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PART 1. RESIN BEAD MASS SPECTROMETRY

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PART 2. RESULTS OF A RESIN BEAD FIELD EXPERIMENT - TASTEX-J

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Part 1. Resin Bead Mass Spectrometry

Introduction and Background

One of the most difficult stages of the nuclear fuel cycle to sample is spent reactor fuel dissolver solutions. These solutions are highly radioactive, containing fission products and actinides, primarily uranium and plutonium. It is nevertheless essential that such materials be sampled for plutonium and uranium for process control and to establish material balances for safeguards purposes.

A technique of using anion resin beads selectively to adsorb plutonium and uranium from highly radioactive solutions for subsequent mass spectrometric analysis was developed at our laboratory in 1974.[1] The method involves the adsorption of both elements on Dowex-1 x 2 anion resin from 8 $\underline{M}$ HNO_3 solutions of the spent fuel. Equilibration of a diluted portion of the sample with a number of beads separates sufficient (several nanograms/bead) plutonium and uranium from the radioactive solution to permit sequential isotopic analysis of both elements from a single bead. The approach aimed at sequential plutonium and uranium analyses in spent fuels was and remains the principal purpose of the method. However, other applications to low-level analysis have been developed, e.g., alloys, waste streams, and environmental samples.

Many investigations of anion exchange resin separations of plutonium and uranium have been reported in the literature.[2-3] Figure 1 shows adsorption characteristics of elements of interest in nitric acid systems on anion resin. This was taken from the work of Buchanan and coworkers at Argonne National Laboratory.[2] As can be seen, plutonium and uranium exhibit adsorption maxima at about 8 $\underline{M}$ HNO_3 concentration. Approximately equal quantities of each element are absorbed as a result of the stronger affinity of the resin for plutonium, which is commonly about 1/100 the concentration of uranium in spent fuel dissolver solutions from uranium-fueled power reactors. Several nanograms of each element are adsorbed on each bead under these conditions. Note also that there is no adsorption of americium or curium, the elements which have isobaric interferences in plutonium analysis. This is important since ^{241}Am is always present from the beta decay of ^{241}Pu ($T_{1/2}$ = 14.35y), and ^{244}Cm would interfere if ^{244}Pu

were to be added as the spike for isotope dilution analysis.

The primary advantages of the method are: 1) beads are simple separations devices for isolating Pu and U from "hot" dissolver solutions, 2) the hazard and cost in shipping are greatly reduced in comparison to conventional samples, 3) beads permit analysis of both Pu and U from a single filament loading, 4) enhancement of the ion emission is achieved from the point source of the bead, and 5) Am and Cm interferences are eliminated in Pu isotopic analysis.

The Batch Resin Bead Method

In the original technique, about ten anion resin beads in the nitrate form were exposed to the diluted sample solution. The solution was adjusted to be 8 $\underline{M}$ HNO_3 and to have about 1 μg U per bead exposed. Up to 48 hours of static contact between beads and solution was required for adsorption of 1-3 ng Pu and U per bead to be achieved. Under these conditions, contamination was a problem at reprocessing facilities where high levels of plutonium and uranium are inevitable.

The batch technique addresses two weaknesses of the original static system: length of adsorption time for sample preparation and the possibility of cross-contamination due to the small amount of uranium (10 μg) involved. The new technique only requires ten minutes adsorption time to provide ∿1000 purified samples for mass spectrometry. Only a few are needed for analysis, but the system has been scaled up to use the same quantity of U (1 mg) that is used for typical solvent extraction preparations often employed in isotope dilution analysis. Thus, the solution is adjusted to have about 100 times more uranium than the static system, but the 1 μg U per bead exposure is maintained. For isotopic dilution work, the quantity of the spike is not considered for estimating the amount to be exposed per bead. The amount of Pu and U adsorbed versus exposure time has been determined; results are given in Table 1. Individual beads were chosen at random from a batch preparation and chemically oxidized with concentrated HNO_3; the plutonium and uranium were spiked with ^{242}Pu and ^{233}U and redissolved. Subsequent isotope dilution analysis gave the quantity of Pu and U per bead, which was then converted to a concentration of Pu and U per μm^3 of bead.

Table 1. Batch Resin Bead Adsorption Study

Time, min	Bead Diameter, µm	Bead Vol. x 10^{-6} µm^3	ng/bead U	ng/bead Pu	ng/µm^3 x 10^{-6} U	ng/µm^3 x 10^{-6} Pu	U/Pu
5	284	12.22	10.7	4.1	0.88	0.34	2.59
10	302	15.48	10.4	5.4	0.71	0.39	1.82
15	248	7.98	5.6	5.0	0.72	0.64	1.13
20	275	11.03	8.8	6.7	0.81	0.61	1.33
30	289	13.11	11.8	7.0	0.90	0.56	1.61
60	256	9.14	13.6	9.2	1.46	1.00	1.46

The above results are the averages for 2 determinations.

The 100-fold increase in the amount of uranium and plutonium in the sample solution should reduce the effect of contamination by the same factor. Successful transfer of the technique from a clean laboratory to a reprocessing facility was carried out in cooperation with the International Atomic Energy Agency and the Power Reactor and Nuclear Fuel Development Corporation (PNC) at Tokai-mura, Japan. Results of this work are described in the next section.

Part 2. Results of a Resin Bead Field Experiment - Tastex-J

Introduction

This part of the report will briefly summarize the results of field tests completed at the Power Reactor and Nuclear Fuel Development Corporation (PNC) reprocessing plant in Tokai-mura, Japan. It was carried out under the TASTEX program, subtask J, sponsored by the International Safeguards Program Office of the U.S.A. with the cooperation of The International Atomic Energy Agency (IAEA).

Field Tests at PNC

The first test was carried out on five spent fuel solutions, using the original small-sample resin bead method, with resin bead samples being prepared by PNC for analysis at ORNL and IAEA; dried residues for preparation of resin beads in the laboratory at both IAEA and ORNL were shipped. The preparation at PNC included spiking and valence adjustment using Fe(II)/nitrite.

The results of the first Tastex-J exercise indicated that the potential problem of failing to obtain chemical equilibration was not a significant factor. Instead, discrepancies were noted in the U concentration measurements which were ascribed to contamination of the samples. Since resin beads contain only nanogram amounts of U and Pu, and very small aliquots of diluted dissolver solutions containing 10 μg - 20 μg of U were used in the original technique, it is necessary to provide clean facilities for their handling. The isotopic measurements on the unspiked samples showed acceptable agreement.

A second test of the resin bead method has taken place as a follow-up to the first Tastex-J experiment. A new bead handling procedure was developed at ORNL and further training of PNC personnel carried out. This new "batch technique", described earlier, was designed to reduce the risk of contamination. It handles one hundred times more U in the final diluted sample which is exposed to a proportionately larger number of beads. A single spent fuel solution was sampled and five subsamples prepared (Figure 2). Each of these was spiked and subjected to the chemical equilibration procedure of Marsh, et al.[4], before bead preparation. Beads were prepared at PNC and distributed to IAEA and ORNL along with dried residues for conventional mass spectrometric analysis at IAEA. Parallel measurements were made at PNC using their normal measurement routines.

The results of all resin bead measurements and those of PNC are in excellent agreement. Shown in Table 2 are the results for the unspiked sample. The largest variation is observed in the ^{238}Pu analysis; otherwise, no large statistical differences are observed in the measurements.

Table 2. Comparison of Isotopic Results - TASTEX - J

	Uranium, wt. %			
Lab-Technique	234	235	236	238
PNC-Conv.	0.0191	1.094	0.375	98.512
SAL-Dried	0.0211	1.088	0.372	98.519
SAL-Beads	0.0206	1.090	0.370	98.519
ORNL-Beads	0.0201	1.096	0.372	98.511
MEAN	0.0202	1.092	0.372	98.515
SD	0.0009	0.004	0.002	0.004

	Plutonium, wt. %				
	238	239	240	241	242
PNC-Conv.	1.458	60.178	22.623	11.515	4.227
SAL-Dried	1.369	60.301	22.642	11.483	4.206
SAL-Beads	1.375	60.171	22.599	11.624	4.231
ORNL-Beads	1.366	60.232	22.635	11.529	4.239
MEAN	1.392	60.220	22.625	11.538	4.226
SD	0.044	0.060	0.019	0.061	0.014

Table 3 contains the comparison of the mean concentration results obtained for the five samples. The variation of the laboratory means are 0.33% for uranium and 0.47% for plutonium.

Table 3. Comparison of Concentration Results - TASTEX-J

Lab-Technique	U, Conc. g/l	Pu Conc. g/l
PNC-Conv	164.70	1.507
SAL-Dried	164.83	1.492
SAL-Beads	164.68	1.498
ORNL-Beads	163.95	1.492
MEAN	164.54	1.497
SD	0.53	0.007

This experiment is the culmination of years of experience with the resin bead technique, performed under actual field conditions. It proved that the resin bead technique meets the accuracies required for the verification of the accountability of spent fuel dissolver solutions and that it can successfully be applied in a reprocessing plant environment.

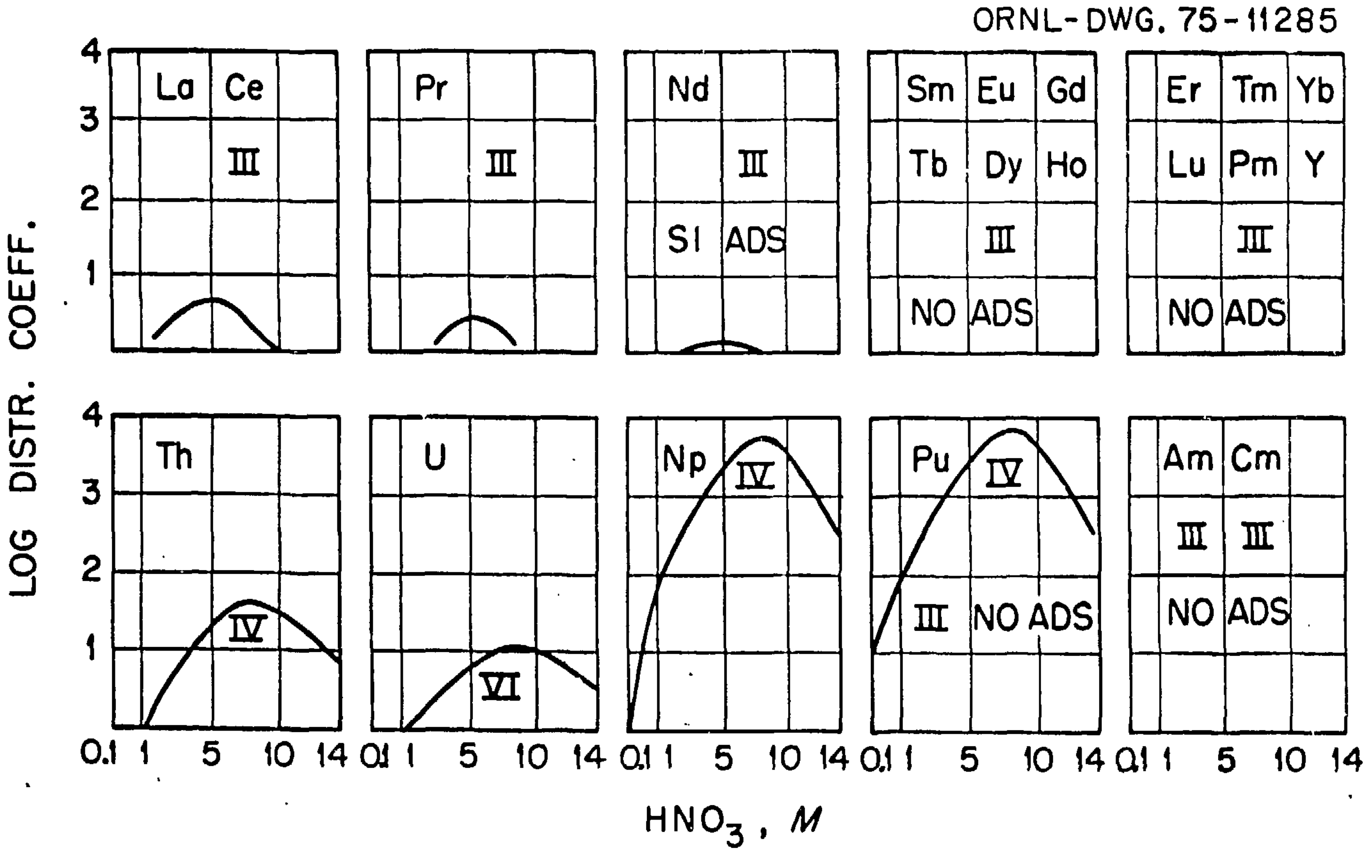
References:

1. R. L. Walker, R. E. Eby, C. A. Pritchard, and J. A. Carter, Anal. Letts. 1, 563 (1974).
2. R. F. Buchanan, J. P. Faris, K. A. Orlandini, and J. P. Hughes, U.S.A.E.C. Report TID-7560 (1928).
3. I. K. Kressin and G. R. Waterbury, Anal. Chem. 34, 1598 (1962).
4. S. F. Marsh, R. M. Abernathy, and J. E. Rein, Anal. Letts. 13(A17), 1487 (1980).

Figures:

1. Ionic Metal Adsorption by Strongly Basic Anion Exchange Resin (Dowex 1-X-2).
2. Outline of TASTEX-J Experiment.

Figure 1



IONIC METAL ADSORPTION BY STRONGLY BASIC ANION EXCHANGE RESIN (Dowex 1-X2)

Figure 2

OUTLINE OF TASTEX-J EXPERIMENT