it.

7.2.12 With the other manipulator, put a clean funnel into the top of the filter column. Pour the solution and beads while swirling into the column.

7.2.13 After the solution has drained, wash the beads with 1 ml of 8 M HNO_3.

7.2.14 Carefully remove the column and replace the cork stopper. Press stopper in firmly.

7.2.15 Pick up the column by grasping the cork stopper and transfer it to the clean 30 ml bottle.

7.2.16 Remove and discard the cork stopper.

7.2.17 Transfer the bottle containing the column with beads out of the cell.

7.2.18 Without handling the bottle, remove the column with plastic gloves.

7.2.19 Touch the tip of the column with a clean tissue to remove any remaining liquid; discard the tissue into radioactive waste container.

7.2.20 Put the original cap on the column and check for radiation and contamination on the outside; if any found, decontaminate.

7.2.21 Put the column inside two plastic bags for shipment to the Mass Spectrometry Laboratory.

8.0 UNSPIKED SAMPLE PREPARATION

8.1 Operations performed in the analytical hot cell with manipulators.

8.1.2 Add ~9 ml of 8 M HNO_3 to a clean, 15 ml polyethylene bottle containing 1000 anion resin beads previously prepared outside the hot cell as for spiked sample (Step 7.1.6).

8.1.3 Deliver an aliquant of the diluted sample containing 1-2 mg U using a pipet or medicine dropper to above bottle.

8.1.4 Follow the procedure given for spiked sample preparation by repeating Steps 7.2.9 through 7.2.21.

9.0 A TECHNIQUE DESIGNED TO DELIVER APPROXIMATELY 1000 RESIN BEADS

9.1. Preparation of resin bead stock mixture.

9.1.1 Using a 10 ml graduated, glass-stoppered centrifuge cone, add anion resin beads in the NO_3^- form to a volume of 4 ml.

9.1.2 Add triple distilled H_2O to cone to a total volume of 7 ml.

9.2 Bead delivery to sample container.

9.2.1 By hand, shake stoppered cone until beads are uniformly mixed and suspended in the water.

9.2.2 Without delay, remove stopper and withdraw a few drops of mixture into a medicine dropper (one that will deliver ∿20 drops per ml).

9.2.3 Quickly deliver one (1) drop of the resin bead-H_2O mixture into a 15 ml polyethylene sample bottle.

9.2.4 (Set aside for later addition of prepared sample solution for bead adsorption step using Vortex mixer.)

10.0 MASS SPECTROMETRIC PROCEDURE

10.1 The mass spectrometer required is described in ASTM Standard Test Method E267; the pulse-counting detection system mentioned in this method is necessary because of the small sample size.

10.2 Calibration of the instrument is accomplished through analysis of NBS certified isotopic standards loaded on resin beads. Details of the procedure are given in ASTM Standard Test Method E267.

10.3 Samples on resin beads are loaded on filaments by use of a stainless steel or tungsten needle.[4] This operation is facilitated by the use of 2 microscopes, one with 60-100X for transferring bead to needle and a second one 6-10X for transferring bead to filament. One bead is loaded per filament and constitutes one sample for the mass spectrometer.

10.4 Pu and U are analyzed sequentially from the same resin bead. Care must be taken to observe the time and temperature instructions to obtain the best data.

10.5 The filament is inserted in the mass spectrometer and pumped down to 4×10^{-6} Pa.

10.6 For analysis, the temperature is raised slowly until a pressure burst signals decomposition of the bead.

10.7 The temperature is slowly increased until Pu^+ ions are observed. Focus conditions are optimized.

10.8 The temperature is slowly increased until the intensity of the signal from the most abundant Pu ion (usually 239) reached 100,000 counts/sec; 1500°C (as read by an optical pyrometer) should not be exceeded to avoid excessive emission of $^{238}U^+$.

10.9 Pu data are accumulated according to Method E267.

10.10 At the end of Pu analysis, the temperature is slowly raised to burn off excess Pu. The 238/239 ratio is monitored, being careful not to damage the detector with excessive $^{239}Pu^+$ counting rates; count rates in excess of 2×10^6 counts sec^{-1} can damage the multiplier if allowed to fall on the first dynode for more than a few minutes. Do not burn off Pu for more than 15 minutes if at all possible.

10.11 When the signal at mass 238 is equal or less than that at mass 239, the temperature is increased until the count rate for the most abundant U isotope is 300-350,000 counts/sec. Recheck focus conditions.

10.12 Accumulate U data according to the procedure described in Method E267.

11.0 CALCULATIONAL PROCEDURES

11.1 The procedures necessary to process the data collected are described in ASTM Standard Test Method E267. Computer programs which are used at ORNL have been published.[5]

12.0 PRECISION AND ACCURACY

12.1 Precision. The precision of the measurement is dependent upon rigid control of all operating parameters and varies with the isotopic ratio.

Isotopic Ratio	Relative Standard Deviation, %
1	0.05 - 0.2
100	0.3 - 0.8
200	0.5 - 1.0
500	0.5 - 1.0
1000	1 - 2

Precisions quoted in the above table are derived from scanning all isotopes for equal lengths of time. The precision on ratios greater than one can be improved a factor of 2-5 by optimizing the scanning times of the minor isotopes.

12.2 Accuracy. The accuracy of an isotopic ratio measurement under ideal conditions will normally fall between 0.20 and 0.50 relative % for an isotopic ratio near unity.

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