

## Liquid-liquid extraction separation of uranium(VI) from associated elements using dibenzo-24-crown-8 from hydrobromic acid medium

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Liquid-liquid extraction of uranium (VI) from hydrobromic acid solutions with dibenzo-24-crown-8 in nitrobenzene have been investigated. Uranium(VI) was quantitatively extracted from 6.0–8.0M hydrobromic acid with 0.001–0.01M dibenzo-24-crown-8 and was quantitatively stripped from the organic phase with 0.1–1.0M hydrochloric acid, 0.5–10M nitric acid, 2–10M perchloric acid, 3.0–10M sulfuric acid or 3.0–10M acetic acid. It was possible to separate uranium(VI) from a number of elements in binary mixtures. Most of the elements showed very high tolerance limit. Uranium(VI) was also separated from a number of associated elements in multicomponent mixtures. The method is very simple, selective, rapid and highly reproducible (approximately  $\pm 2\%$ ) and was applied to the analysis of uranium in geological samples.

### Introduction

The crown ether compounds have received much attention as new types of extractants in liquid-liquid extracting systems. The use of crown ethers for the separation of uranium(VI) from associated elements is very limited.<sup>1</sup> The partitioning behavior of uranyl ion and other actinides was investigated with 15-crown-5 and 18-crown-6 from polyethylene glycol and ammonium sulphate.<sup>2</sup> Synergistic extraction studies of uranium and other actinide elements are reported with 1-phenyl-3-methyl-4-benzylpyrazolone (PMBP)<sup>3</sup> and thenoyl trifluoroacetone (TTA).<sup>4</sup> The trends in uranium extraction with various crown ethers from nitric acid medium were studied<sup>5</sup> and it was found that they were weak extractants for uranium. Synergistic extraction of uranium(VI) has been carried out using various crown ethers and  $\beta$ -diketones from nitric acid medium and the extraction constants of chelates and the synergistic factors were evaluated.<sup>6</sup> From the literature survey it is clear that no systematic efforts have been made for the separation of uranium(VI) from the associated elements using this type of compound. This paper describes the systematic investigation of the liquid-liquid extraction separation of uranium(VI) from thorium, cesium, rubidium, lanthanum, cerium, lithium, beryllium and yttrium with dibenzo-24-crown-8 in nitrobenzene from hydrobromic acid medium. The method has been applied for the analysis of uranium in geological samples.

### Experimental

#### Equipment and reagents

A Zeiss spectrophotometer, a digital pH meter, with glass and calomel electrodes, a digital flame photometer, a wrist action flask shaker and 125 ml separating funnels were used.

A stock solution of uranium(VI) was prepared by dissolving 2.166 g of uranyl nitrate hexahydrate (AnalaR BDH) in 1000 ml of distilled deionised water and standardized gravimetrically.<sup>7</sup> A solution containing 100  $\mu\text{g/ml}$  of uranium(VI) was prepared by appropriate dilution of the standard stock solution.

Solutions of crown ethers were prepared from 15-crown-5, benzo-15-crown-5, 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6, dibenzo-24-crown-8, dicyclohexano-24-crown-8 (Aldrich, USA) without further purification. Hydrobromic acid (Merck) was also used as received.

#### General procedure

Hydrobromic acid was added in the concentration range of 0.5–8.0M in a total volume of 10 ml to an aliquot of a solution containing 100  $\mu\text{g}$  uranium(VI). The solution was then transferred to a separating funnel and was equilibrated with 10 ml of a 0.005M solution containing suitable crown ether with nitrobenzene as the diluent for 10 minutes, 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 and determined spectrophotometrically with PAR at 530 nm.<sup>8</sup> The concentration of uranium(VI) was calculated from the calibration graph.

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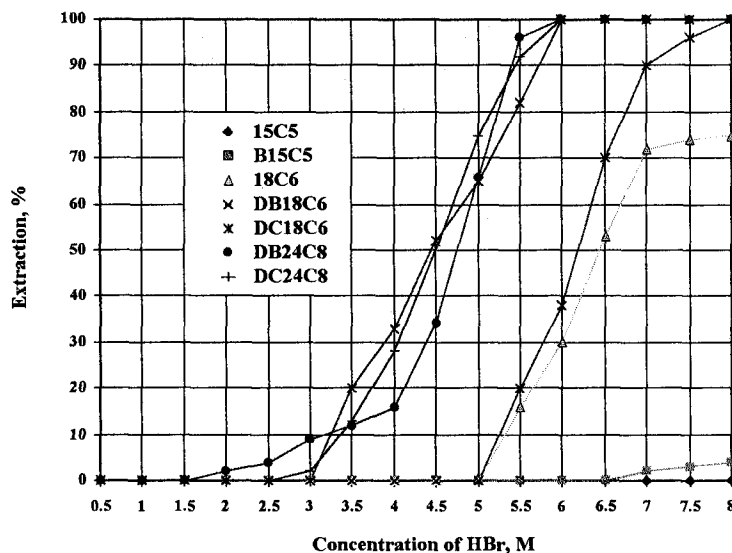


Fig. 1. Extraction of uranium as a function of hydrobromic acid concentration with various crown ethers

## Results and discussion

### *Extraction of uranium as a function of hydrobromic acid concentration with various crown ethers*

In order to ascertain the optimum concentration of hydrobromic acid required for the quantitative extraction of uranium, various studies were conducted with a range of crown ethers with 0.005M concentration in nitrobenzene. The hydrobromic acid concentration was varied from 0.5 to 8M. The results in Fig. 1 show that uranium(VI) was not extracted with 15-crown-5 from 0.5–8.0M HBr. Benzo-15-crown-5 showed extraction to the extent of 4%, 18-crown-6 extracted uranium(VI) to the extent of 75% and dibenzo-18-crown-6 showed 100% extraction at 8.0M HBr. Amongst other crown ethers, dicyclohexano-18-crown-6, dicyclohexano-24-crown-8 and dibenzo-24-crown-8 showed quantitative extraction of uranium(VI) from 6.0–8.0M HBr. For further studies of uranium(VI) extraction, dibenzo-24-crown-8 was preferred over other crown ethers because it is not soluble in the aqueous phase, whereas dicyclohexano derivatives showed a partial aqueous solubility.

To study the effect of hydrobromic acid concentration on the extraction of uranium, extractions were performed using 0.005M dibenzo-24-crown-8 in nitrobenzene by varying the concentration of hydrobromic acid in the range of 0.5 M to 8.0 M. It was observed that the extraction of uranium started at 2.0M (2%), it was 16% at 4.0M and increased with increase in hydrobromic acid concentration and was quantitative

from 6.0M to 8.0M of hydrobromic acid. For further extraction studies of uranium 7.0M hydrobromic acid was used.

### *Effect of varying concentration of dibenzo-24-crown-8*

The extraction of uranium was carried out from 7.0M hydrobromic acid with dibenzo-24-crown-8 in nitrobenzene. The concentration of dibenzo-24-crown-8 was varied from 0.0001 to 0.01M. The studies revealed that the extraction of uranium was 5% at 0.0001M, 22% at 0.0002M, 54% at 0.0004M, 87% with 0.0006M, 98% with 0.0008M and was quantitative (100%) from 0.001–0.01M of dibenzo-24-crown-8. Further extraction studies of uranium were carried out using 0.005M dibenzo-24-crown-8 in nitrobenzene.

### *Effect of various diluents*

In order to study the effect of diluents on the extraction of uranium, extractions were performed from 7.0M hydrobromic acid medium using 0.005M dibenzo-24-crown-8 in various of solvents, such as benzene, toluene, xylene, carbon tetrachloride, chloroform, kerosene, dichloromethane, 1,2-dichloroethane, tetrachloroethane and nitrobenzene. From the organic phase, uranium was stripped with 2M nitric acid. It was observed that there was no extraction of uranium with any of the diluents except nitrobenzene. Nitrobenzene proved to be an efficient diluent for the quantitative extraction of uranium. Therefore, further extractions studies of uranium were carried out from nitrobenzene.

*Choice of stripping agents*

After extraction of uranium from 7.0M hydrobromic acid with 0.005M dibenzo-24-crown-8 in nitrobenzene as a diluent, it was stripped from the organic phase with various stripping agents such as nitric acid, hydrochloric acid, acetic acid, sulfuric acid and perchloric acid in the concentration range of 0.1–10M. The stripping of uranium was quantitative with 0.1–1.0M hydrochloric acid, 0.5–10M nitric acid, 2.0–10M perchloric acid, 3.0–10M sulfuric acid and acetic acid. For further studies of uranium 2M nitric acid was employed as a strippant.

*Separation of uranium(VI) from binary mixtures*

Uranium was extracted with 0.005M dibenzo-24-crown-8 in nitrobenzene from 7.0M hydrobromic acid in the presence of a wide range of ions (Table 1). The tolerance limit was set at the amount of foreign ions required to cause a  $\pm 2\%$  error in the recovery of uranium. Most of the s-block elements were not extracted and hence showed very high tolerance limit. Amongst d-block elements only iron(III) and molybdenum(VI) were extracted quantitatively along with uranium. The separation of uranium(VI) from iron(III) and thorium is shown in multicomponent mixture separation. Other d-block elements were not extracted and showed high tolerance limits. From p-block elements gallium(III), indium(III) and thallium(III) showed co-extraction with uranium(VI). Most of the p-block elements, anions of organic and inorganic acids showed very high tolerance limits.

*Separation of uranium from multicomponent mixtures*

Separation of uranium was carried out from a number of other elements in multicomponent mixtures. The separation of iron(III), uranium(VI) and thorium(IV) was carried out as follows. The mixture containing uranium(VI), iron(III) and thorium(IV) in 7.0M hydrobromic acid was extracted with 0.005M dibenzo-24-crown-8 in 1,2-dichloroethane, (from 1,2-dichloroethane uranium(VI) is not extracted while iron(III) is quantitatively extracted). Under these conditions only iron(III) was extracted leaving behind uranium and thorium in the aqueous phase from which uranium was extracted with 0.005M dibenzo-24-crown-8 in nitrobenzene thorium remaining in the aqueous phase. Iron(III) and uranium(VI) were stripped out from the respective organic phases with 2M HNO<sub>3</sub>.

When a mixture containing uranium, Rb(I)/Cs(I) and Th(IV)/Ce(III)/La(III)/Be(II)/Li(I) was extracted with 0.005M dibenzo-24-crown-8 in nitrobenzene from 7.0M hydrobromic acid, uranium was extracted while

Rb(I)/Cs(I) and Th(IV)/Ce(III)/ La(III)/Be(II)/ Li(I) remained in the aqueous phase. From the organic phase uranium was stripped out with 2M nitric acid. The aqueous phase containing Rb(I)/Cs(I) and Th(IV)/Ce(III)/ La(III)/Be(II)/ Li(I) was extracted with dibenzo-24-crown-8 in nitrobenzene from 0.001M picric acid. Under these conditions Rb(I)/Cs(I) were extracted leaving behind Th(IV)/Ce(III)/ La(III)/Be(II)/ Li(I) in the aqueous phase. From the organic phase Rb(I)/Cs(I) was stripped out with 2M nitric acid. The separation of uranium from Ba(II) and other elements was accomplished by following a similar methodology (Table 2).

Table 1. Separation of uranium(VI) from binary mixtures

Ion	Added as	Tolerance limit, mg
Li <sup>+</sup>	LiCl	20.0
Na <sup>+</sup>	NaCl	7.0
K <sup>+</sup>	KCl	30.0
Rb <sup>+</sup>	RbCl	25.0
Cs <sup>+</sup>	CsCl	30.0
Be <sup>2+</sup>	Be(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	20.0
Mg <sup>2+</sup>	MgCl <sub>2</sub> ·6H <sub>2</sub> O	15.0
Ca <sup>2+</sup>	CaCl <sub>2</sub>	25.0
Sr <sup>2+</sup>	Sr(NO <sub>3</sub> ) <sub>2</sub>	20.0
Ba <sup>2+</sup>	Ba(NO <sub>3</sub> ) <sub>2</sub>	8.0
Co <sup>2+</sup>	CoCl <sub>2</sub> ·6H <sub>2</sub> O	5.0
Ni <sup>2+</sup>	NiCl <sub>2</sub> ·6H <sub>2</sub> O	5.0
Zn <sup>2+</sup>	ZnCl <sub>2</sub>	5.0
Hg <sup>2+</sup>	HgCl <sub>2</sub>	20.0
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	1.5
Cr <sup>3+</sup>	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	2.0
Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	7.0
La <sup>3+</sup>	La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	15.0
Ce <sup>3+</sup>	CeCl <sub>3</sub> ·6H <sub>2</sub> O	30.0
Ga <sup>3+</sup>	GaCl <sub>3</sub>	1.5
In <sup>3+</sup>	InCl <sub>3</sub> ·3H <sub>2</sub> O	6.0
Tl <sup>3+</sup>	Tl(NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	5.0
Sb <sup>3+</sup>	SbCl <sub>3</sub>	15.0
Ge <sup>4+</sup>	Na <sub>2</sub> GeO <sub>3</sub>	2.5
Th <sup>4+</sup>	Th(NO <sub>3</sub> ) <sub>4</sub>	25.0
Zr <sup>4+</sup>	Zr(NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	7.0
V <sup>5+</sup>	NH <sub>4</sub> VO <sub>3</sub>	2.5
Mo <sup>6+</sup>	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O	5.0
W <sup>6+</sup>	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	5.0
Cl <sup>-</sup>	HCl	15.0
I <sup>-</sup>	HI	12.0
NO <sub>3</sub> <sup>-</sup>	HNO <sub>3</sub>	15.0
SCN <sup>-</sup>	NaSCN	10.0
CH <sub>3</sub> COO <sup>-</sup>	CH <sub>3</sub> COOH	20.0
ClO <sub>4</sub> <sup>-</sup>	HClO <sub>4</sub>	15.0
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	20.0
PO <sub>4</sub> <sup>3-</sup>	H <sub>3</sub> PO <sub>4</sub>	15.0
BO <sub>3</sub> <sup>3-</sup>	H <sub>3</sub> BO <sub>3</sub>	25.0
Citrate	Citric acid	15.0
Ascorbate	Ascorbic acid	15.0
Tartrate	Tartaric acid	10.0

U: 100  $\mu$ g/10 ml, 7.0M hydrobromic acid, dibenzo-24-crown-8 0.005M in nitrobenzene, strippant 2M HNO<sub>3</sub>.

Table 2. Separation of uranium from multicomponent mixtures

No.	Mixture	Taken, $\mu\text{g}$	Found, $\mu\text{g}$	Recovery, %	Extractant
1	Fe(III)	100	100	100	DB24C8(EtCl <sub>2</sub> ) - 7M HBr
	U(VI)	100	100	100	DB24C8 (NO <sub>2</sub> Bz)-7M HBr
	Th(IV)	200	196	98	Aqueous phase
2	U(VI)	100	100	100	DB24C8 - 7M HBr
	Rb(I)/Cs(I)	100	100	100	DB24C8 - 0.001M Pic.
	Th(IV)	200	196	98	Aqueous phase
3	U(VI)	100	99	99	DB24C8 - 7M HBr
	Rb(I)/Cs(I)	100	100	100	DB24C8 - 0.001M Pic.
	Ce(III)	200	198	99	Aqueous phase
4	U(VI)	100	100	100	DB24C8 - 7M HBr
	Rb(I)/Cs(I)	100	100	100	DB24C8 - 0.001M Pic.
	La(III)	200	198	99	Aqueous phase
5	U(VI)	100	100	100	DB24C8 - 7M HBr
	Rb(I)/Cs(I)	100	100	100	DB24C8 - 0.001M Pic.
	Be(II)	200	198	99	Aqueous phase
6	U(VI)	100	100	100	DB24C8 - 7M HBr
	Rb(I)/Cs(I)	100	100	100	DB24C8 - 0.001M Pic.
	Li(I)	200	200	100	Aqueous phase
7	U(VI)	100	100	100	DB24C8 - 7M HBr
	Ba(II)	100	100	100	DB24C8 - 0.001M Pic.
	Th(IV)	200	198	99	Aqueous phase
8	U(VI)	100	100	100	DB24C8 - 7M HBr
	Ba(II)	100	100	100	DB24C8 - 0.001M Pic.
	Ce(III)	200	200	100	Aqueous phase
9	U(VI)	100	100	100	DB24C8 - 7M HBr
	Ba(II)	100	100	100	DB24C8 - 0.001M Pic.
	La(III)	200	198	99	Aqueous phase
10	U(VI)	100	100	100	DB24C8 - 7M HBr
	Ba(II)	100	100	100	DB24C8 - 0.001M Pic.
	Be(II)	200	200	100	Aqueous phase
11	U(VI)	100	100	100	DB24C8 - 7M HBr
	Ba(II)	100	100	100	DB24C8 - 0.001M Pic.
	Li(I)	200	198	99	Aqueous phase

EtCl<sub>2</sub> = 1,2-dichloroethane, NO<sub>2</sub>Bz = Nitrobenzene.  
Strippant 2M HNO<sub>3</sub> unless aqueous phase is indicated.

### Applications

The proposed method was applied for the determination of uranium in geological samples such as syenite rock sample (SY-II) and monazite sample. The samples were brought in to solution by the procedure described elsewhere.<sup>1</sup> Iron from the SY-II sample was separated as per procedures described in multi-component mixture separation. An aliquot of sample

solution containing uranium was extracted with 0.005M dibenzo-24-crown-8 in nitrobenzene from 7M HBr. Under these conditions only uranium was extracted which was then stripped with 2M HNO<sub>3</sub> and determined spectrophotometrically. The amount of uranium found in SY-II sample was 282 ppm as against the reported value of 280 ppm.<sup>9</sup> In monazite sand it was 0.31% as against the standard value of 0.30%.

### Conclusions

A simple extraction method has been developed for the separation and determination of uranium at trace levels using dibenzo-24-crown-8 from aqueous hydrobromic acid medium. The concentration of crown ether required is very low. The important feature of this method is that it permits the separation of uranium from other elements such as iron, rubidium, cesium, potassium, barium, strontium, thorium, cerium, lanthanum, beryllium and lithium. The method is simple, rapid, selective, reproducible and exemplifies an interesting use of crown ethers as extracting agent for uranium and was applied to the analysis of uranium from geological samples.

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