

CHROMATOGRAPHIC SEPARATION OF URANIUM FROM EXCESS ACCOMPANYING ELEMENTS IN A MEDIUM OF DIETHYLENE-TRIAMINE-N,N,N',N'',N'''-PENTAACETIC ACID

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A procedure for the separation and determination of uranium has been proposed, based on selective sorption of uranyl ions on a silica gel column from solution containing excess accompanying ions, using a diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid medium.

In a previous work¹, the values of the distribution coefficients for uranyl and thorium(IV) ions were determined in a system containing silica gel and a polyaminopolycarboxylic acid. Chromatographic separation of the two ions at various concentration ratios is most efficient in media of diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid (DTPA) and triethylenetetramine-N,N,N',N'',N''',N''''-hexaacetic acid (TTHA) (ref.²). Consequently, the present work deals with the use of DTPA in the chromatographic separation of trace amounts of uranyl ions from excess accompanying components.

EXPERIMENTAL

Instruments and Chemicals

Spectrophotometric measurements were carried out on a Unicam SP 800 instrument. For the determination of the amounts of metals sorbed on silicagel, atomic absorption spectrometers Perkin-Elmer 306, 300 and Techtron AA 4 with a PE-HGA 70 graphite cuvette were employed. Trace amounts of mercury were determined on a Coleman MAS 50 instrument. The preparation procedures for DTPA and TTHA solutions and for silica gel columns were described in a previous work².

RESULTS

Analytical Methods Used for Evaluation of the Sorption Properties of Silica Gel

A spectrophotometric determination of uranium with ArsenazoIII (AZO) reagent in the presence of Th^{4+} in solutions containing a monochloroacetate buffer and TTHA was described in detail in a previous paper³. The effect of the other accom-

panying elements under the conditions given in the final procedure in the paper cited is summarized in Table I. Especially Ce^{3+} , La^{3+} and Y^{3+} ions, which are not sufficiently strongly complexed by TTHA at the given pH, exhibit strong interference and cause a considerable positive error. Titanium also interferes, but in the presence of TTHA and H_2O_2 it forms a very stable ternary complex, enabling the determination of uranium in the presence of more than a three-hundred-fold excess of titanium. The stability of the uranyl ion chelate with AZO is not affected by the addition of dilute hydrogen peroxide (0.5 ml of 3% H_2O_2 in 50 ml). Excess ferric ions cause a small positive error; when they are reduced to Fe^{2+} with ascorbic acid, the U-AZO chelate is destroyed probably due to the strong reducing properties of the Fe(II)-TTHA complex.

During the study of the efficiency of the chromatographic separation, most elements were determined employing atomic absorption spectrometry with acetylene-air or acetylene-nitrous oxide flames. Some elements (*e.g.* Pt) were determined by the flameless technique in a graphite cuvette. The initial solution volumes were 5–100 ml. the content of Ce, La, Y, Zr and Th was determined spectrophotometrically using the AZO reagent (*ref.*⁴). Spectrophotometry was also used for the determination

TABLE I
Effect of Some Ions on the Photometric Determination of Uranium with AZO

Element, mg	Error in the determination U, rel %	Element, mg	Error in the determination U, rel %
5.6 Fe(III)	4.2	1.0 Sb(III)	1.0
1.0 Ti	15.5	1.0 Cu	15.9
0.5 Ti	5.0	1.0 Cd + 1.0 Zn	-0.5
10.0 Ti ^a	0.0	1.2 Ni + 1.0 Hg	2.6
5.0 Ca	20.6	1.0 Pb + 1.2 Co	0.5
5.4 Al + 4.9 Mg + 1.1 Mn	3.0	0.05 Pt	-3.0
2.0 Ba	-2.1	0.05 Pd	-2.0
2.0 Sr	4.1	0.05 Au(III)	0.0
0.05 La	36.4	1.0 Cr(III)	1.0
0.05 Ce(IV)	30.0	1.0 V(V)	5.0
0.05 Y	26.7	1.0 Mo	3.0
0.1 Sc	7.7	1.0 In	1.5
0.5 Be	2.9	10 PO_4^{3-}	1.5
0.5 Sn(IV)	0.5	1.0 Ga	0.0
0.11 Ag	5.1	1.0 Zr	2.9
0.10 Tl(I)	2.6		

^a Addition of 0.4 ml of 3% H_2O_2 ; 35.7 μg U(VI), volume 50 ml, pH 2.0; 0.01M-TTHA.

TABLE II

Sorption of Metal Ions on Silica Gel at Various Ionic Strengths

Ionic strength adjusted with NaCl, volume 100 ml, column with 2 g silica gel.

Taken mg	Sorbed, %			
	$I \leq 0.1$	$I = 1$	$I \leq 0.1$	$I = 1$
	pH 5		pH 7.5	
135 Al	0.8	1.2	2.9	7.3
135 Al ^d	0.7	1.2	2.6	6.5
1.08 Ag ^e	0.7	1.5	0.1	0.1
0.5 Au(III)	0.7	<0.2	1.8	0.4
10.1 Ba	<1.0	<1.0	<1.0	<1.0
0.1 Be	59	85	86	87
10.4 Bi	<0.2	<0.2	<0.2	<0.2
300 Ca	0.01	0.01	0.003	0.01
2 Ce(IV)	0.7	1.3	0.8	1.0
2 Ce(IV) ^b	0.08	<0.05	<0.05	0.2
10 Cd	<0.02	<0.02	<0.02	<0.02
11.8 Co	<0.03	<0.03	<0.03	<0.03
10 Cr(III)	0.02	0.05	0.05	0.1
10 Cu	<0.02	<0.02	<0.02	<0.02
195 Fe(III)	0.003	0.01	0.05	0.15
10.5 Ga	1.3	2.1	0.2	1.3
1.0 Hg	0.02	0.02	0.02	0.02
10.5 In	<0.2	<0.2	<0.2	<0.2
10 La	0.1	0.1	0.1	0.1
194 Mg	<0.003	0.001	<0.003	<0.002
110 Mn(II)	0.001	0.004	0.001	0.001
10 Mo	<0.02	<0.02	<0.02	<0.02
11.7 Ni	<0.03	<0.03	<0.03	<0.03
10 Pb	0.1	0.1	0.1	0.1
0.5 Pd(II)	<1.0	<1.0	<1.0	<1.0
0.5 Pt(IV)	<0.05	<0.08	0.8	0.2
10 Sb(III)	4.0	5.5	79.6	78.5
10 Sc	<0.05	<0.05	<0.05	<0.05
1 Sn(IV)	<1.0	<2.0	23.4	49.1
9.8 Sr	<0.05	<0.05	<0.05	<0.05
120 Ti	2.9	7.1	15.3	19.6
120 Ti ^c	0.01	0.03	2.5	15.4

TABLE II
(Continued)

Taken mg	Sorbed, %			
	$I \leq 0.1$	$I = 1$	$I \leq 0.1$	$I = 1$
	pH 5		pH 7.5	
65 Ti ^d	2.0	1.7	—	—
1 Ti(I) ^e	<0.7	<0.7	<0.7	<0.7
10 V	<0.01	<0.01	0.04	0.03
10 W(VI)	0.09	0.2	0.07	0.05
10 Y	0.04	0.08	0.1	0.1
9.8 Zn	<0.03	<0.03	<0.03	<0.03
10 Zr	0.6	0.7	0.6	1.7

^a After pH adjustment boiled 5 min cooled and pH checked; ^b 0.2 ml of 30% H₂O₂ added before pH adjustment, boiled for 10 min, cooled and pH adjusted; ^c addition of 5 ml of 30% H₂O₂, boiled for 10 min and pH adjusted; ^d 1 g of tartaric acid added; ^e eluted with 1M-HNO₃ — sorbed from NaNO₃.

of tungstate, by reaction with CNS⁻ after preliminary reduction with a TiCl₃ solution, and aluminium as a coloured complex with chromazurol S. Mercury was determined using the Coleman MAS 50 mercurimeter.

Sorption of Accompanying Elements as a Function of the pH

Taking into account the determined values of the distribution coefficients for uranyl ions on silica gel in a medium of DTPA and the results obtained in a previous work², the sorption of accompanying metals was studied at pH 5.0 and 7.5 in solutions with an ionic strength of $I \leq 0.1$ and $I = 1$.

The results obtained by the procedure described at the end of this work are given in Table II. The values found are in agreement with the facts obtained previously. The amount of metals deposited increases with increasing pH and ionic strength. The noble metals (Au³⁺, Ag⁺, Pt⁴⁺) are exceptional; in this case, the amount sorbed on the gel is probably given by the sum of the partial reactions combined with reduction and absorption of the reduced form. The amount of titanium deposited is substantially higher compared with EDTA media⁵; however, its sorption is substantially decreased by addition of tartaric acid. The most effective substance for its masking during sorption is hydrogen peroxide, similar to Ce³⁺. The amount of Al³⁺ deposited is lower than in EDTA; in view of the analogy with Al³⁺, the value of

1% Ga^{3+} sorbed is not surprising. Be^{2+} , Sn^{4+} and Sb^{3+} are deposited on silica gel to a considerable degree, which is in agreement with the published data⁵⁻⁷.

Separation of Uranium from Accompanying Elements

Experiments were carried out according to the final procedure given in the present paper at $I \leq 0.1$ and $I = 1$, generally at pH 5–6, where the selectivity of the chromatographic process is highest. A 50% excess of DTPA over the ions separated was added to the solutions. As illustrated by the results obtained (Table III), the efficiency of the chromatographic separation of uranium is good even in complex mixtures. Because of the excess of DTPA used, larger columns (6.5 g) must be used, otherwise part of the uranium passes into the eluate. Tartaric acid increases the selectivity of the sorption process, especially when large titanium excesses are to be separated. The effective masking of Ti^{4+} with hydrogen peroxide creates the danger of incomplete sorption of uranium. When the content of Ti^{4+} is small, the hydrogen peroxide is not consumed by the formation of the ternary complex and anionic uranium peroxo-complexes, which are not quantitatively deposited on silica gel, are formed. Moreover, catalytic decomposition of peroxide occurs in the presence of iron, titanium (*e.g.* mixture 1 in Table III), DTPA, H_2O_2 and tartaric acid; decomposition products of the Fe^{3+} and Ti^{4+} complexes are formed and sorbed and are very difficult to elute. They cause brown colouration of the sorbent and a decrease in its sorption efficiency (mixture 1, 2 in Table III).

An excess of seriously interfering Ce^{3+} , Y^{3+} and La^{3+} ions, together with basic rock-forming elements, can be reliably separated by a single chromatographic operation. Among anions, chloride, nitrate and sulphate do not interfere. Sorption of uranium is quantitative even in the presence of fluoride; anionic complexes, incompletely sorbed on silica gel, are formed in the presence of a large excess of phosphate. However, sorption of uranium is quantitative up to a $\text{U(VI)} : \text{PO}_4^{3-}$ ratio of 1 : 700.

These results unambiguously indicate very good prospects for the use of DTPA in chromatographic isolation of trace amounts of uranium from complex solutions obtained on treatment of mineral materials. The selectivity of sorption from DTPA media is substantially higher than from EDTA (ref.⁸). The procedure proposed is simpler and easier to apply to a wide range of inorganic materials.

The following procedure is based on the described experiments: To a solution containing 10–200 μg U(VI) and the given accompanying elements (Table III), 0.1M-DTPA is added in a 50% excess or a 0.02M excess in a final volume of 250 ml of solution. The solution with an ionic strength of $I = 1$, with the pH adjusted to 5–6 is passed through a column containing 6.5 g of silica gel at a flow-rate of 1–1.5 ml/min. The column is washed with 50 ml of 0.02M-DTPA of the same pH and ionic strength and 50 ml of water. The sorbed uranium is then eluted with 50 ml of 1M-HCl. The solution is evaporated to a volume of 0.1–0.5 ml and 4 ml of 6M-HCl, 5 ml of

TABLE III
Separation of Uranium from Accompanying Elements with Various Components Added

pH	U sorbed, %	pH	U sorbed, %
mixture 1		mixture 6	
5.0	85.7 ^{b,e}	5.0	101.8 ^{a,d}
5.0	100 ^{a,e}	5.5	101.0 ^{a,d}
5.0	99.4 ^{a,d}	mixture 7	
5.5	95.8	5.0	99.6 ^d
5.0	96.2	5.5	99.1 ^d
5.5	99.0	mixture 8	
6.0	97.5	5.0	100.4 ^d
5.0	74.3 ^{a,c,d}	5.5	100.6 ^d
mixture 2		mixture 9	
5.0	100.8 ^{a,d}	5.0	100.5
5.0	83.5 ^{b,e}	5.5	101.5
5.5	101.7	mixture 10	
5.5	100.8	5.0	100.0 ^d
6.0	101.5	5.5	94.1
mixture 3		5.5	104.0 ^{a,d}
4.7	72.5	mixture 11	
5.0	50.0 ^d	5.0	99.4
5.5	52.5 ^d	5.5	98.1
6.0	88.2 ^a	mixture 12	
mixture 4		5.0	100.0
5.0	97.7	mixture 13	
5.5	94.1	5.5	100.6
mixture 5			
5.0	101.7 ^a		
5.5	98.6		
6.0	100.3 ^a		

35.7^a or 47.6 μg U(VI); the given amounts of oxides and metals added in the form of chlorides or nitrates, fluoride as NaF and phosphate as KH_2PO_4 . The column contained 6 or 2^b g of silica gel; volume of the sorbed solutions, 250 ml; 0.1M-DTPA at 50% excess. $I = 1$ (NaCl); 1 ml of 30% H_2O_2 added before sorption and the solution boiled for 2 min^c. The separation was performed with 5 g of tartaric acid added, or with Ig^d or in its absence^e.

TABLE III
(Continued)

mixture 1, mg:	204 Al ₂ O ₃ ; 100 Fe ₂ O ₃ ; 81 MgO; 84 CaO; 53 TiO ₂ ; 11 MnO
2	: ditto + 19 F ⁻
3	: ditto + 50 PO ₄ ³⁻
4	: ditto + 35 PO ₄ ³⁻
5	: ditto + 20 PO ₄ ³⁻
6	: ditto + 50 B ₂ O ₃ + 50 As(III)
7	: ditto + 0.1 (La, Y, Ce(IV))
8	: ditto + 5 (Cu, Ni, Pb, Cd, Zn, Co, Hg(II)).
9	: ditto + 5 (Sr, Bi); 1 (Sb(III), Sn(IV), Be)
mixture 10, mg:	ditto + 10 Cr(III) + 5 (V, Mo, W)
11	: ditto + 10 Ba + 1 (Ga, Sc) + 0.1 (Pt(IV), Pd(II), Au(III))
12	: ditto + 20 PO ₄ ³⁻ + 10 F + 5 (Cu, Pb, Zn, Ni, Co, Cr ^{III} , B ₂ O ₃) + 2 Sr + + 1 (V(V), Mo, Hg(II), Zr, Sn(IV), Bi, Ga, As(III)) + 0.1 Be + 0.05 Pt(IV)
13:	: ditto + 20 PO ₄ ³⁻ + 10 F ⁻ + 5 (Cu, Pb, Zn, Ni, Co, Cr(III), B ₂ O ₃) + 2 Sr + + 1 (Th, V(V), Mo, Hg(II), Zr, Sn(IV), Bi, Ga, As(III)) + 0.5 (Ce(IV), Y, Sc) + + 0.1 Be + 0.05 Pt(IV)

0.1M-TTHA, 0.5 ml of 3% H₂O₂ and 10 ml of 2.5M-monochloroacetic acid are added. The solution pH is adjusted to a value of 2.0 with 5M-NaOH. To the solution is then added 0.5 ml of 0.25% AZO, the mixture is diluted to the mark and the absorbance is measured at a wavelength of 656 nm against a reference solution containing AZO, TTHA, monochloroacetic acid and H₂O₂. Deviations from this procedure, during measurement of some dependences, are specified in the text.

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