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THE SEPARATION OF URANIUM
FROM ITS FISSION PRODUCTS BY
COMBINED ION EXCHANGE-SOLVENT EXTRACTION

by

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THE SEPARATION OF URANIUM
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INTRODUCTION

Until recently, separation and purification of inorganic ions by ion-exchange methods have been one-dimensional. By this is meant that in both cation and anion exchange systems, the separation of ions is usually achieved solely by the ion-exchange mechanism, and little use is made of the solvent or liquid-liquid extraction mechanisms potentially inherent in the system. A separation system involving both mechanisms would be likely to increase the efficiency of column exchange operations and would initiate a new realm of separation possibilities.

Such a two-dimensional system, known simply as combined ion exchange-solvent extraction (CIESE), has been proposed by Korkisch.¹ The research discussed in this report is involved with the application of the CIESE principle to the cation exchange separation of uranium from its fission products in a mixed aqueous-organic solvent system.

BACKGROUND

The systematic investigation of feasible methods for separating uranium from rare-earth and transition elements by cation exchange in organic solvent media began with the study of the hydrochloric acid-organic solvent media. Korkisch *et al.*² found that UO_2^{2+} (VI) is easily separated from Th(IV), Zr(IV), and Ce(III) in various solutions of 0.6M HCl and aliphatic alcohols, acetic acid, or tetrahydrofuran, but that separations from other transition metals are poor. The best results are obtained when the medium consists of 90% organic solvent and 10% 6M-12M HCl, the resultant acid concentration being 0.6M-1.2M HCl. Of particular interest is the 90% tetrahydrofuran (THF)-10% 12M HCl system in which Th(IV), Zr(IV), Ce(III), and Al(III) are adsorbed on the cation column, but in which all other elements tested pass through the column with the UO_2^{2+} (VI) and are thus inseparable from the uranyl ion.

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When the same organic solvents are used with nitric acid, there is a vast improvement in the separations.^{2,3} In all instances, of the elements tested, the 90% organic solvent-10% 12M HNO₃ media offer excellent separations from uranium, the only inseparable elements being Mo(VI), V(V), and Bi(III). Of the various mixed systems, the 90% THF-10% 12M HNO₃ medium offers the best results.

Since the THF-HNO₃ cation exchange separations worked so well, it was decided to test the feasibility of the same solvent system for the uranium-uranium fission-product separations. If proven worthwhile, the method will not only provide an excellent analytical purification procedure for uranium, but will also further corroborate the CIESE theory.

EXPERIMENTAL PROCEDURE

Reagents and Solutions

In all experiments, the strong acid cation exchange resin Dowex 50 (BioRad AG 50W, X8, 100-200 mesh, hydrogen-form) was used. For the column experiments, the necessary amount of this resin was soaked for at least 30 min in the THF-HNO₃ solution before being transferred to the column. For the determination of the distribution coefficients using the batch equilibrium method, the air-dried form of the resin was employed.

The THF-HNO₃ solvent mixture was prepared by mixing nine parts of tetrahydrofuran (THF) (Mallinkrodt A.R.) with one part of 12M HNO₃ (Baker Reagent), resulting in a 90% THF-10% 12M HNO₃ (v/v) solution (eluent solution). To ensure stability and freshness, these THF-HNO₃ solutions were made as needed.

The uranium carrier solution (stock solution) consisted of 10.55 gm of uranyl nitrate, UO₂(NO₃)₂ · 6H₂O (chemically pure), dissolved in 50 ml of the stock THF-HNO₃ solution. When made according to these specifications, the carrier solution has a uranium concentration of 100 mg/ml. For the qualitative analytical detection of the uranium in the preliminary experiments designed to determine the proper elution volume, the uranium-sensitive potassium ferrocyanide test was used. A 5% (w/v) solution of K₄[Fe(CN)₆] · 3H₂O (Merck Reagent) in distilled water was the reagent solution.

Standard and feed solutions of many radioactive tracer elements were made from laboratory HCl stock solutions of the elements. Depending on the activity of the solution, an amount of the HCl solution was treated with concentrated HNO₃, heated and evaporated to near dryness, and then diluted with 1-2 ml of water. In this manner, all elements were in the

necessary nitrate form. The standard and feed solutions for the column and batch experiments were then prepared by spiking various cold $\text{UO}_2^{2+}(\text{VI})$ -THF- HNO_3 or THF- HNO_3 solutions with 25-100 $\mu(\lambda)$ of a particular tracer.

Apparatus

A 1-gm resin column with a diameter of 0.5 cm was used for all column experiments.

Gamma-ray counting was performed by either the RIDL 200-channel analyzer, Model 40-7, which has a thallium-activated NaI crystal detector, or by the RIDL 400-channel, Model 34-12B, lithium-drifted germanium detector. For beta-particle analyses, an ANL 2π open-window β -counter was used.

Procedures

Proper Preparation of the Exchange Column

The two required features of an ion-exchange resin column are that the resin must be free of air pockets and that the proper drop rate is obtained. To prevent air pockets and bubbles from forming in the column, the empty column is first filled with the THF- HNO_3 solution. After a small cotton plug, presoaked in THF- HNO_3 , is packed into the bottom tip of the column to act as a resin bed support, the resin-THF- HNO_3 presoaked mixture is slowly added to the solution within the column with a transfer pipet. In this manner, the resin is constantly in the THF- HNO_3 solution, and by being allowed to merely settle to the bottom of the column, there is no chance for air-pocket formation. This feature is a necessity in column operations, for a moving air pocket can easily promote the formation of continuous air channels in the resin and destroy the needed solution flow pattern through the resin.

The drop rate preferred in this work is 0.25-0.50 ml/min. To obtain this rate, either of two methods can be used if the initial resin-column drop rate is too fast. Oftentimes, the mere packing of the resin column with a glass stirring rod "tightens" the resin enough to give the needed rate. If this is still not slow enough, a cotton plug may be set upon the top of the column and packed down accordingly. This slow drop rate is necessary to give the microquantities of elements used in the column runs adequate time to exchange with the resin.

Determination of the Proper THF- HNO_3 Elution Volume

To recover all the $\text{UO}_2^{2+}(\text{VI})$ fed onto the cation column, it is necessary to determine what volume of the THF- HNO_3 solution must be passed through the column (elution volume) after the $\text{UO}_2^{2+}(\text{VI})$ feed solution has

been introduced to the column. Qualitative-analysis and activity-counting methods are used for this elution volume determination.

For the qualitative-analysis method, 1 ml of the stock $\text{UO}_2^{2+}(\text{VI})$ solution was loaded onto the resin column. Fifty-drop ($\approx 1\text{-ml}$) effluent fractions were collected; the effluent solution consists of the $\text{UO}_2^{2+}(\text{VI})$ coming through the column along with the THF- HNO_3 eluent used to wash the column. Two drop rates (44 drops or $\approx 0.7\text{ ml/min}$, and 24 drops or $\approx 0.4\text{ ml/min}$) were tested; in each case, 30-40 ml were collected in the 50-drop fractions. After the fraction collection was complete, 1 ml of the $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution was added to each fraction. The appearance of a brown solution indicated the presence of uranium.

The determination of the elution volume using the activity method followed nearly the same procedure. The 1-ml feed solution this time consisted of 0.9 ml of THF- HNO_3 , $\approx 0.02\text{ ml}$ of the $\text{UO}_2^{2+}(\text{VI})$ carrier, and $\approx 0.08\text{ ml}$ of a U^{232} tracer used as a spike. Fifty-drop fractions were again collected at a 24-drop/min rate, and the γ -ray activity of each was counted on the NaI(Tl) detector.

The detailed results of these two methods are presented in the Results and Discussion section of this report. For now, it will suffice to mention that 20 ml of THF- HNO_3 was the elution volume finally settled upon.

Preliminary Separations of Individual Elements from Uranium

After the elution volume needed to completely recover the $\text{UO}_2^{2+}(\text{VI})$ was determined, the next step was to separate various elements in their tracer forms from the uranium feed solution. All these column operations followed the same pattern and were done to estimate their separation factors.

In each case, the feed solution was 1 ml of the $\text{UO}_2^{2+}(\text{VI})$ carrier, spiked with 20 λ of the tracer element. An identical standard solution was also prepared for later comparisons. After two 10-ml effluent samples were collected, the solutions were counted for a short time, the exact length of time depending upon the relative activity of the tracer. The ratio

$$\frac{\text{count rate in standard solution}}{\text{count rate in effluent solution}}$$

then indicates how well the element was adsorbed by the resin. A high ratio value indicates complete or nearly complete separation; the lower the value becomes, the greater is the amount of the element that passes through the column with the $\text{UO}_2^{2+}(\text{VI})$.

Batch Equilibrium Determinations of K_D

The most important preliminary experiment is that dealing with K_D value determinations for the possible fission-product elements. The distribution coefficient, K_D , is defined by Mayer and Tompkins⁴ as

$$K_D = \frac{\mu\text{g of element per gm of resin}}{\mu\text{g of element per ml of solution.}}$$

If the K_D is known for each element, it is possible to predict what fission products will be adsorbed on the resin column and separated from uranium. Determinations of this type will also supplement the K_D values previously determined by Korkisch *et al.*² for the 90% THF-10% 12M HNO_3 system and give a broader picture of the possible separation uses of this solvent system.

The batch equilibrium experiments were carried out in the following manner: To a suspension of 1 gm of resin in 20 ml of THF- HNO_3 was added 100 λ of the tracer. This mixture was then shaken to equilibrium for approximately 2 hr. Meanwhile, a standard solution consisting of 10 ml of THF- HNO_3 plus 50 λ of the tracer was prepared. After shaking, 10 ml of the equilibrated solution was withdrawn, and both it and the standard solution were counted. The K_D calculations are simplified by making sure that there is twice as much spike in the sample as there is in the standard, since, after shaking, the 10 ml withdrawn from the sample will then be equivalent to the 10-ml standard solution. The γ -active element solutions such as Co^{60} , Cs^{137} , etc., were put in polyethylene bottles and counted directly on the detectors, while the β -active elements such as Sr^{90} and Tc^{99} had to be treated with concentrated HCl and plated on tantalum discs before counting on the open-end β -counter.

In this manner, K_D values for about 20 elements were determined. For those elements of interest for which no isotope tracers were available, the K_D values were determined as accurately as possible from spectrographic analysis of experimental solutions. For Cr(III) and Cu(II), which formed deeply colored solutions in the THF- HNO_3 , the K_D values could be visually approximated during a column run.

Separation of Uranium from the Fission Products

After the K_D values are determined, the final step of the experiment becomes a simple column-exchange procedure. Identical standard and feed solutions of the actual fission products are converted to the nitrate form. The feed solution is passed through the resin bed, followed by elution with 20 ml of THF- HNO_3 . The effluent and standard solutions are then analyzed on the Ge(Li) detector. Since the detector is calibrated to corresponding energy values, it becomes a matter of identifying the peaks and determining which elements of the fission-product "pot" solution are separated from uranium on the cation exchange column.

RESULTS AND DISCUSSION

The first column run designed to determine the proper THF-HNO₃ elution volume was done at a ≈ 0.7 -ml/min drop rate. In light of later experiments, this flow rate proved to be too fast, as a positive ferrocyanide-uranium test was still being obtained in the 50-drop fractions after 30 ml of eluent had passed through the column.

For the U²³² tracer experiment, the drop rate was reduced to ≈ 0.4 ml/min. Figure 1 gives the results of the γ -activity analysis.

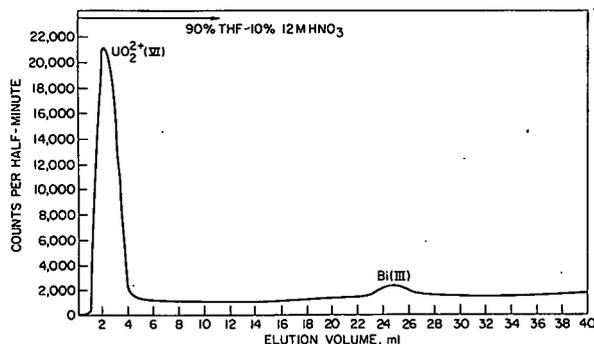


Fig. 1. THF-HNO₃ Elution-volume Data for Uranium Separation

As can be seen from Fig. 1, most of the U²³² activity passes through the column with the first 3 ml of eluent; the minimum is reached at ≈ 10 ml. Thereafter, however, the activity again increases slightly, reaches a peak at ≈ 25 ml, and then levels off up to 40 ml.

The second peak in Fig. 1 is the result of γ -emission by possible uranium daughter products present in the tracer and carrier solution that may be eluted from the column more slowly than the U²³² itself. Of the possibilities, bismuth is a likely suspect, as earlier studies^{2,3} indicated a very low K_d for bismuth in this same THF-HNO₃ system. The ferrocyanide test on these same active solutions shows that no more U²³² is present after 12-14 ml of eluent have passed.

Apparently, then, all the uranium is eluted by 10-14 ml of THF-HNO₃ at the slower 0.4-ml/min drop rate. For this reason, all further column experiments were run at a drop rate of 0.25-0.4 ml/min, and 20 ml of eluent were used to wash the column.

Figure 2 summarizes the important K_d values as determined by the three methods mentioned earlier. The batch equilibrium values are the most accurate and important, as they are obtained from quantitative activity counts. The spectrographic results lack sufficient accuracy to assign explicit number values, while the visual K_d values are merely estimated according to surrounding values in the periodic table.

According to these findings, V(V), P(V), Tc⁹⁹, Ru¹⁰⁶, Ag¹¹⁰, Ir¹⁹², and Bi²⁰⁷ pass through the resin with the UO₂²⁺(VI).^{*} Of these, only Tc⁹⁹ and Ru¹⁰⁶ are possible fission products and need to be considered. All the other tested fission-product elements are either strongly adsorbed by the column, or are

*Pu(IV) is also coeluted with the uranium.

identifiable is that at channel 19 (0.076 MeV). However, since this element is completely adsorbed by the resin, it presents no separation problems and can remain unidentified.

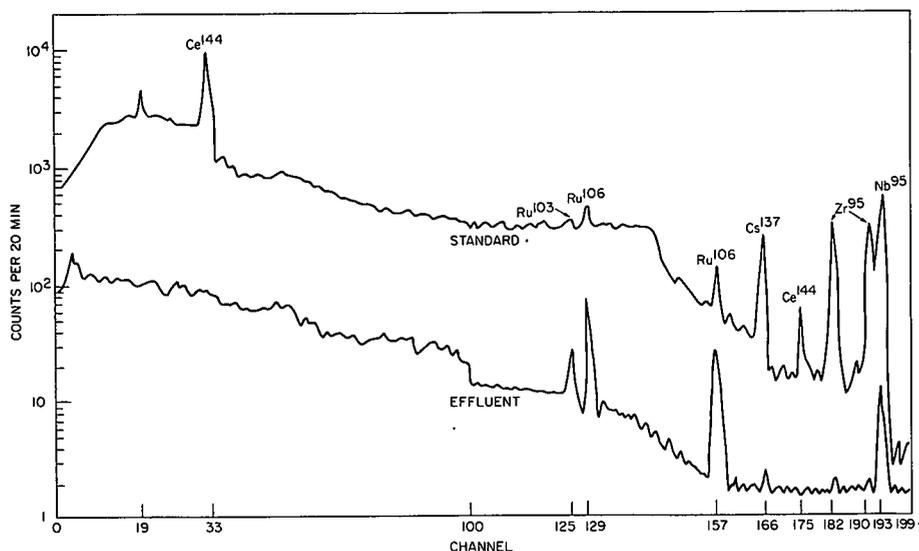


Fig. 3. Logarithmic Display of γ -activity in Uranium-Fission Product Solutions Used for Column-separation and Decontamination-factor Calculations. Note the high machine background interference in the standard solution.

No analysis was done for β -emitting fission products. Sr^{90} and Tc^{99} are likely fission products, but there is no way of determining this with the open-window counter. All the elements are β -emitters, and a count of the massive β -activity could not be divided into individual element contributions. One only needs to realize that Sr^{90} would be strongly adsorbed ($K_D = 16,850$), while Tc^{99} ($K_D = 7.3$) would likely be eluted with the ruthenium and niobium.

Table I summarizes the fission-product separation data and presents decontamination-factor values, the decontamination factor being defined (as on p. 7) as

$$\frac{\text{count rate in standard solution}}{\text{count rate in effluent solution}}$$

As with the K_D values, the higher the decontamination-factor value, the better the separation from uranium. The values were determined by comparing the relative heights of the peaks in the standard and effluent solutions for each element, using the effluent background readings as the base line. More important than the decontamination values, however, are the graphic results (shown in Fig. 3), which clearly indicate that Ru^{103} , Ru^{106} , and Nb^{95} must be further separated from the uranium.

TABLE I. Decontamination Factors for Fission-product Elements

Element	Channel	γ -energy, MeV	Decontamination Factor
a	19	0.076	4,400
Ce ¹⁴⁴	33	0.132	9,000
Ru ¹⁰⁶	129	0.516	6.2
Ru ¹⁰⁶	157	0.628	5
Cs ¹³⁷	166	0.664	260
Zr ⁹⁵	182	0.728	340
Zr ⁹⁵	190	0.760	340
Nb ⁹⁵	193	0.772	40

^aUnidentified peak.

The advantages² and potential uses of the bidimensional CIESE principle are many. After the uranium has been completely eluted from the column by the THF-HNO₃ eluent, the other metal ions adsorbed on the column can be eluted. The separation procedure is free of interferences since no salting-out agents or high acid concentrations are necessary. Of particular importance is the fact that the bulk constituent of the mixture (in this case, uranium) may be present in gram amounts without interfering with the isolation of trace amounts of the other metals. Considering these advantages, then, extensive analytical applications of CIESE are possible and forthcoming.

Besides the analytical separation and purification of uranium, the THF-HNO₃ system may also be used for the separation of any two elements showing extremes in their K_D values. Another immediate application of this system will be in the preliminary separation work needed for the γ -ray characterization of Th²³⁵. The laboratory has a sample of U²³⁸ which contains small amounts of Th²³⁴. Thorium has a high K_D in the THF-HNO₃ medium and can readily be separated from the uranium. The Th²³⁴ will then be bombarded with neutrons to produce the Th²³⁵ necessary for these investigations.

REFERENCES

1. Korkisch, J., Separation Sciences 1, 159 (1966).
2. Korkisch, J., F. Feik, and S. S. Ahluwalia, Talanta 14, 1069 (1967).
3. Korkisch, J., and S. S. Ahluwalia, Anal. Chem. 38, 497 (1966).
4. Tompkins, E. R., and S. W. Mayer, J. Am. Chem. Soc. 69, 2859 (1947).
5. Crouthamel, C. E., Applied Gamma-ray Spectrometry, New York, Pergamon Press, 1960, pp. 347-393.