CHROMATOGRAPHIC SEPARATION OF URANIUM FROM EXCESS OF THORIUM ON SILICA GEL COLUMN

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Conditions have been found for the chromatographic separation of uranium from excess of thorium on a column of silica gel from the medium of triethylenetetraminehexaacetic acid (TTHA), diethylenetriaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA). Under optimum conditions, *i.e.* from the TTHA medium of pH 5—6 and $I = 1$, uranium may efficiently be separated from the $8 . 10^4$ excess of thorium.

In previous paper[1] the distribution coefficients of uranyl (D^U) and thorium (D^{Th}) ions have been determined for silica gel and solutions of polyaminopolycarboxylic acids. In this paper the obtained data are further employed in the chromatographic separation of uranium from excess of thorium from solution of triethylenetetramine--N,N,N′,N″,N‴,N‴-hexaacetic acid, diethylenetriamine-N,N,N′,N″,N″-pentaacetic acid and nitrilotriacetic acid.

EXPERIMENTAL AND RESULTS

All used apparatus and solutions have already been described in the previous paper[1]. For column separations, glass columns, with a sintered glass disc, 25 cm long and 8 mm internal diameter, were used. Such columns were packed with 2 g of the gel, previously dried at 120°C for 2 hours. Thorium nitrate $Th(NO_3)_4 . 5 H_2O$ (Schuchardt) was purified in the laboratories of the Uranium Industries, and contained $<2 . 10^{-4}\%$ uranium.

Separation of Uranium and Thorium from Solutions of TTHA

The sorption of uranyl and thorium ions was studied on the column of silica gel in the pH range 4—9. The following procedure was used: 50—150 ml of a solution containing 0—119 μg U(VI) and 0—1 g Th^{4+} was taken and 0·1M-TTHA added so that 0·02M excess remained. If necessary 4M-NaCl was added and pH adjusted by the addition of diluted (1 + 5) ammonia. The resulting solution having the ionic strength $I \leq 0·1$ or $I = 1$ (NaCl) was passed through the column packed with 2 g of silicagel previously washed with 50 ml 0·02M-TTHA of the same pH and ionic strength. The flow rate was kept in the range of 1·0—1·5 ml/min. After all solution has soaked into silicagel the column was washed with 50 ml 0·02M-TTHA of required pH and ionic strength and finally with 50 ml water. The retained uranyl ions were eluted with 25 ml 1M-HCl (added in 5 ml increments) into a 50 ml beaker. The eluate was evaporated to dryness and the residue then dissolved in 2 ml concentrated HCl. After the addition of 2—10 ml 0·1M-TTHA (depending on the amount

of thorium[2]) and 10 ml 2·5M monochloroacetic acid, pH 2·0 was adjusted by 5M-NaOH. The solution was transferred into a 50 ml volumetric flask and 0·5 ml of 0·25% solution of Arsenazo III added. The volume was then made up to the mark, solution mixed and the absorption spectrum recorded in 40 mm cells. The absorbance was measured at 656 nm against blank containing HCl, TTHA and monochloroacetic acid.

TABLE I

Sorption of Th^{4+} from TTHA Medium

Volume of solution from which sorption took place 100—150 ml; 0·02M excess TTHA.

pH	μg Th^{4+} retained from the original amount			
	100 mg		1 000 mg	
	$I \leqq 0·1$	$I = 1$	$I \leqq 0·1$	$I = 1$
4	3·0	4·6	18·2	9·0
5	2·6	3·8	18·3	3·9
6	3·2	5·8	18·0	8·5
7	3·6	4·2	13·0	14·0
8	3·3	3·2	15·0	18·2
9	3·6	4·6	13·0	18·0

TABLE II

Separation of Uranium and Thorium from TTHA Medium

Measured values were corrected for uranium content in the used thorium nitrate; volume 150 ml; 0·02M excess TTHA; $I = 1$.

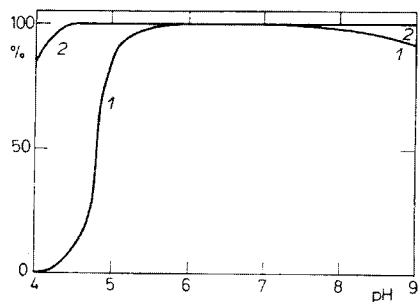| pH | Given μg U(VI) | Found % U(VI) in the presence of | |
		100 mg Th^{4+}	1 000 mg Th^{4+}
5·0	11·9	100·0	87·2
	35·7	101·0	99·0
	59·5	102·8	104·4
	119·0	100·7	103·2
5·5	35·7	103·5	101·0
	119·0	99·8	98·2
6·0	11·9	100·0	118·0
	35·7	99·7	99·4
	59·5	101·6	105·0
	119·0	101·1	104·7

FIG. 1

Sorption of Uranyl Ions from TTHA Medium
Curve 1: $I \leq 0.1$; 2: $I = 1$. 59.5 µg U(VI);
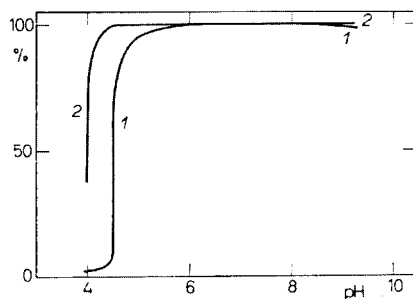volume 50 ml; 0.02M-TTHA.

FIG. 2

Sorption of Uranyl Ions from DTPA
Medium
Curve 1: $I \leq 0.1$; 2: $I = 1$. 59.5 µg U(VI);
volume 50 ml; 0.02M-DTPA.

To study the sorption of thorium, the elution was carried out by 40 ml 3.75M-HCl directly into a 50 ml volumetric flask. After 0.5 ml of 0.25% Arsenazo III had been added the absorption spectrum was recorded and absorbance measured at 665 nm against blank containing the agent in 3M-HCl.

The performed experiments were used to determine the efficiency of the sorption of uranyl ions as a function of pH at ionic strength $I \leq 0.1$ and $I = 1$. The sorption of Th^{4+} was followed by the same method. The obtained results are presented in Fig. 1 and in Tables I and II. The optimum conditions found were used for the separation and determination of uranium in

TABLE III

Sorption of Th^{4+} from DTPA Medium

Given 100 mg Th^{4+}; volume of solution from which sorption took place 50 ml; 0.02M excess DTPA

| pH | µg Th^{4+} retained | |
	$I \leq 0.1$	$I = 1$
4.5	—	3.0
5	1.4	8.8
6	18.0	39
7	46	420
8	290	2 300
9	1 600	2 300

TABLE IV

Separation of Uranium and Thorium from DTPA Medium

Measured values were corrected for uranium content in the used thorium nitrate; volume 50 ml; 0.01M excess DTPA; 100 mg Th^{4+} given; sorption at pH 6.

| µg Uranium given | % Uranium found | |
	$I \leq 0.1$	$I = 1$
11.9	100.0	102.0
35.7	98.7	100.3
59.5	98.0	101.4
59.5[a]	96.2	99.5
117.8	102.0	100.2

[a] pH 5.

the presence of ecxess of thorium (Table II). Having in mind further applications of TTHA for the separation of other accompanying ions, the chromatographic separation was carried out at pH 5, 5·5 and 6 at $I = 1$.

Separation of Uranium and Thorium from Solutions of DTPA

The sorption of uranyl and thorium ions from solutions of DTPA was studied under identical conditions as those mentioned for TTHA at ionic strength $I \leqq 0·1$ and $I = 1$ in the pH range $4-9$ (UO_2^{2+}) and $4·5-9$ (Th^{4+}) respectively. 50 ml of the starting solution contained excess of DTPA of $0·01-0·02M$. The elution and final determination was completed by the already mentioned method. The chromatographic separation of uranium and thorium was carried out at pH $5-6$ and ionic strength $I \leqq 0·1$ and $I = 1$. Results are shown in Tables III and IV and in Fig. 2.

Separation of Uranium and Thorium from Solutions of NTA

The experiments were performed by the method described for TTHA at pH $4-9$ (UO_2^{2+}) and $4·5-9$ (Th^{4+}) respectively and ionic strength $I \leqq 0·1$ and $I = 1$. The separation of uranium from excess of thorium was studied at pH 4·5 and 5. The results are presented in Table V and in Fig. 3.

DISCUSSION

Consistently with the already determined distribution coefficients and separation factors[1] the best medium for the chromatographic separation of uranium from excess of thorium (in the system silica gel–UO_2^{2+}, Th^{4+}–solution of polyaminopoly-carboxylic acid) proved to be TTHA. Promising however seems also the application of DTPA and NTA.

TTHA. In solutions of this polyaminopolycarboxylic acid the quantitative sorption of uranyl ions $(>95\%)$ takes place at pH $5·5-9$ $(I \leq 0·1)$ and pH $4·5-9$ $(I = 1)$ respectively. In accordance with the measured values of D^U, the sorption efficiency increases with increasing pH and ionic strength, as seen on Fig. 1. The sorption of thorium was studied under the same conditions. Determined values, presented in Table I, prove the high selectivity of the sorption process. Even at extreme excess of thorium $(1 \text{ g } Th^{4+})$ not more than 18 µg Th^{4+} is retained by the column, which is less than $0·002\%$ of the original amount of thorium. This amount is practically constant on the wide acidity range (pH $4-9$) and does not even change with the in-creasing ionic strength. Consistently with the course of dependence of D^{Th} on pH the amount of retained Th^{4+} does not increase in the alkaline region. It is therefore obvious that sorption of these microgram amounts of thorium is determined by other factors, such as the size and shape of the column, quality of its surface, method of the preparation of the sorbent, *etc.*

The entire studied pH range in which UO_2^{2+} is completely retained by the column, *i.e.* pH $5·5-9$ for $I \leqq 0·1$ and pH $4·5-9$ for $I = 1$, may be employed for the separa-tion of uranium from excess of thorium. With regard to future possibilities of the

separation of uranium from other accompanying ions simultaneously with thorium, pH $5-6$ at $I = 1$ was adopted for the chromatographic separation. Results which describe the efficiency of the chromatographic process are shown in Table II. Presented method facilitates a number of applications such as the determination of 0·001% uranium in spectral grade thorium compounds. High selectivity of the chromatographic separation is combined with increased selectivity of the final spectrophotometric determination[2].

DTPA. Distribution coefficients of values which would enable practical separation were found in solutions of pH $4-9$. For this reason the sorption of uranyl ions on a column of silica gel was studied in the same concentration range of hydrogen ions. Quantitative sorption of uranium takes place at pH $5-9$ $(I \leqq 0\cdot1)$ or pH $4\cdot5-9$ $(I = 1)$ as seen on Fig. 2. The sorption of thorium was followed in the same pH ranges and conditions. The obtained results, presented in Table III, are in accordance with the values of D^{Th}. The sorption of thorium is increasing with decreasing concentration of hydrogen ions. At pH $> 6\cdot5$ the value of $D^{Th} > 100$ which causes a marked increase in the sorption of thorium $(i.e. > 1\%$ at pH 9$)$. At pH $5-6$ however, the amount of retained thorium is $10^{-2}-10^{-3}\%$ which makes the chromatographic separation of uranium from excess of thorium possible (Table IV). Presented method allows the determination of less than 0·005% uranium in, for example, thorium nitrate.

NTA. Quantitative sorption of uranium from solutions of NTA takes place at pH $5-9$ $(I \leqq 0\cdot1)$ or pH $4-9$ at $I = 1$ as seen on Fig. 3. At pH 6 and $I = 1$ thorium starts to be notably sorbed but this sorption decreases with the increasing concentration of hydrogen ions. At pH $4\cdot5$ it amounts only to 0·02% of the initial 100 mg Th^{4+}. In solutions of low ionic strength $(I \leqq 0\cdot1)$ only 0·05% Th^{4+} is sorbed at pH 5·0 but

TABLE V

Sorption of Th^{4+} from NTA Medium

Given 100 mg Th^{4+}; volume of solution from which sorption took place 50 ml; 0·02M excess NTA.

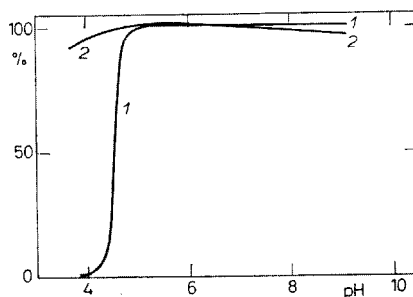| pH	µg Th^{4+} retained	
	$I \leqq 0\cdot1$	$I = 1$
4·5	—	20
5	5	—
6	—	5 500
7	580	—
8	—	> 29 000
9	> 29 000	—

Fig. 3

Sorption of Uranyl Ions from NTA Medium

Curve *1*: $I \leqq 0\cdot1$; *2*: $I = 1$. 59·5 µg U(VI); volume 50 ml; 0·02M-NTA.

with decreasing concentration of hydrogen ions this amount sharply increases as indicated in Table V. The separation of uranium and thorium might therefore be carried out quantitatively at pH 5 and $I \leqq 0.1$ or at pH 4.5 and $I = 1$ at the ratio 1 : 2000.

To summarize all obtained results one may say that the separation and subsequent determination of uranium from excess of thorium can be carried out in all studied chelating systems. In accordance with the determined values od D^U and D^{Th} and the corresponding separation factors, the most convenient chelating agent for the chromatographic separation of UO_2^{2+} and Th^{4+} is TTHA which allows the application of a wide acidity range. .For DTPA the concentration of hydrogen ions must be kept in the range of pH 5—6. The separation from solutions of NTA may be carried out but only under very definite conditions.

The obtained results are going to be used for the isolation of uranium from complex solutions which often occur in analyses of various inorganic raw materials. When rocks containing highly resistant minerals (*e.g.* zircon) are decomposed, the most general decomposition method being the fusion with Na_2O_2, the resulting solutions have a high ionic strength. The increase of the sorption efficiency with increasing ionic strength renders silicagel more applicable under conditions where the high content of neutral salts causes that common ion-exchangers could not be used.

REFERENCES

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