Separation of Uranium from Fission Products using Cellulose

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Cellulose column chromatography has been extensively used for the separation of uranium from other metals1), thorium from rare earths2), uranium from thorium3), uranium from plutonium4) and so on.

This method has the advantage that minor components or impurities are adsorbed and collected onto cellulose. This is the opposite of the ion exchange or solvent extraction method, which extracts the main component, such as uranium or thorium.

The applicability of this method to the separation of uranium from fission products has been briefly mentioned by the author5). Because the amounts of fission products in irradiated uranium are very small, this method seems especially suitable for this separation. In this paper a detailed treatment of this program is presented.

Experimental

Reagents.—*Cellulose.*—Cellulose powder, 100~200 meshes for chromatography, was obtained from Toyo Roshi Co., Ltd., and was used after treatment with dilute nitric acid according to the method of Burstall1).

The irradiation of the uranium was performed in a JRR-1 reactor. A uranium(IV) oxide pellet was irradiated for one week, and after a coling period of 30 to 100 days it was dissolved in nitric acid; then the excess nitric acid and water were evaporated off, leaving the uranyl nitrate hexahydrate.

Separation by Column Method.—One gram of cellulose was packed in a glass tube 18 mm. in

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1) F. H. Burstall and R. A. Wells, *Analyst*, **76**, 396 (1951).

2) N. F. Kember, ibid., **77**, 78 (1952).

3) C. A. Barnett, E. Furby and A. M. Thomas, AERE C/R 1183.

4) J. A. F. Delsiel, AERE C/R 704.

5) N. Oi, This Bulletin, **33**, 1617 (1960).

diameter. Uranyl nitrate containing fission products was dissolved in an organic solvent keeping the concentration of uraniun about 0.2 M, and this solution was passed through the column. Then the column was washed with ten milliliters of the organic solvent, and then 30 ml. of one molar nitric acid was passed to elute the adsorbed fission products. The fractions of the organic solution, nitric acid and remaining cellulose were analyzed by a single-channel γ-scintillation spectrometer.

Separation by Batch Methed.—To obtain the distribution ratios of individual fission products at various uranium concentrations in an organic solvent, the following method was employed. About one microcurie of nuclides in nitric acid was evaporated to dryness in a beaker under an infrared lamp. Then, various concentrations of uranyl nitrate in organic solution were added, and the nuclide was dissolved by stirring. This solution was then transferred to a graduated glass cylinder with a stopper, and 100~200 mg. of cellulose was added. The activities of the solution before and after the equilibration (one hour was enough) were measured by a scintillation counter, and the K_d value was calculated by the following equation:

$$K_d=\frac{\text{Activity adsorbed per g. of cellulose (c.p.m./g.)}}{\left(\begin{array}{c}\text{Activity per ml. in solution at equilibrium}\\ \text{(c.p.m./ml.)}\end{array}\right)}$$

Results

Selection of the Solvent. — Almost all the works ever published on cellulose column separation have used as an organic solvent, either ethyl ether, isopropyl ether, or, in some cases, ethyl methyl ketone. In order to establish a rule for the selection of the organic solvent, about forty solvents which can dissolve uranyl nitrate were tested (Table I). In this experiment, one gram of uranyl nitrate hexahydrate was dissolved in 30 ml. of organic solvent together with cerium-144 and was passed through the column. The eluted organic fraction was counted to calculate the percentage of the eluted cerium. The K_d values obtained for cesium-137 proved more clearly the rule for the selection of the organic solvent, as shown in Fig. 1. These two results agreed well in that the solubility of water in the solvent here plays a main role in the separation. A water-insoluble ether or an acetate, such as ethylether, *n*-butylacetate or isoamylacetate, showed good results. On the other hand, alcohols, acetone and tri-*n*-butylphosphate did not give good results.

TABLE I. SEPARATION OF URANIUM FROM CERIUM-144. SELECTION OF THE SOLVENT

Organic solvent	Cerium-144 eluted %	Solubility of water in the solvent*
Alcohol		
Methanol	98	∞
Ethanol	96	∞
Isopropanol	13	∞
n-Butyl alcohol	18	20.1
Isobutyl alcohol	12	15
Isoamyl alcohol	29	2.6
n-Hexyl alcohol	29	7.2
2-Ethylhexyl alcohol	0	2.6
Cyclohexanol	65	—
Ketone		
Acetone	67	∞
Ethyl methyl ketone	28	11.8
Methyl propyl ketone	0	3.3
Isobutyl methyl ketone	0	1.8
Amyl methyl ketone	0	1.5
Diacetonealcohol	90	∞
Cyclohexanol	50	8.7
Mesityloxide	9	3.4
Isophorone	11	4.3
Acethylacetone	35	—
Ester		
Ethyl formate	10	4.5
Ethyl acetate	4	3.3
n-Butyl acetate	0	1.2
Isopropyl acetate	0	1.8
Isoamyl acetate	0	1.0
2-Ethoxyethyl acetate	20	—
Ethyl acetoacetate	70	4.9
Tri-*n*-butyl phosphate	42	7.0
Cellusolve		
Methylcellusolve	99	∞
Ethylcellusolve	96	∞
Butylcellusolve	76	∞
Ether		
Ethyl ether	0	1.3
Isopropyl ether	0	0.57
Butyl ether	0	0.17
Dioxane	21	
Nitromethane	5	—

* These data were taken from "Physical Properties: Synthetic Organic Chemicals", the Union Carbide Chemicals Co. (1961).

Influence of Nitric Acid and Water.—All of the published works have used a mixture of inorganic acid and an organic solvent, such as nitric acid and ether, hydrofluoric acid and ethyl methyl ketone. As to the influence of nitric acid, Burstall and Wells[1] pointed out that nitric acid was necessary for the quantitative recovery of uranium or thorium, while large amounts of nitric acid caused an increase in the solubility of other metals.

In this work we used only organic solvent. For the separation of uranium from fission products, free nitric acid must be eliminated. In this case, however, the complete recovery

TABLE II. INFLUENCE OF NITRIC ACID

Solvent	Content of nitric acid vol, %*	γ-Activity eluted %	Ratios of eluted nuclides**			
			$^{144-1}$Ce	$^{103-6}$Ru	^{131}I	^{95}Zr-Nb
Ethyl ether	0	1.2	1	1	1	1
	3	4.5	1	18	1.5	1
	5	6.6	1	27	1.5	1
n-Butyl acetate	0	1.7	1	1	1	1
	3	4.4	1	6.5	1.5	1

* $d=1.38$ nitric acid
** No nitric acid was taken as unity.
*** One week irradiated, four weeks cooled uranium was used.
Uranyl nitrate hexahydrate, one gram.

TABLE III. INFLUENCE OF WATER

Crystal water of uranyl nitrate	Water present in this system mg.	Eluted γ-activity, %	Decontamination factor		Uranium loss mg.
			$^{103-6}$Ru	^{95}Zr-Nb	
$2H_2O$	72	2.1	18	50	1.0
$3H_2O$	108	0.88	37	110	1.8
$6H_2O$	248	0.31	59	380	16
$6H_2O$*	700	0.23	43	400	23

Uranium: One gram as uranyl nitrate hexahydrate
Solvent: *n*-Butyl acetate
Fission products: Mixed fission products (ORNL) $\sim 10^8\ \gamma$ c.p.m.
* Solvent was saturated with water.

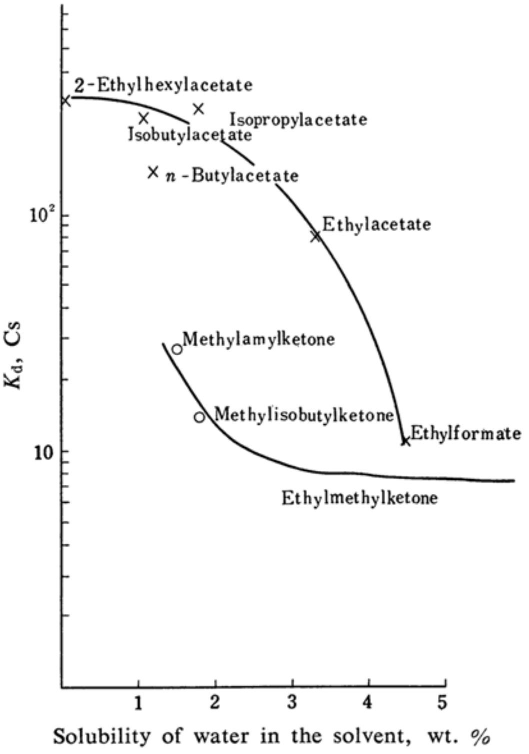

Fig. 1. Distribution ratios of cesium-137 as a function of water-in solubility of the solvent.

of uranium becomes difficult. From Table II, it is clear that the adsorption of fission products, especially ruthenium, decreased rapidly with the addition of nitric acid. The adsorption of uranium and its daughter nuclides also decreased, while adsorptions of cerium⁶⁾ and zirconium were little influenced. The increase in the elution of ruthenium is perhaps due to the formation of a trinitrato nitrosyl complex.

On the contrary, the presence of water is necessary for this separation, as is shown in Table III. This indicates also that water, namely partition, is a key factor for the adsorption. But the addition of water in excess must be avoided because the loss of uranium will increase.

Distribution Ratios for Individual Nuclides. — Irradiated uranyl nitrate cooled for four weeks was dissolved in *n*-butyl acetate and was passed through the cellulose column. Eluted fractions were collected and analyzed for uranium and fission products. The results are shown in Fig. 2. This pattern indicates that the adsorption of fission products onto cellulose is influenced by the concentration of uranium in the organic solvent. This phenomenon becomes clear with the determination of the K_d values of the fission products. Figure

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6) Ce-144 was completely retained on the cellulose when 20% of HNO_3 in ethylether was used.

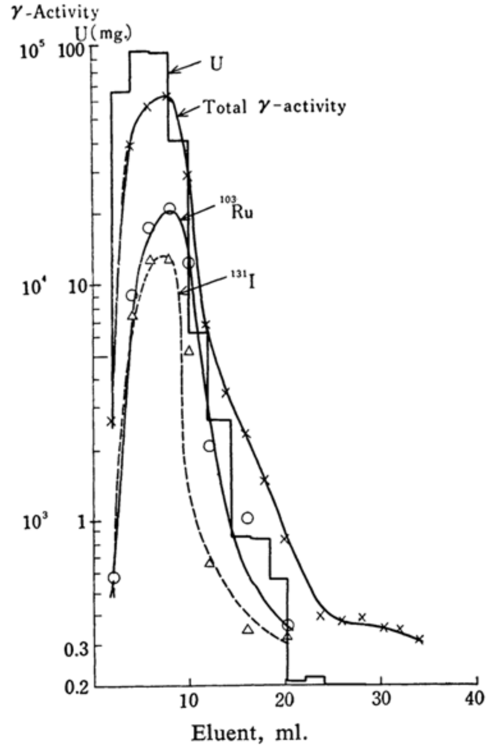

Fig. 2. Elution of uranium and fission products using *n*-butyl acetate.

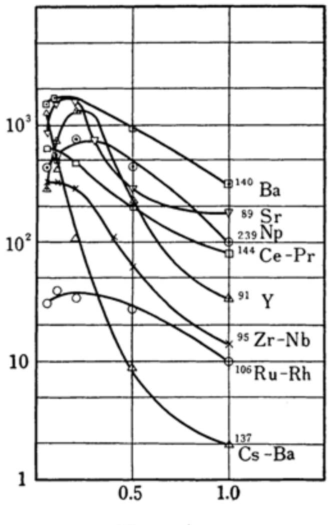

Fig. 3. Distribution ratios of fission products and neptunium as a function of uranium concentration in *n*-butyl acetate.

3 shows the K_d values for comparatively long-lived fission products and neptunium at various concentrations of uranium in *n*-butyl acetate. Here, the adsorption of fission products decreased rapidly with an increase in the uranium concentration. These values correspond well to the behavior of the nuclides in the column. Ruthenium is the most troublesome nuclide, and its degree of adsorption always determines the decontamination factor for total gamma activity. Cesium was found to elute when the uranium concentration was high. Consequently, uranium concentrations which passed through the column were limited to below 0.2 M.

Treatment of Irradiated Uranium. — As an example, the treatment of one-week-irradiated and 100 day-cooled uranium was conducted. The results are shown in Table IV. It must be noted that these results are valid only for this amount of uranium. Figure 4 shows the γ-spectrographs for the sample of uranium, the eluted organic solution and the activity remaining on the cellulose after the passage of one molar nitric acid. About 20~40% of zirconium was found to remain on cellulose without its being eluted by nitric acid.

TABLE IV. TREATMENT OF 100 DAY-COOLED URANIUM

Solvent	Eluted γ-activity, %	Decontamination factor	
		$^{103-6}$Ru	^{95}Zr-Nb
Ethyl ether	0.42	47	1360
n-Butyl acetate	0.68	37	1700
Isoamyl acetate	0.89	12	5000
Isopropyl acetate	1.1	11	1800
Isobutyl methyl ketone	3.1	6	320

Uranyl nitrate hexahydrate: 1 g.
(10^8 γ-c.p.m.)

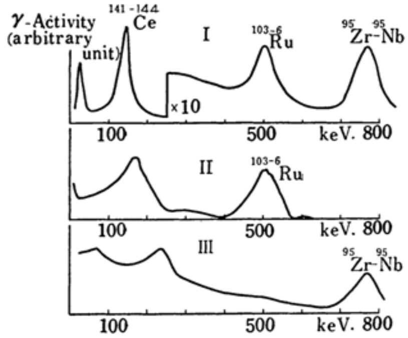

Fig. 4. Treatment of 100 day-cooled, irradiated uranium using *n*-butyl acetate.

I Total activity (sample of uranium)
II Eluted organic solution
III Activity remained on cellulose after the passage of one molar nitric acid

Discussion

As has been mentioned, for the separation of uranium from fission products by cellulose, we can not use nitric acid to keep off the elution of ruthenium. For this reason, large amounts of organic solvent are necessary for the complete recovery of uranium. But when one to two grams of uranium are to be treated, 99% or more of uranium recovery and 99% or more of fission products removal can be accomplished easily by using less than 40 ml. of organic solvent and one gram of cellulose.

As to the treatment of large amounts of irradiated uranium, it requires much further investigation. Because the K_d values for fission products nuclides are of the order of 10^2 to 10^3, even at a uranium concentration of 0.2 M the amount of uranium to be treated by one gram of cellulose seems to be limited.

This method has the advantage that the fission products are collected onto cellulose. This makes easier further treatment such as waste disposal or the recovery of potential radioisotopes. The selective elution of fission products nuclides from cellulose will be made possible by the use of a combination of complexing agents. This remains for further investigation.

The mechanism of this separation is not yet known. As has been mentioned, partition will be a large factor, while adsorption by ion exchange seems to be a factor, too.

Summary

The separation of uranium from fission products by using cellulose has been demonstrated. Uranyl nitrate hexahydrate containing fission products was dissolved in an organic solvent that had low solubility of water, and this solution was passed through the column of cellulose. Almost all the fission products were retained on the cellulose, while uranium passed almost unadsorbed. The most labile nuclides were found to be ruthenium and cesium. Free nitric acid must be eliminated to prevent the elution of ruthenium.

The distribution ratios of individual fission products and neptunium between cellulose and an uranyl nitrate solution in *n*-butyl acetate were determined, and it was found that the adsorption of fission products decreased with the increase in the uranium concentration of the organic solvent. Therefore, the concentration of uranium that passed through the column was limited to below 0.2 M.

It was also found that water was necessary. This indicated partition as one of the mechanisms of this separation.

In this method the mass transfer of uranium between two different phases is not performed, so the contamination of fission products is rather small. Moreover, uranium can be easily recovered and fission products are condensed on a small amount of cellulose.

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