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SOLVENT EXTRACTION SEPARATION OF URANIUM(VI) WITH DIBENZO-24-CROWN-8

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Uranium(VI) was quantitatively extracted with 0.01M DB-24-crown-8 in nitrobenzene from 6 to 10M hydrochloric acid. From the organic phase uranium was stripped with 2M nitric acid and determined spectrophotometrically with PAR at 530 nm. Uranium(VI) was separated from a large number of elements in binary mixtures as well as from multicomponent mixtures. The method was extended to the analysis of uranium in geological samples and animal bone.

Introduction

In view of nuclear industry, separation of uranium from associated elements is very important. Crown ethers have been used for the extraction analysis studies[1] and also for the evaluation of thermodynamic parameters of uranium[2] with various crown ethers. 18-Crown-6 and its derivatives have been used for the complexation studies of UO_2^{2+} in propylene carbonate by using a Na^+ selective glass electrode[3] and by potentiometric and spectrophotometric methods.[4–6] In photoreduction studies, 18-Crown-6 was used to bind photoreduced uranium(III) from uranium(IV) using a high peak power KrF laser.[7] Synergistic extraction studies of uranium(VI) with crown ethers have been reported in presence of di(1-methylheptyl) methyl phosphonate,[8] HTTA[9] and acylpyrazolones.[10] Exraction constants and other thermodynamic parameters were determined for uranium(VI) from nitric acid media with various crown ethers in methylene chloride[11] and benzonitrile[12] as diluents. An unsuccessful attempt was made for extraction of uranium from nitrate, chloride, acetate and perchlorate media with crown ethers in dichloroethane and cyclohexanone as diluents.[13] Isotope separation of uranium(IV)[14] and uranium(VI)[15] have been reported with various crown ethers. Dicyclohexano derivatives of crown ethers have been used for the extraction of uranium(IV)[16] and uranium(VI)[17–19] from hydrochloric acid media, where in the ratio of metal to ligand was 1 : 2. The effect of HCl and LiCl concentration was studied on the distribution of uranium(VI) with various crown ethers in dichloroethane as diluent.[20] The extraction of

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tetra- and hexavalent uranium was studied with DB-18-crown-6 from hydrochloric acid medium in which extraction of uranium increased when a small amount of potassium was added.[21] Extractive separation studies of uranium(VI) have been reported with dicyclohexano-18-crown-6 in chloroform as diluent[22] but with dibenzo-24-crown-8 the extraction of uranium(VI) was less than 10%.

So far no systematic efforts have been made for the use of dibenzo-24-crown-8 for the investigation on the possible extraction of uranium(VI). This paper describes the systematic investigation of the solvent extraction separation of uranium(VI) from associated elements with dibenzo-24-crown-8 in nitrobenzene as diluent from hydrochloric acid medium. The method has been extended to the separation of uranium(VI) from a large number of elements and also to the analysis of uranium in real samples.

Experimental

Equipment and reagents

A 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 wrist action flask shaker were used.

About 2.166 g of uranyl nitrate hexahydrate (AnalaR B.D.H.) was dissolved in 1000 ml of distilled water containing 1% nitric acid. The solution was standardized gravimetrically.[23] It contained 1 mg/ml of uranium(VI), diluted solutions containing 50 μg/ml of U(VI) were prepared by appropriate dilution.

Nitrobenzene solutions (0.01M) of 18-crown-6 (Fluka, A. G.), 12-crown-4, 15-crown-5, DB-18-crown-6, DC-18-crown,-6, DB-24-crown-8 and DC-24-crown-8 (Aldrich) were used without further purification.

General procedure

To an aliquot of a solution containing 50-90 μg uranium(VI), hydrochloric acid was added so as to reach a concentration of 7M in a total volume of 10 ml. The solution was then transferred to a separating funnel and was equilibrated with 10 ml of 0.01M suitable crown ether with nitrobenzene as the diluent for 10 min on a wrist action flask shaker. The two phases were allowed to settle and separate. Uranium(VI) was stripped from the organic phase with 10 ml of 2M nitric acid. It was then determined spectrophotometrically with PAR at 530 nm.[24] The concentration of uranium(VI) was calculated from the calibration curve.

Results and discussion

Extraction of uranium as a function of hydrochloric acid concentration

The extraction of uranium was studied at various hydrochloric acid concentrations. The optimum acid concentration for the quantitative extraction of uranium was ascertained by extracting uranium with 0.01M of various crown ethers in nitrobenzene as the diluent. The hydrochloric acid concentration was varied from 1 to 10M. The results in Fig. 1 show that amongst various crown ethers DB-24-crown-8 proved to be suitable for the quantitative extraction of uranium from 6 to 10M hydrochloric acid concentration. The extent of the extraction of uranium was 76% at 6M HCl with 18-crown-6, 90% at 9M HCl with DB-18-crown-6, 84% with DC-18-crown-6 and 88% with DC-24-crown-8 at 5-6M HCl. There was no extraction with 12-crown-4, 15-crown-5 in the concentration range of 1 to 10M hydrochloric acid. The main feature of the method using DB-24-crown-8 instead of DC-18-crown-6[22] is that the latter has high water solubility, whereas DB-24-crown-8 is not soluble in water, which helps in repeated use of the extractant. At the same time the concentration of DC-18-crown-6 required was fairly high. With DC-18-crown-6 the extraction of uranium(VI) was 67% at 0.0005M, 85.7% at 0.01M and was quantitative from 0.01825M of DC-18-crown-6,

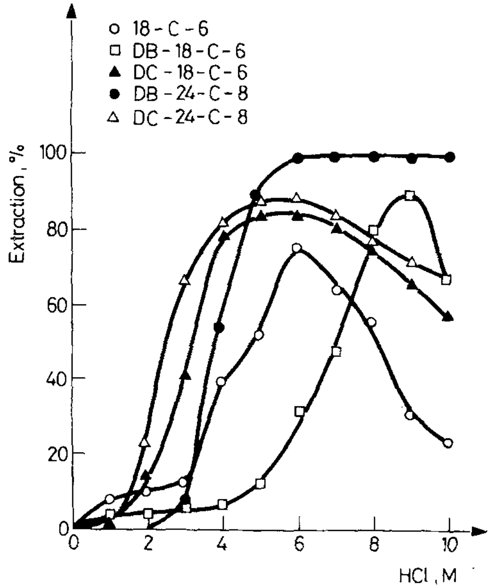

Fig. 1. Extraction of uranium as a function of HCl concentration with various crown ethers and nitrobenzene as diluent

whereas with DB-24-crown-8 there was quantitative extraction of uranium using the crown ether of 0.004 to 0.1M concentration. For further studies DB-24-crown-8 in nitrobenzene was used and the extraction experiments were carried out at 7M HCl concentration. In order to study the effect of anion on the extraction of uranium, an attempt was made to extract uranium in the presence of 0.01M picric acid with 0.01M DB-24-crown-8 in nitrobenzene. It was found that there was no extraction of uranium from 0.01M picric acid. This condition was exploited for the separation of uranium from elements (see later).

Effect of crown ether concentration

The optimum concentration of DB-24-crown-8 required for the quantitative extraction of uranium was ascertained by extracting uranium at 7M hydrochloric acid with varying concentrations of DB-24-crown-8 in nitrobenzene. The extraction started at 0.0003M (10%) and was quantitative (100%) with 10 ml of 0.004M of DB-24-crown-8. For further studies 10 ml of 0.01M DB-24-crown-8 in nitrobenzene was used.

Effect of the solvents used

The extraction of uranium was carried out with DB-24-crown-8 at 7M hydrochloric acid with various solvents such as benzene, toluene, xylene, carbon tetrachloride, chloroform, methylene chloride, ethylene chloride, tetrachloroethane, nitrobenzene and nitromethane. The phase volume ratio was maintained at unity. The studies revealed that there was quantitative extraction of uranium with nitrobenzene and nitromethane as diluents, whereas with the other solvents the extraction was less than 5%. Because of the very low solubility of nitrobenzene in water further studies were carried out with nitrobenzene.

Nature of the extracted species

An attempt was made to ascertain the probable composition of the extracted species by extracting uranium at 7M hydrochloric acid with DB-24-crown-8 in nitrobenzene in the concentration range of 0.0001 to 0.004M. The extraction of uranium(VI) was 2% with 0.0001M, 24% with 0.0005M, 53% with 0.001M and was quantitative (100%) with 0.004M DB-24-crown-8. The plot of log D vs. log {DB-24-crown-8} gave a slope of 1.88. Hence the probable composition of the extracted species is 1 : 2 ($H_2UO_2Cl_4$: 2DB-24-C-8). Uranium(VI) forms the anionic species $(UO_2Cl_4)^{2-}$. This finding is in agreement with earlier work.[21]

Time of equilibration and choice of stripping agents

In order to ascertain the optimum time of extraction, the equilibrations were performed for various periods of time (1-60 min). It was found that with 1 minute of equiilibration, there was quantitative extraction of uranium. Further studies were carried out with 10 min equilibration period.

After extraction of uranium from 7M hydrochloric acid with DB-24-crown-8 in nitrobenzene as diluent, uranium from the organic phases was stripped with various stripping agents in the concentration range of 0.01 to 10M. The stripping of uranium was quantitative with 0.01 to 2M hydrochloric acid, 0.5 to 4M nitric acid, 4 to 8M sulfuric acid, 0.01 to 0.1M acetic acid. With 6M perchloric acid stripping was only 86%; with 7-8M hydrobromic acid there was back-extraction of uranium into the organic phase due to formation of extractable bromo complex species.

Separation of uranium from binary mixtures

Uranium was extracted in the presence of various ions (Table 1). Most of the foreign ions were added as either metal chloride or metal nitrate salts and in case of Ti(IV), Nb(V) and Ta(V) their oxalate salts were used. The tolerance limit was set as the amount of foreign ions required to cause ±2% error in the recovery of uranium.

Table 1
Separation of uranium(VI) from binary mixtures; U = 0.05 mg, DB-24-crown-8, 0.01M in nitrobenzene, 7M HCl

Ion	Added as	Tolerance limit, mg
Li^+	$LiCl$	7.50
Na^+	$NaCl$	6.50
K^+	KCl	6.00
Rb^+	$RbCl$	1.00
Cs^+	$CsCl$	0.85
NH_4^+	NH_4Cl	5.00
Be^{2+}	$Be(NO_3)_2 \cdot 4H_2O$	0.10
Mg^{2+}	$MgCl_2 \cdot 6H_2O$	1.20
Ca^{2+}	$CaCl_2$	8.50
Sr^{2+}	$Sr(NO_3)_2$	7.00
Ba^{2+}	$Ba(NO_3)_2$	3.50
Co^{2+}	$CoCl_2 \cdot 6H_2O$	0.30
Ni^{2+}	$NiCl_2 \cdot 6H_2O$	1.00
Pb^{2+}	$Pb(NO_3)_2$	0.40
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	1.00
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	3.50

Table 1 cont.

Ion	Added as	Tolerance limit, mg
Fe^{3+}	$FeCl_3 \cdot 6H_2O$	0.30
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	1.80
Y^{3+}	$Y(NO_3)_3$	0.30
La^{3+}	$La(NO_3)_3 \cdot 6H_2O$	2.00
Ce^{3+}	$CeCl_3 \cdot 6H_2O$	1.00
Bi^{3+}	$Bi(NO_3)_3 \cdot 5H_2O$	0.50
Ru^{3+}	$RuCl_3 \cdot XH_2O$	5.00
Rh^{3+}	$RhCl_3 \cdot XH_2O$	5.50
Sb^{3+}	$SbCl_3$	6.00
Ti^{4+}	$K_2TiO(C_2O_4)_2 \cdot 2H_2O$	0.50
V^{4+}	$VOSO_4 \cdot H_2O$	0.40
Th^{4+}	$Th(NO_3)_4$	0.60
Zr^{4+}	$Zr(NO_3)_4 \cdot 4H_2O$	0.05
V^{5+}	NH_4VO_3	0.10
Ta^{5+}	$(NH_4)_3\{TaO(C_2O_4)_3\}$	3.00
Nb^{5+}	$(NH_4)_3\{NbO(C_2O_4)_3\}$	0.80
W^{6+}	$Na_2WO_4 \cdot 2H_2O$	0.05
Mo^{6+}	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.05
Br^{+}	HBr	8.00
I^{-}	HI	5.00
NO_3^{-}	HNO_3	7.00
SCN^{+}	NaSCN	2.00
ClO_4^{-}	$HClO_4$	1.20
CH_3COO^{-}	CH_3COOH	2.50
SO_4^{2-}	H_2SO_4	1.00
C_2O_4	$H_2C_2O_4$	4.00
PO_4^{3-}	H_3PO_4	0.50
BO_3^{3-}	H_3BO_3	2.00
Ascorbate	Ascorbic acid	3.00
Tartrate	Tartaric acid	2.00
EDTA	EDTA	5.00

Amongst the transition metals tungsten(VI), zirconium(IV) and molybdenum(VI) were tolerated in a 1 : 1 ratio. Alkali and alkaline earth metals were tolerated in higher ratios. For beryllium and vanadium(V) the tolerance limit was lower (1:2). Most of the non-transition elements and anions were tolerated in higher ratios. Amongst the diverse ions only molybdenum(VI) and iron(III) were co-extracted with uranium and their tolerance limit was very low.

Separation of uranium from multicomponent mixtures

Uranium(VI) was extracted with DB-24-crown-8 in nitrobenzene as diluent from 7M hydrochloric acid. Under these conditions there was no extraction of barium and rubidium, but from 0.01M picric acid there was quantitative extraction of barium and rubidium with DB-24-crown-8 in nitrobenzene. This property was exploited for the separation of uranium from multicomponent mixtures using DB-24-crown-8. A mixture of uranium(VI), barium and thorium was separated by extracting uranium(VI) from 7M hydrochloric acid with 0.01M DB-24-crown-8. When barium and thorium remained in the aqueous phase, the aqueous phase was evaporated to dryness and was then treated with water from which barium was extracted with 0.01M DB-24-crown-8 in nitrobenzene after addition of 0.01M picric acid, whereas thorium remained in the aqueous phase. Uranium(VI) and barium from the respective organic phases were stripped with 2M nitric acid.

A mixture of uranium(VI), rubidium and strontium was separated by extracting uranium(VI) from 7M hydrochloric acid with 0.01M DB-24-crown-8. When rubidium and strontium remained in the aqueous phase, the aqueous phase was evaporated to dryness and was treated with water, from which rubidium was extracted with 0.01M DB-24-crown-8 in nitrobenzene after addition of 0.01M picric acid, whereas strontium remained in the aqueous phase. Uranium(VI) and rubidium from the respective organic phases were stripped with 2M nitric acid.

When a mixture containing uranium(VI), barium and cerium(III) was extracted with 0.01M DB-24-crown-8 from 7M hydrochloric acid, barium and cerium(III) remained in the aqueous phase, which was then evaporated to dryness and was treated with water from which barium was extracted with 0.01M DB-24-crown-8 in nitrobenzene from 0.01M picric acid. Cerium(III) remained in the aqueous phase. Uranium(VI) and barium from the respective organic phases were stripped with 2M nitric acid. 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

Syenite rock sample (SY-II) was brought into solution by the procedure described earlier.[25] 1.0 g of monozite sample was dissolved in a mixture of nitric and sulfuric acid. Silica was separated by filtration and the solution was diluted to 100 ml with distilled water. 1.0 g animal bone sample (IAEA-A-3/1) was dissolved in a mixture of nitric and perchloric acid. After evaporation it was extracted with distilled water and diluted to 25 ml. In case of syenite rock an aliquot of sample solution was taken and iron was removed by ether extraction from 6M hydrochloric acid and then it was used for

Table 2
Analysis of uranium(VI) in ternary mixtures

No.	Mixture	Taken, mg	Found, mg	Recovery, %	Extractant	Stripping agent
1	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M picric acid	2M HNO_3
	Th	0.50	0.50	100	Aqueous phase	–
2	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Rb	1.00	0.99	99	DB-24-C-8, 0.01M picric acid	2M HNO_3
	Sr	0.50	0.50	100	Aqueous phase	–
3	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M picric acid	2M HNO_3
	Ce(III)	0.50	0.50	100	Aqueous phase	–
4	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Rb	1.00	0.98	98	DB-24-C-8, 0.01M picric acid	2M HNO_3
	Th	0.50	0.50	100	Aqueous phase	–
5	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	0.99	99	DB-24-C-8, 0.01M picric acid	2M HNO_3
	Sr	0.50	0.49	98	Aqueous phase	–
6	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Rb	1.00	1.00	100	DB-24-C-8, 0.01M picric acid	2M HNO_3
	La	1.00	0.99	99	Aqueous phase	–
7	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M picric acid	2M HNO_3
	Ru	1.00	1.00	100	Aqueous phase	–
8	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M picric acid	2M HNO_3
	La	1.00	1.00	100	Aqueous phase	–
9	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M picric acid	2M HNO_3
	Cr(III)	1.00	1.00	100	Aqueous phase	–
10	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	0.98	98	DB-24-C-8, 0.01M picric acid	2M HNO_3
	Y	0.20	0.20	100	Aqueous phase	–

uranium extraction. To an aliquot of solution containing uranium, 2 mg of EDTA was added to mask other elements and then it was extracted with 0.01M DB-24-crown-8 in nitrobenzene from 7M hydrochloric acid. Under these conditions thorium, cerium, yttrium, calcium, and sodium were not extracted. From the organic phase uranium was stripped with 2M nitric acid and determined spectrophotometrically. The amount of uranium found in syenite rock sample was 284 ppm as opposed to the reported value of 280 ppm. In monozite sand it was 0.29% as against the standard value of 0.30% and in animal bone the amount of uranium found was 390 ppm as compared to the reported value of 400 ppm.

Conclusion

The important feature of the method described is that it permits the separation of uranium from thorium, cerium, barium, rubidium, strontium, lanthanum, yttrium, chromium, which are usually present in nuclear fission products. The method was used for the analysis of uranium in geological samples and an animal bone sample. The extractant DB-24-crown-8 in nitrobenzene can be reused. The method is simple, rapid, selective and reproducible.

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