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Application of a Pretreated Straw Column to the Separation of Thorium and Uranium

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Abstract

Straw pretreated with concentrated nitric acid has been used as an adsorbent in columns. This adsorbent has been shown to possess high adsorbability and high affinity for thorium, and it is based on this property that the pretreated straw is used to separate thorium from uranium and its daughters. The affinity of this column for thorium and uranium was studied, and a number of eluants have been investigated for the desorption. We found that several economical ammonium salts [0.2 *M* $(NH_4)_2SO_4$, 1 *N* $(NH_4)_2CO_3$, 1.5 *N* NH_4Cl, and 2 *N* NH_4NO_3] could be used for the separation of thorium and uranium successfully. Finally, this column was successfully used to separate trace amounts of thorium from uranyl nitrate hexahydrate and to remove the daughters from thorium nitrate dodecahydrate.

INTRODUCTION

A method was given by Burstall and Wells (*1*) in which the use of ethyl ether containing 5%, v/v, of nitric acid as solvent and cellulose pulp as adsorbent had been proved successfully in the separation of uranium from minerals, ores, and other products, while Kember (*2*) succeeded in the separation of both thorium and uranium on the same sample by using ether containing 5%, v/v, of nitric acid to separate uranium or containing 12.5%, v/v, of nitric acid to separate thorium. Feldman and Ellenburg (*3*) used this method to separate rare earths from thorium nitrate dodecahydrate and uranium nitrate hexahydrate. This method is reasonably simple and

speedy in operation. But pure cellulose is expensive, and the ethyl ether is not only expensive but also easy to evaporate and burn. Thus much work remains to be done to improve this method.

Our previous observation (*4*) has shown that cheap rice straw pretreated with concentrated nitric acid is an excellent adsorbent. It was considered that this special adsorbent might be good for the separation of thorium and uranium. The present work describes the use of this adsorbent in a column for the separation of thorium and uranium. The adsorption capacity and the affinity of this column for thorium and uranium were studied in detail. Attempts were made to elute thorium and uranium from this column with a number of different complexing agents. It was found that several economical ammonium salts could be used for the separation of thorium and uranium successfully. Finally, this column was actually applied to the separation of trace amounts of the daughters in uranyl nitrate hexahydrate, and to the separation of the daughters of thorium nitrate dodecahydrate.

EXPERIMENTAL

Chemical Reagents

All chemical reagents used in the experiments were of C.P. grade without further purification.

99.9% pure U_3O_8, uranium nitrate hexahydrate, and thorium nitrate dodecahydrate were obtained from Johnson Matthey Chemicals Limited, England.

Preparation of Solutions

Aqueous reagents were prepared with deionized water. The standard uranium feed solution was prepared by dissolving a known amount of 99.9% pure U_3O_8 in nitric acid, evaporating the solution just to dryness, then dissolving and diluting with deionized water. The standard thorium solution was prepared by dissolving thorium nitrate dodecahydrate in deionized water, and then standardizing gravimetrically. Ether containing X%, v/v, of nitric acid was prepared by adding X ml of concentrated nitric acid (sp. gr. 1.42) to each 100 ml of ether.

Preparation of a Column

Natural rice straw was steeped in concentrated nitric acid for 24 hr and

then filtering with a Whatman No. 1 filter paper. The mat was washed free from nitric acid with deionized water while it was on the filter, then dried by exposure to room conditions. Two grams of this dry adsorbent were weighed into a beaker, mixed with deionized water to give a semidry pulp, then poured it into a glass column, 20 cm long, 1.5 cm i.d. with a fritted disk. The bed dimension was 1.77 cm^2 × 20 cm. A well-packed column flows evenly, and the column should never be allowed to run dry. If it dries, it shrinks away from the tube and leaves channels. The solution passes freely through the column at a rate of approximately 0.25 ml/(min)$(cm)^2$.

Apparatus and Methods

The spectra of the radioactive daughters of natural uranium and thorium were analyzed by a Ge(Li) detector, with an active volume of 33 cm^3, coupled with the HP 5401B 4096-Channels Pulse Height Analyzer.

The concentration of uranyl ion was determined by a Metrohm Herisau polarecord E 261 polarograph, in which a well-defined wave for the reduction of uranyl ion in a supporting electrolyte of 0.1 *N* HCl was obtained.

The concentration of thorium was determined by the indirect polarographic method (*5*). *m*-Nitrobenzoic acid was used to precipitate thorium as the tetra-(*m*-nitrobenzoate).

The concentrations of uranium and thorium could also be visually estimated by $K_4Fe(CN)_6$ and oxalic acid, respectively.

Measurements of Thorium and Uranium Adsorption Capacity of the Column

A series of solutions of equal volume but containing different concentrations (from 10 mg/50 ml to 1000 mg/50 ml) of uranium was passed through each column, then washed with deionized water. By the change of the concentration, the uranium adsorption capacity of the column was determined. The thorium adsorption capacity of the column was determined in the same way as described above. All measurements were carried out at 25°C.

Measurements of the Affinity of the Column for Thorium and Uranium

The relative affinities of thorium and uranium were demonstrated by passing series of mixtures of equal volume (50 ml) but containing different ratios of thorium to uranium through each column, then washing with

deionized water. The affinity of the column was determined by the change of the ratio.

Desorption of Thorium and Uranium from the Column

After thorium and uranium were adsorbed on each column, a number of mineral acids, ammonium salts, and ether containing 1 to 15% nitric acids were used as eluants to desorb thorium and uranium. By measuring the concentration of thorium and uranium of each fraction (5 ml), we could find which eluant was able to separate thorium and uranium.

An Application of the Column to the Separation of the Daughters of Uranium and Thorium

By comparing the gamma-ray spectrum of uranyl nitrate hexahydrate solution which was passed through the column with the original gamma-ray spectrum, we found that daughters of the natural uranium were adsorbed by the column. The thorium nitrate dodecahydrate solution was passed through a column, and the adsorbed daughters were then washed out by one column volume of deionized water.

RESULTS AND DISCUSSION

The amounts of uranium adsorbed in the column are shown in Fig. 1 as a function of the concentration of uranium in the feed solution at 25°C. It is shown that the adsorption capacity of the column for uranium is about 500 mg. The adsorption capacity of the column for thorium is about the same.

Table 1 shows the adsorption results from a mixed thorium and uranium solution by the column at 25°C. In Samples 3–5 the amount of thorium is higher than the adsorption capacity of the column. This shows that only a very little amount of uranium was adsorbed. In Samples 6–10 the total amount of thorium and uranium is equal to 500 mg (the adsorption capacity of the column). It is seen that thorium is 100% adsorbed while uranium is only about 30% adsorbed. In Sample 11 the total amount of thorium and uranium is less than the adsorption capacity of the column; thorium is about 100% adsorbed and uranium is still about 30%. In Sample 12, although the amount of uranium is higher than the adsorption capacity of the column, thorium is still 100% adsorbed and uranium is adsorbed less than 150 mg, corresponding to about 30% of the capacity

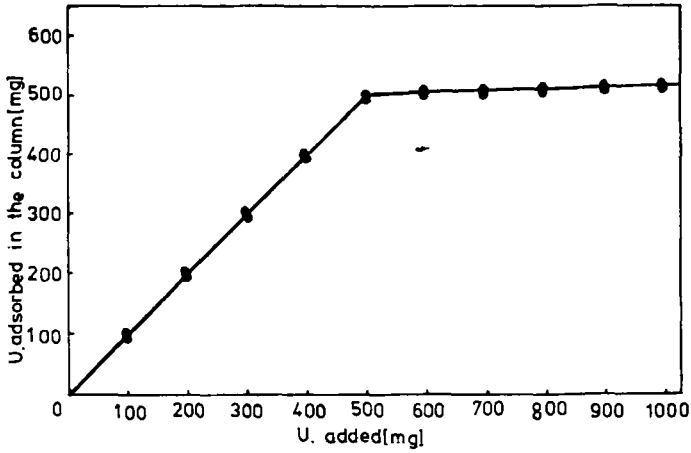

FIG. 1. Uranium adsorption of the column as a function of the concentration of the feed solution at 25°C. The volume of feed solution added is 50 ml for each case.

TABLE 1

Adsorption from a Thorium and Uranium Mixture Solution by the Column at 25°C

Sample no.	Composition of mixture		Thorium adsorbed		Uranium adsorbed	
	Th (mg)	U (mg)	Amount (mg)	%	Amount (mg)	%
1	0	500	0	0	500	100
2	500	0	500	100	0	0
3	>500[a]	0	500	—	0	0
4	>500[a]	10	500	—	3	30
5	>500[a]	100	500	—	10	10
6	400	100	400	100	30	30
7	350	150	350	100	48	32
8	250	250	250	100	87	34
9	150	350	150	100	115	31
10	100	400	100	100	130	32
11	100	100	100	100	31	31
12	100	>500[a]	100	100	150	—

[a]Including 500 mg, 1000 mg, 2000 mg, etc.

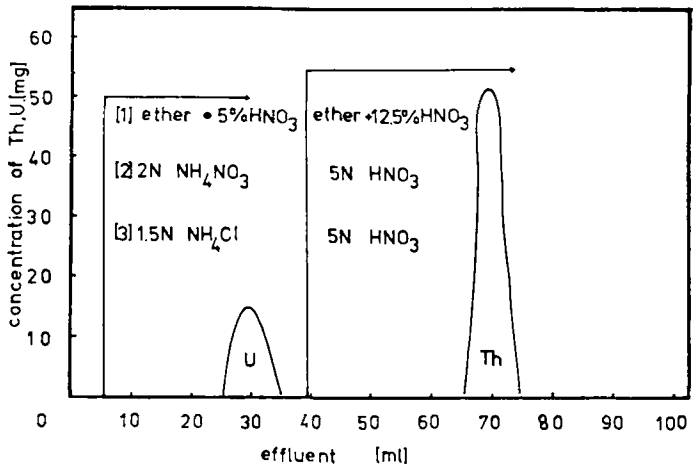

FIG. 2. Desorption of thorium and uranium with three different series of eluants. Bed dimension: 1.77 cm^2 × 20 cm. Flow rate: 0.25 ml min^{-1} cm^{-2}.

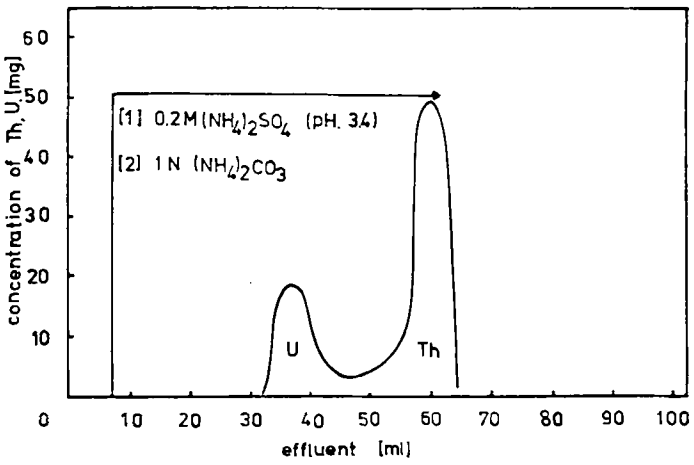

FIG. 3. Desorption of thorium and uranium with 0.2 *M* $(NH_4)_2SO_4$ (pH. 3.4) or 1 *N* $(NH_4)_2CO_3$. Bed dimension: 1.77 cm^2 × 20 cm. Flow rate: 0.25 ml min^{-1} cm^{-2}.

of the column. All these results show that this column has a marked affinity for thorium and that the adsorption of thorium is not affected in the presence of uranium. When the amount of thorium is below the capacity of the column, the adsorption of thorium is always 100%, irrespective how much uranium is present. On the other hand, the presence of thorium will reduce the adsorption capacity of uranium to less than about 30% of that for pure uranium.

Some agents attack this adsorbent, and therefore they cannot be used as elutriants. We endeavored to find the optimal elutriants by testing a large number of different agents. It was found that several ammonium salts such as 0.2 *M* $(NH_4)_2SO_4$, 1 *N* $(NH_4)_2CO_3$, 1.5 *N* NH_4Cl, and 2 *N* NH_4NO_3 could be used successfully for the separation of thorium and uranium. The good elution curves of thorium and uranium obtained are shown in Figs. 2 and 3. The success of the elutions may be due to the formation of the water-soluble ammonium complex of thorium and uranium. Since the major constituent of the straw is cellulose, the column may be an ion-exchange rather than a chromatographic column. The ion-exchange property of this straw-cellulose column may be due to the carboxylic groups' ion-exchange behavior which can be increased by pretreating the cellulose with nitric acid (*6*, *7*). By such a simple elution, thorium and uranium can be recovered. The adsorption capacity of this adsorbent did not diminish after several successive adsorption–elution cycles.

Figure 4 shows gamma-ray spectra of the uranyl nitrate hexahydrate; the lower one is the spectrum of the original uranium solution, and the upper one is the spectrum of the same solution after it was passed through the column. The peaks of ^{234}Th and ^{234}Pa disappeared because they were retained in the column. The spectrum of ^{234}Th and ^{234}Pa remaining in the column is presented in Fig. 5. Since ^{234}Pa is the daughter of ^{234}Th, with a half-life very short compared with that of ^{234}Th, both of them always appear together. The gamma-ray spectra of the thorium nitrate dodecahydrate are shown in Fig. 6; the lower one is the spectrum of the column after the original thorium solution was passed. The peaks are all due to the daughters of ^{232}Th. After the column was washed with one column volume of deionized water, most of the thorium daughters were washed down, as can be seen in the upper spectrum of Fig. 6. If it is treated once more by one column volume of water, all daughters of the thorium can be removed. It is seen that the method can be used for preparing carrier-free ^{234}Th tracer from aged uranium and for the removal of daughters from aged thorium.

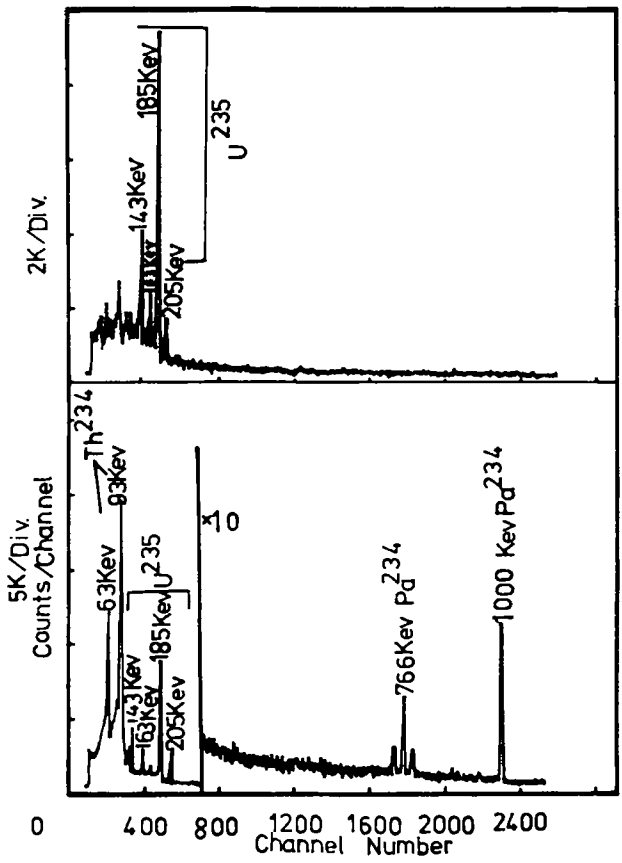

FIG. 4. Gamma-ray spectra of the uranyl nitrate hexahydrate. The lower one is the spectrum of the original uranium solution, and the upper one is the spectrum of the same solution after it was passed through the column. Counting time: 50 min.

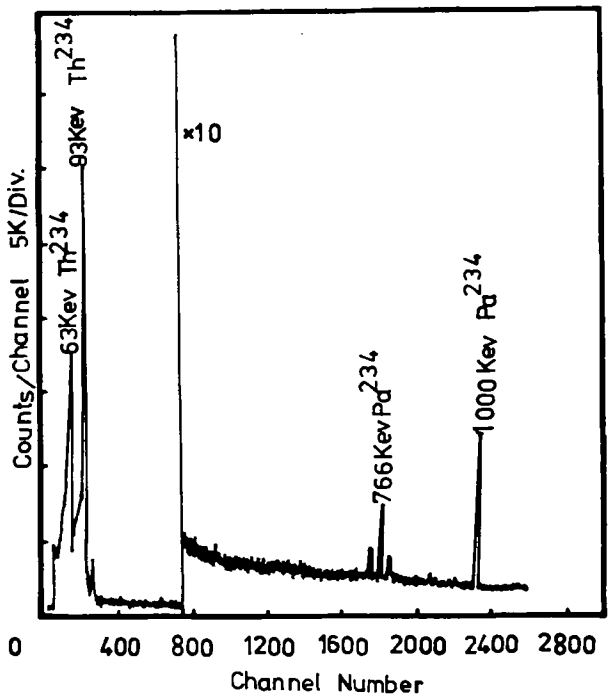

FIG. 5. Gamma-ray spectrum of ^{234}Th and ^{234}Pa in the column. Counting time: 50 min.

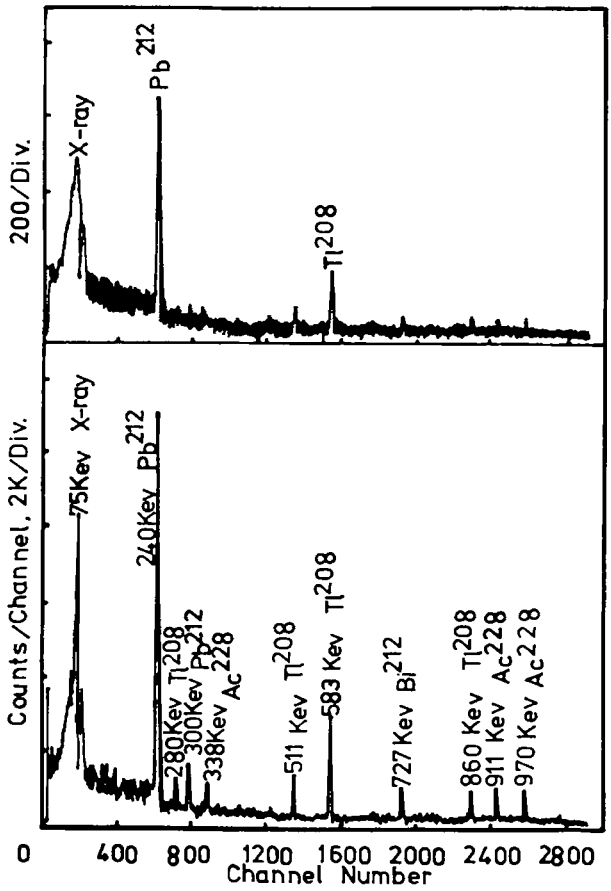

FIG. 6. Gamma-ray spectra of the thorium nitrate dodecahydrate (daughters of ^{232}Th). The lower one is the spectrum of a column after a thorium solution was passed, and the upper one is the spectrum of the same column after it was washed with one column volume of water. Counting time: 50 min.

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