ANION EXCHANGE SEPARATION OF THORIUM FROM URANIUM

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(Received March 13th, 1961)

The first comprehensive study of the adsorption of the elements by strong base anion exchange was reported for hydrochloric acid media by KRAUS AND NELSON[1] at "The First International Conference on the Peaceful Uses of Atomic Energy" at Geneva, Switzerland, in 1955. These authors as well as HYDE[2] showed that thorium cannot be adsorbed on such resins even at the highest possible hydrochloric acid concentration, because of the low tendency of the thorium ions to form negatively charged chloride complexes. The adsorption of uranyl ions, on the other hand, shows a steady increase with increasing hydrochloric acid concentration of the solutions, so that separation of thorium from uranium could be achieved in such media, although a simultaneous adsorption of thorium and uranium was out of the question.

Previous research work by KORKISCH AND TERA[3] in the field of anion exchange in mixed solvents, has shown that thorium tetrachloride can be adsorbed on strongly basic resins from solutions containing aliphatic alcohols and hydrochloric acid. This adsorption, however, is only high if aliphatic alcohols of greater chain length than methanol are applied in high concentrations (85–99 %). The highest adsorption coefficients of thorium on Amberlite IRA-400 could be obtained in mixtures consisting of 96 % propyl-, butyl- or amyl alcohol and 4 % hydrochloric acid. Since, under the same conditions, uranyl ions are also very strongly held, a simultaneous adsorption of both these elements is possible.

In the present paper the distribution coefficients of thorium and uranium between butanol–and methanol–HCl mixtures and Dowex 1 were determined. The results showed that both thorium and uranium have very high distribution coefficients in butanol–HCl mixtures. In methanol–HCl mixtures, however, only uranium is held on the resin with sufficient strength, thereby insuring a clear cut separation of these two radio elements from each other. By means of column operations thorium and uranium can thus be adsorbed simultaneously on the resin from a butanol–HCl mixture. By treating the exchanger with a methanol–HCl mixture thorium is eluted whereas uranium still remains adsorbed. Afterwards the elution of uranium can be achieved by means of 1 *N* hydrochloric acid.

EXPERIMENTAL PART

Solutions and reagents

Air-dried Dowex 1, X8 (100–200 mesh, chloride form) was used. The aliphatic alcohols (methanol and *n*-butanol) were reagent grade solvents. The standard solutions of

thorium and uranium contained the reagent grade chlorides of these elements dissolved in 6 *N* hydrochloric acid. Thorium was determined quantitatively with thoronol (0.1 % aqueous solution)[4] using a Beckman model B spectrophotometer. The absorbance measurements were carried out in 1 cm cells at 545 mμ using a blue sensitive photocell. The column operations were carried out in columns (containing about 1 g resin each) of the same type and dimensions as those described earlier[5].

Quantitative determination of thorium and uranium

The methods used for the quantitative determination of thorium and uranium in the filtrates of the mixtures used for the determination of the distribution coefficients and in the eluates after the column operations are exactly the same as those described in earlier papers[3,5,6].

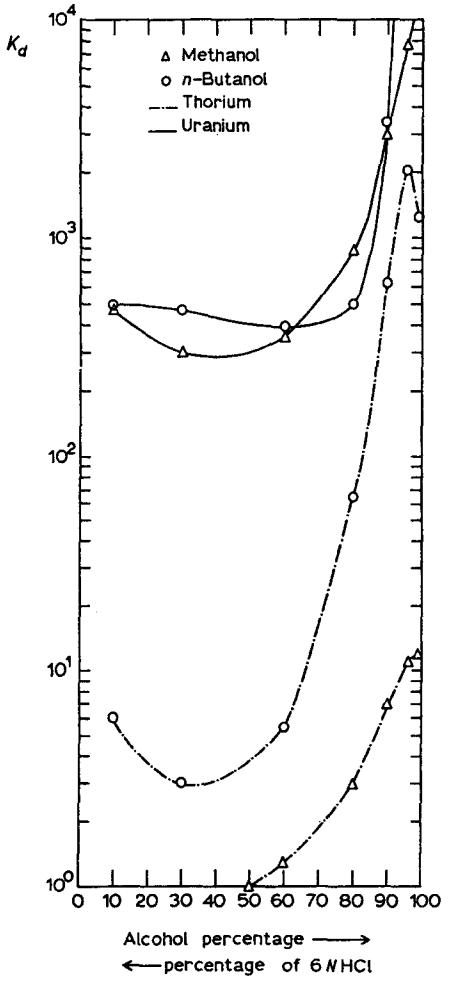

Fig. 1. Effect of *n*-butanol, methanol and 6 *N* HCl concentration on the distribution coefficients K_d of uranium and thorium.

Determination of distribution coefficients

The distribution coefficients of uranium and thorium were always determined in mixtures of 25 ml volume containing 5000 μg thorium or uranium.

Example: For mixtures containing 96% butanol or methanol, 1 ml of either the uranium or thorium standard solution (containing 5000 μg thorium or uranium per ml) was mixed with 24 ml of the corresponding alcohol, using a conical flask. After preparing the solution, 1 g of resin was added, and the stoppered flask was shaken thoroughly on a shaking machine for 24 h. The resin was then filtered off, and the thorium or uranium was determined in the filtrate as described above. The results shown in Fig. 1 were obtained using this procedure.

Column operations (separation of thorium from uranium)

After filling the ion exchange column with resin suspended in methanol the resin bed was pretreated portionwise with in total 50 ml of a mixture consisting of 45 ml *n*-butanol and 5 ml 6 *N* hydrochloric acid. Then the sorption solution (45 ml *n*-butanol + 5 ml 6 *N* hydrochloric acid) containing the thorium and uranium was passed through the column at a flow rate of 15 ml/h. The column was then washed (flow rate 30 ml/h) with 150 ml of a mixture consisting of 90% methanol and 10% 6 *N* hydrochloric acid. During this step the thorium is eluted and can be found up to 90% in the first 50 ml of the effluent. The other 50 ml contained the residual amount of thorium, while in the last 50 ml no trace of thorium could be detected. At the same time the uranium remains strongly adsorbed on the resin (5000 μg uranium occupy a resin zone of less than 1 cm height, which is practically not shifted during the elution of thorium). Afterwards the uranium was eluted with 100 ml 1 *N* hydrochloric acid.

All separations of thorium from uranium were completely quantitative (see Table I), owing to the fact that the distribution coefficient for thorium in the methanol–HCl medium employed for elution is 7, whereas that for uranium is 3000.

RESULTS

Fig. 1 shows the effect of the *n*-butanol and methanol concentration on the distribution coefficient K_d which is given by the following equation:

$$K_d = \frac{\mu\text{g thorium (uranium)/g resin}}{\mu\text{g thorium (uranium)/ml solution}}$$

From this figure it can be seen that the distribution coefficient of thorium and uranium increases with increasing alcohol concentration. From 90% alcohol (methanol or butanol) upwards very high values for uranium were obtained. In this figure the distribution coefficients for uranium in 99% and 96% butanol and 99% methanol are not shown, in order to avoid extending the scale of the figure further. The corresponding distribution coefficients are 833,300, 75,750 and 12,100 respectively.

The curves for thorium show that this element has the highest distribution coefficients in 80–99% butanol only, whereas at all methanol concentrations its

distribution coefficient is rather low. These great differences in the distribution coefficients of thorium and uranium in methanol–hydrochloric acid medium are the basis for the separation method described.

In Table I the results of a series of separation experiments (see experimental part) are recorded. From these results it is seen that this method of separation proves to be quite suitable for the separation of micro- and semi-macro quantities of thorium and uranium.

TABLE I

SEPARATION OF THORIUM AND URANIUM

Amounts taken		*Amounts recovered*	
thorium μg	*uranium* μg	*thorium* μg	*uranium* μg
10	10	11	9.8
100	100	105	102
1000	1000	1010	999
5000	5000	5040	5012
50	5000	50	5020
5000	50	5040	49
10	5000	11	4980
5000	10	5060	10.5

This method could be applied preparatively for the continuous separation of the thorium isotopes that are formed by the natural decay of uranium. In this case the column loaded with uranium has to be washed every now and then with the methanol–hydrochloric acid mixture employed for the separation of thorium from uranium. The effluent will contain the thorium isotopes formed during the time that has passed between two successive washings.

ACKNOWLEDGEMENTS

The research reported above, was sponsored by the International Atomic Energy Agency and the United States Atomic Energy Commission under contract number 67/US. The generous support from these agencies is gratefully acknowledged.

SUMMARY

The present work was carried out in order to develop a method for separating thorium and uranium. Equilibrium studies have shown that the adsorption of both tetravalent thorium and hexavalent uranium as negatively charged chloride complexes on the strongly basic anion exchanger Dowex 1 from solutions containing butanol and hydrochloride acid is very high, so that these two radio elements can be adsorbed on the resin simultaneously. Separation is possible due to the fact that thorium can be readily eluted with a methanol–hydrochloric acid mixture, whereas uranium is still very strongly retained on the resin under the same conditions. After the removal of thorium the uranium is eluted with 1 *N* hydrochloric acid.

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