Column Chromatographic Separation of Uranium(VI) with Poly(dibenzo-18-crown-6) from Hydrochloric Acid Medium

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A very simple method has been developed for the column chromatographic separation of uranium(VI) using poly(dibenzo-18-crown-6). The adsorption studies were carried out from hydrochioric acid medium in the concentration range of 0.5—10.0 mol dm^{-3}. The adsorption of uranium(VI) started from 3.0 mol dm^{-3} hydrochloric acid and was quantitative from 5.5—10.0 mol dm^{-3} hydrochloric acid. Various eluting agents such as hydrobromic acid, perchloric acid, sulfuric acid, acetic acid were used for the elution of uranium(VI). The capacity of poly(dibenzo-18-crown-6) for uranium(VI) was found to be 2.5 mmol g^{-1} of crown polymer. Uranium(VI) was separated from large number of elements from the binary as well as from multicomponent mixtures. The method was applied to the analysis of uranium from real samples.

During the past two decades a variety of crown ethers has been synthesized. In an analytical application, by polymerization or immobilisation on support materials, these crown ether ligands have been utilized as stationary phases for chromatographic separations. EDTA–diaminodibenzo-18-crown-6 condensation polymer was used[1] for the adsorption studies of uranium(VI). Sorption studies of uranium(VI) were carried out from various mineral acid medium using DB-18-C-6 carrier powder,[2] aliphatic dibasic acid condensation polymer with DB-18-C-6,[3] poly(B-15-C-5), poly(DB-24-C-8),[4] and divinylbenzene cryptand polymer.[5]

From the literature survey it is clear that no systematic efforts have been made for the use of poly(dibenzo-18-crown-6), abbrev. to poly(DB-18-C-16), for the adsorption chromatographic separation of uranium(VI) from other elements in binary as well as in multicomponent mixtures. We have therefore undertaken a systematic investigations of the adsorption chromatographic separation studies of uranium(VI) from hydrochloric acid medium on poly(DB-18-C-6) resin column.

Experimental

Apparatus and Reagents. Zeiss Spectrophotometer (German), a digital pH meter (Model LI-120 ELICO, India) with glass and calomel electrodes, a digital flame photometer (PEI, Model No. 041, India) and a Pyrex glass chromatographic colum (20×0.8 cm i.d.) with a glass wool plug at the bottom were used.

About 2.166 g of uranyl nitrate hexahydrate (AnalaR B.D.H.) was dissolved in 1000 cm^3 of distilled water containing 1% nitric acid. The solution was standardised gravimetrically.[6] It contained 1 mg cm^{-3} of uranium(VI), diluted solutions containing 50 μg cm^{-3} of uranium(VI) were prepared by appropriate dilution.

A crown ether polymer, (Poly(DB-18-C-6)) Merck (German) was used after screening to 100—200 mesh. Poly(DB-18-C-6) (0.8 g) was slurried with distilled deionized water and poured into a pyrex glass chromatographic column. The column was used after preconditioning with hydrochloric acid.

General Procedure. An aliquot of solution containing 50 μg of uranium(VI) was mixed with hydrochloric acid in the concentration range of 0.5—10.0 mol dm^{-3}. The solution was then passed through the column, perconditioned with hydrochloric acid of the same acidity as that of the sample solution, at a flow rate of 0.5 cm^3 min^{-1}. The colum was washed subsequently with hydrochloric acid of the same acidity. The adsorbed uranium(VI) was then eluted with different eluting agents (described later) at a flow rate of 0.5 cm^3 min^{-1}, 2 cm^3 fractions were collected, after evaporating the acid it was extracted with water and the uranium(VI) content was determined spectrophotometrically with 4-(2-pyridylazo) resorcinol (PAR) at 530 nm.[7] The concentration of uranium(VI) was calculated from the calibration curve.

Results and Discussion

Adsorption of Uranium(VI) as a Function of Hydrochloric Acid concentration on Poly(DB-18-C-6). In order to ascertain the optiumum concentration of hydrochloric acid required for the quantitative adsorption of uranium, systematic studies of the adsorption of uranium(VI) on poly(DB-18-C-6) were conducted by varying the concentration of hydrochloric acid from 0.5—10 mol dm^{-3} (Fig. 1). It was found that there was no adsorption of uranium(VI) from 0.5—2.0 mol dm^{-3} hydrochloric acid. Adsorption started at 2.5 mol dm^{-3} (2%). It was 92% at 0.5 mol dm^{-3} and was quantitative from 5.5—10.0 mol dm^{-3} hydrochloric acid. Hence subsequent adsorption studies of uranium(VI) were carried out from 6 mol dm^{-3} hydrochloric acid concentration.

Elution Studies of Uranium(VI). After adsorption, uranium(VI) was eluted from the column with various eluents such as hydrobromic acid, perchloric acid, sulfuric acid, acetic acid in the concentration range of 0.5—7.0 mol dm^{-3} and hydrochloric acid in the cencentration range of 0.5—2.5 mol dm^{-3}. Various elution studies revealed that there was quantitative elution of uranium(VI) from 0.5—2.5 mol dm^{-3} hydrochloric acid. 0.5—2.0 mol dm^{-3} hydrobromic acid. From 3.0—7.0

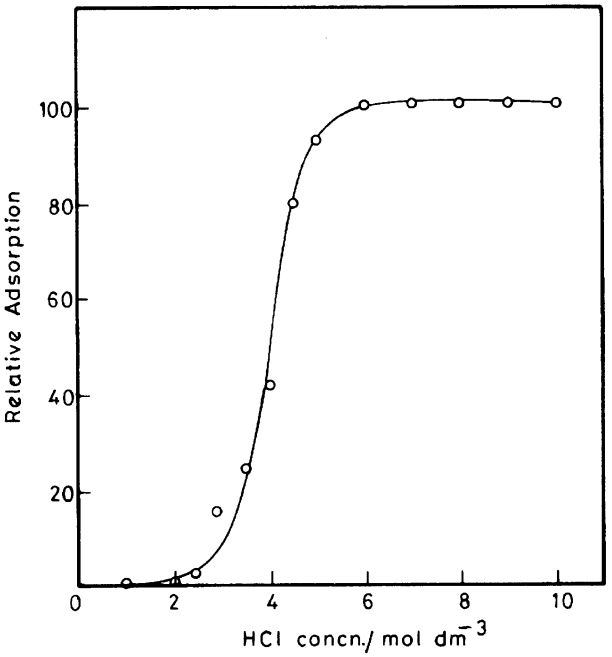

Fig. 1. Adsorption of uranium(VI) as a function of HCl concentration on poly(dibenzo-18-crown-6).

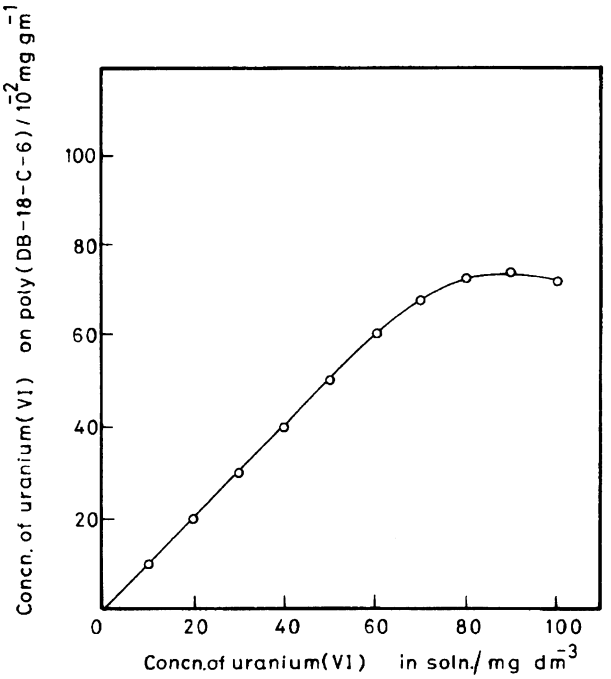

Fig. 2. Adsorption isotherm of uranium.

mol dm^{-3} hydrobromic acid, the recovery of uranium was decreased continuously probably because of formation of adsorbable bromo complex. With 3 mol dm^{-3} hydrobromic acid the recovery of uranium(VI) was 98%, with 5 mol dm^{-3} hydrobromic acid it was 88%, and with 7 mol dm^{-3} hydrobromic acid the recovery was only 18%. With perchloric acid there was quantitative elution of uranium(VI) from 1.0—7.0 mol dm^{-3}. With sulfuric acid, there was quantitiative elution in the concentration range of 0.5—7.0 mol dm^{-3} but with acetic acid there was 72% elution with 0.5 mol dm^{-3}, 90% with 3.0 mol dm^{-3} and quantitative at 4 mol dm^{-3} again the elution of uranium(VI) decreased from 0.5—7.0 mol dm^{-3} acetic acid. The total volume of the eluent required for the recovery of uranium(VI) was in the range of 10—15 cm^3. For further studies 1 mol dm^{-3} hydrochloric acid was used as eluting agent.

Effect of Varying Concentration of Uranium(VI). Adsorption studies of uranium(VI) were carried out from 6 mol dm^{-3} hydrochloric acid on 1.0 g of poly(DB-18-C-6) resin column. The concentration of uranium was varied from 10—100 mg dm^{-3}. 10 cm^3 solution was passed through the column. After adsorption, uranium(VI) from the column was eluted with 1 mol dm^{-3} hydrochloric acid. From Fig. 2 it is clear that there was quantitative adsoprtion of uranium(VI) upto 60 mg dm^{-3} concentration. The extent of adsorption decreased with an increase in the concentration of uranium(VI). The adsorption isotherm of uranium(VI) is shown in Fig. 2. The capacity of poly(DB-18-C-6) for uranium(VI) was calculated from Langmuir plot.[8] The capacity of poly(DB-18-C-6) for uranium(VI) was found to be 2.52 mmol g^{-1}.

Separation of Uranium(VI) from Binary Mixtures. An aliquot of solution containing uranium(VI) and the foreign ions to be tested was taken and hydrochloric acid was added so that its concentration was 6 mol dm^{-3} in a total volume of 10 cm^3. The tolerance limit was set as the amount of foreign ion required to cause ±2% error in the recovery of uranium(VI). The solution was then passed through poly(DB-18-C-6) resin column preconditioned with 6 mol dm^{-3} hydrochloric acid at a flow rate of 0.5 cm^3 min^{-1}. Subsequently the column was washed with 6 mol dm^{-3} hydrochloric acid. Those foreign ions which were not adsorbed on the poly(DB-18-C-6) resin passed through the column. The effluent was collected and was analysed for the foreign ion content. Most of the foreign ions were not adsorbed (Table 1). Amongst the alkali metals sodium was adsorbed to the extent of 70%, potassium 80%, and rubidium 90%. Amongst the alkaline earth elements, only strontium and barium were adsorbed quantitatively. From the nontransiiton metals thallium(III) and from transition elements molybdenum(VI) was adsorbed quantitatively. Most of the anions were tolerated in higher proportions. At 1.5 mol dm^{-3} hydrochloric acid concentration uranium(VI) and sodium were not adsorbed, whereas thallium(III), potassium(I), and lead(II) were adsorbed quantitatively, whereas rubidium(I) (80%), molybdenum(VI) (90%). The adsorbed potassium and rubidium at 1.5 mol dm^{-3} hydrochloric acid could be eluted by washing the column with water and lead was eluted with 6 mol dm^{-3} hydrochloric acid and molybdenum(VI) was eluted with 0.5 mol dm^{-3} aqueous ammonia. These conditions could be

Table 1. Separation of Uranium(VI) from Binary Mixtures

Ion	Added as	Tolerance limit/mg
1	2	3
Li(I)	LiCl	5.0
*Na(I)	NaCl	7.0
*K(I)	KCl	8.0
*Rb(I)	RbCl	8.0
Cs(I)	CsCl	6.0
NH_4(I)	NH_4Cl	7.0
Be(II)	$Be(NO_3)_2 \cdot 4H_2O$	6.0
Mg(II)	$MgCl_2 \cdot 6H_2O$	8.0
Ca(II)	$CaCl_2$	7.5
*Sr(II)	$Sr(NO_3)_2$	4.0
*Ba(II)	$Ba(NO_3)_2$	3.0
Co(II)	$CoCl_2 \cdot 6H_2O$	1.0
Ni(II)	$NiCl_2 \cdot 6H_2O$	2.0
Cu(II)	$CuCl_2 \cdot 2H_2O$	0.5
Zn(II)	$ZnCl_2$	2.0
Mn(II)	$MnCl_2 \cdot 4H_2O$	2.0
Sn(II)	$SnCl_2 \cdot 2H_2O$	2.0
Pb(II)	$Pb(NO_3)_2$	1.5
Cr(III)	$Cr(NO_3)_3 \cdot 9H_2O$	6.0
Fe(III)	$FeCl_3 \cdot 6H_2O$	0.2
Al(III)	$Al(NO_3)_3 \cdot 9H_2O$	2.5
La(III)	$La(NO_3)_3 \cdot 6H_2O$	8.0
Ce(III)	$CeCl_3 \cdot 6H_2O$	6.0
Bi(III)	$Bi(NO_3)_3 \cdot 5H_2O$	1.0
In(III)	$InCl_3$	3.5
*Tl(III)	$Tl(NO_3)_3 \cdot 3H_2O$	0.5
Sb(III)	$SbCl_3$	4.0
Ge(IV)	Na_2GeO_3	2.5
Th(IV)	$Th(NO_3)_4$	4.0
V(V)	$VOSO_4 \cdot H_2O$	5.0
*Mo(VI)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1.0
W(VI)	$Na_2WO_4 \cdot 2H_2O$	3.0
Br^-	HBr	9.0
I^-	HI	12.0
NO_3^-	HNO_3	10.0
SCN^-	NaSCN	7.0
ClO_4^-	$HClO_4$	6.0
CH_3COO^-	CH_3COOH	10.0
$C_2O_4^{2-}$	$H_2C_2O_4$	6.0
PO_4^{3-}	H_3PO_4	7.0
BO_3^{3-}	H_3BO_3	6.0
Ascorbate	Ascorbic acid	7.0
Tartrate	Tartaric acid	6.0
Citrate	Citric acid	6.5
EDTA	EDTA	8.0

* Adsorbed. U(VI), 50 μg, Poly(DB-18-C-6), 6 mol dm^{-3} HCl (adsorption), 1 mol dm^{-3} HCl (elution).

exploited for the separation of uranium(VI) from potassium, rubidium, lead, molybdenum and other elements.

Separation of Uranium(VI) from Multicomponent Mixtures. In developing a method for the separation of uranium(VI) from various elements in multicomponent mixtures the adsorbing property of uranium(VI) at different hydrochloric acid concentration was explored. When a mixture containing uranium(VI), potassium(I)/rubidium(I), lead(II), and molybdenum(VI) was passed through the column at 1.5 mol dm^{-3} hydrochloric acid at a flow rate of 0.5 cm^3 min^{-1}, uranium(VI) was not adsorbed on the column, hence passed through the column, whereas potassium(I)/rubidum(I), lead(II), and molybdenum(VI) were adsorbed quantitatively. The adsorbed potassium(I)/rubidium(I) was eluted by washing the column with water. Lead was then eluted with 6 mol dm^{-3} hydrochloric acid and finally molybdenum was eluted with 0.5 mol dm^{-3} aqueous ammonia.

When a mixture of lead, uranium and molybdenum was passed through the column at 6 mol dm^{-3} hydrochloric acid, lead was not adsorbed, hence passed through the column. The adsorbed uranium was eluted with 1 mol dm^{-3} hydrochloric acid and finally molybdenum was eluted with 0.5 mol dm^{-3} aqueous ammonia.

When a mixture of thorium, uranium, and molybdenum was passed through the column at 6 mol dm^{-3} hydrochloric acid, thorium was not adsorbed hence passed through the column. The adsorbed uranium was eluted with 1 mol dm^{-3} hydrochloric acid and finally molybdenum was eluted with 0.5 mol dm^{-3} aqueous ammonia.

When a mixture of cerium, uranium, and molybdenum was passed through the column at 6 mol dm^{-3} hydrochloric acid, cerium was not adsorbed, hence passed through the column. The adsorbed uranium was eluted with 1 mol dm^{-3} hydrochloric acid and finally molybdenum was eluted with 0.5 mol dm^{-3} aqueous ammonia.

The separation of uranium(VI) from other multicomponent mixtures was accomplished similarly (Table 2).

Application to Analysis of Uranium from Geological Samples and Animal Bone. The synite rock sample (SY-II), monizite sand, and animal bone sample (IAEA-A-3/1) was brought into solution as per the procedure described earlier.[9] An aliquot of sample solution was then treated with hydrochloric acid so as to have its concentration of 6 mol dm^{-3} in a total volume of 10 cm^3. The solution was then passed through poly(DB-18-C6) resin column, preconditioned with 6 mol dm^{-3} hydrochloric acid, at a flow rate of 0.5 cm^3 min^{-1}. Under these conditions thorium, cerium, yttrium, calcium were not extracted whereas uranium, sodium, potassium, rubidium, strontium, barium were extracted. From the coumn only uranium(VI) was eluted with 2 mol dm^{-3} hydrochloric acid. The effluent was evaporated and extracted with water and the uranium content was determined spectrophotometrically with PAR. The amount of uranium found in synite rock sample was 282 ppm as against the reported value of 280 ppm. In monizite sand it was 0.31% as against the standard value of 0.30% and in animal bone the amount of uranium found was 395 ppm as against the reported value of 400 ppm.

The important feature of this method is that the column chromatographic separation of uranium(VI) from hydrochloric acid medium on poly(DB-18-C-6) has been achieved. The separation of uranium has been carried

Table 2. Separation of Uranium(VI) from Multicomponent Mixtures

No.	Mixture	Taken	Found	Recovery	Adsorbing	Eluent
		mg	mg	%	condition	
1	2	3	4	5	6	7
1	U(VI)	0.05	0.05	100	1.5M HCl,NAPC	—
	K/Rb	0.10	0.10	100	1.5 M MCl	H_2O
	Pb	0.05	0.05	100	1.5 M HCl	6 M HCl
	Mo(VI)	0.50	0.49	98	1.5 M HCl	0.5 M aq NH_3
2	Pb	0.05	0.05	100	6 M HCl,NAPC	—
	U(VI)	0.05	0.049	98	6 M HCl	1 M HCl
	Mo(VI)	0.50	0.50	100	6 M HCl	0.5 M aq NH_3
3	Th	0.10	0.10	100	6 M HCl, NAPC	—
	U(VI)	0.05	0.05	100	6 M HCl	1.0 M HCl
	Mo(VI)	0.50	0.50	100	6 M HCl	0.5 M aq NH_3
4	Ce(III)	0.10	0.099	99	6 M HCl,NAPC	—
	U(VI)	0.05	0.05	100	6 M HCl	1.0 M HCl
	Mo(VI)	0.50	0.49	98	6 M HCl	0.5 M aq NH_3
5	Cr(III)	1.00	0.99	99	6M HCl, NAPC	—
	U(VI)	0.05	0.05	100	6M HCl	1.0 M HCl
	Mo(VI)	0.50	0.49	98	6M HCl	0.5M aq NH_3
6	La	0.10	0.10	100	6M HCl, NAPC	—
	U(VI)	0.05	0.05	100	6M HCl	1.0 M HCl
	Mo(VI)	0.50	0.50	100	6M HCl	0.50 M aq NH_3
7	V(V)	0.10	0.10	100	6M HCl, NAPC	—
	U(VI)	0.05	0.05	100	6M HCl	1.0 M HCl
	Mo(VI)	0.50	0.49	98	6M HCl	0.5 M aq NH_3
8	Co	0.10	0.098	98	6M HCl, NAPC	—
	U(VI)	0.05	0.05	100	6M HCl	1.0 M HCl
	Mo(VI)	0.50	0.50	100	6M HCl	0.5 M aq NH_3
9	Cs	0.10	0.10	100	6M HCl, NAPC	—
	U(VI)	0.05	0.05	100	6M HCl	1.0 M HCl
	Mo(VI)	0.50	0.49	98	6M HCl	0.5 M aq NH_3

1 M=1 mol dm^{-3}, NAPC: No adsorption passing through the column.

out from potassium/rubidium, lead, molybdenum, and other elements such as thorium, cerium, chromium, lanthanum, vanadium, cobalt, cesium. The separation of uranium from thorium, cesium, lead, molybdenum is of great significance because these elements are usually associated with nuclear fission product and medium active waste. The method has been used for the analysis of uranium in real sample. The method is very simple, rapid, selective, and reproducible. The recovery of uranium in all instances from duplicate determinations is 100±2%. The reproducibility of the procedure is ±2%.

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