

Separation studies of Uranium (VI) from Iron (III) With Dicyclohexano-18-Crown-6 from Hydrobromic Acid Medium

S.H. Burungale

Laboratory of Analytical Chemistry, PG Department of Chemistry, Yashwantrao Chavan College of Science, Karad -415124, India

Abstract: A novel method has been developed for the solvent extraction of Uranium (VI) from 6.5M hydrobromic acid with 0.001M Dicyclohexano-18Crown-6 in nitrobenzene. Uranium (VI) from the organic phase was determined spectrophotometrically at 530 nm. Extraction was found to be quantitative in the range of 6-8 M hydrobromic acid. When the concentration of Dicyclohexano-18Crown-6 was varied from 0.05-20% in nitrobenzene, it showed that optimum concentration was 3%. Amongst diluents like nitrobenzene was found to be an effective diluent. Effect of shaking time, concentration of metal ion. Tolerance limits of various diverse ions were studied. Uranium (VI) was separated from associated elements in its ternary mixtures with Fe (III), Bi (III) and Cu (II), Au (III). The proposed method was applied for separation and determination of Uranium (VI) in rocks.

Keywords: Solvent extraction; Determination of Uranium (VI); Dicyclohexano-18Crown-6; Analysis of real samples.

1. Introduction

Much attention has been paid to the development of ion selective macrocyclic compounds for the separation of lanthanides either as a group or as elements. The macrocyclic crown ethers achieved considerable importance for separation and determination of a large number of metal ions¹. Crown ethers showed selective extraction for metal ions, especially alkali and alkaline earth metals, in terms of the correspondence between the extracted metal ion crystal radii and the cavity size of the crown ethers used. Due to their ion size selective nature and ability to transfer metal ions into organic media, crown ethers have been frequently used as extractants and phase transfer reagents in solvent extraction and liquid membrane processes. The use of crown ethers for the separation of uranium (VI) from associated elements is very limited. The synergistic extraction of uranyl ion from dilute nitric acid medium employing HIT All-phenyl-3-methyl-4-benzoyl-S-pyrazolone (HPMBP) in toluene and their mixture with several structurally modified monoamides viz. di-2-ethylhexylacetamide (D2EHAA), di-2-ethylhexylpropanamide (D2EHPrA), di-2-ethylhexylisobutyramide (D2EHIBA), di-2-ethylhexylpivalamide (D2EHPvA) has been investigated. The nature of the extracted species for the binary and ternary extraction systems were reported as UO_2A_2 and $UO_2A_2.B$, respectively, where A = TTA or PMBP and B = D2EHAA, D2EHPrA, D2EHIBA or D2EHPvA. A linear correlation was observed between the basicity of the amide and the corresponding adduct formation constants.[1],[2],[3]. The former criterion requires some understanding of the coordination chemistry and particularly, knowledge of the solution speciation of the cation and the extractants. However, remarkably few studies of synergistic extraction have probed the cation coordination environment[4],[5],[6],[7]. The portioning behavior of uranyl ion and other actinides was investigated with 15-crown-5. The partitioning of uranium(VI) by mixtures of 1,3-diketones and various CE's has been investigated, but the extraction systems are not yet well. Macrocyclic rings of 12, 15, 18 or 24 members, including the common cyclohexyl or

benzo derivatives, were shown to synergize uranium(VI) extraction into benzene[8],[9]. Based on the synergism observed for macrocyclics containing 12 and 18 members, it appears that the cavity size is not an important factor in the synergism of uranium(VI) extraction by these CE's and 18-crown-6 from polyethylene glycol and ammonium sulphate.[9],[10]. The introduction of cation selectivity into synergistic solvent extraction is best accomplished by the use of crown ethers that form both stable in-cavity complexes with the target cation and have adequate functionalisation to impart organophilicity. Hence in the present study, the extraction of uranium (VI) with dicyclohexano-18-crown-6 in the nitrobenzene and various crown ethers, 15-crown-5(15C5), 18-crown-6(18C6), DB18-crown-6(DB18C6) has been investigated with a view to improve the selectivity between these actinides. When these two criteria are met, the crown ether is both an effective ligand and an effective extractant.

2. Experimental

2.1 Apparatus

A Zeiss spectrophotometer, a digital pH meter, with glass and Calomel electrodes, a digital Flame photometer and 125 ml separating funnels were used. A stock solution of Uranium (VI) was prepared by dissolving 2.166 g of uranyl nitrate hexahydrate (BDH) in 1000 ml of distilled deionized water and standardized gravimetrically (230). The solution was found to contain 1.0 mg/ml of Uranium (VI). A solution containing 100 µg/ml of Uranium (VI) was prepared by appropriate dilution of the standard stock solution. Solutions of crown ether were prepared from Dicyclohexano-18-crown-6 (DC18C6) without further purification. All other chemicals were of guaranteed grade and were used without further purification.

2.2 Procedure

Solvent Extraction. 100 µg of Uranium (VI) was mixed with hydrobromic acid in the concentration range of 0.5M to 8 M in a total volume of 10 mL. The solution was then transferred to a separating funnel and was equilibrated with 10 ml Dicyclohexano-18-crown-6(DC18C6) crown ether (0.001M) in nitrobenzene as a diluent for 5 min. on a wrist action flask shaker. Two phases were allowed to settle and separate. From the organic phase Uranium (VI) was then stripped with 10 ml of stripping agent like 0.5M Hydrochloric and was determined spectrophotometrically at 530 nm. The concentration of Uranium (VI) was calculated from the calibration curve.

3. Results and Discussion

3.1 Extraction of Uranium (VI) 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 (VI), the extraction studies were performed with a range of crown ethers of 0.001 M concentration in nitrobenzene. The hydrobromic acid concentration as varied from 0.5 to 8. The results of extraction studies are shown in Table- 1. It is clear that amongst various crown ethers only Solutions of crown ethers were prepared from 15-crown-5(15C5), 18-crown-6(18C6), DB18-crown-6 (DB18C6) and Dicyclohexano-18-crown-6 (DC18C6), could quantitatively extract uranium (VI) where as other crown ethers were not efficient extractants for the quantitative extraction of uranium (VI). There was only 0% extraction of uranium (VI) with 15-crown-5, 4% Benzo-15-crown-5, 75 % with 18-crown-6(18C6), 95% with Dibenzo-18-crown-6(DB18C6) at 6.5 M hydrobromic acid. The extraction of Uranium (VI) was quantitative with Dicyclohexano-18-crown-6(DC18C6) from 6-8 M hydrobromic acid. Further extraction studies of Uranium (VI) was carried out with 0.001M DC-18-Crown-6 with nitrobenzene as diluents.

Table 1: Extraction of Uranium (VI) as a function of hydrobromic acid Concentration with various crown ethers. Uranium (VI -100 µg, Strippant-0.5M HCl Crown Ether-0.001M in Nitrobenzene

HBr Acid M	Uranium (VI) Extraction %				
	15C5	B15C5	18C6	DB18C6	DC18C6
0.5	0	0	0	0	0
1.5	0	0	0	0	0
2	0	0	0	0	0
2.5	0	0	0	0	0
3	0	0	0	0	0
3.5	0	0	0	0	20
4	0	0	0	0	33
4.5	0	0	0	0	52
5	0	0	0	0	88
5.5	0	0	15	0	98
6	0	0	30	30	100
6.5	0	0	50	38	100
7	0	2	70	70	100
7.5	0	3	74	90	100
8	0	4	75	100	100

3.2 Effect of varying Concentration of Dicyclohexano-18-crown-6

In order to ascertain the optimum concentration of DC-18-Crown-6 required for the quantitative extraction of Uranium (VI), the extraction studies were performed with a range of hydrobromic acid of 6.5 M with varying the concentration of DC-18-Crown-6 in nitrobenzene. The concentration of DC-18-Crown-6 was varied from 0.0001-0.01M. The results of extraction studies are shown in Table- 2 and fig-1 which indicate that the extraction of Uranium (VI) was increased with increase in DC-18-Crown-6 concentration and was quantitative from 0.001 – 0.01M DC-18-Crown-6. Further extraction studies of Uranium (VI) were carried out using 10 ml of 0.001M DC-18-Crown-6 in nitrobenzene as a diluent.

Table 2: Effect of varying Concentration of Dicyclohexano-18-crown-6 Uranium (VI -100 µg, Strippant-0.5M HCl

DC-18-Crown-6 Conc.M	Extraction %E	Distribution D	DC-18-Crown-6 Conc.M	Extraction %E	Distribution D
0.0001	05	0.087	0.002	100	∞
0.0002	22	0.136	0.003	100	∞
0.0003	40	0.190	0.004	100	∞
0.0004	50	0.220	0.005	100	∞
0.0005	70	0.250	0.006	100	∞
0.0006	95	0.538	0.007	100	∞
0.0007	99	7.333	0.008	100	∞
0.0008	100	∞	0.009	100	∞
0.0009	100	∞	0.01	100	∞
0.001	100	∞			

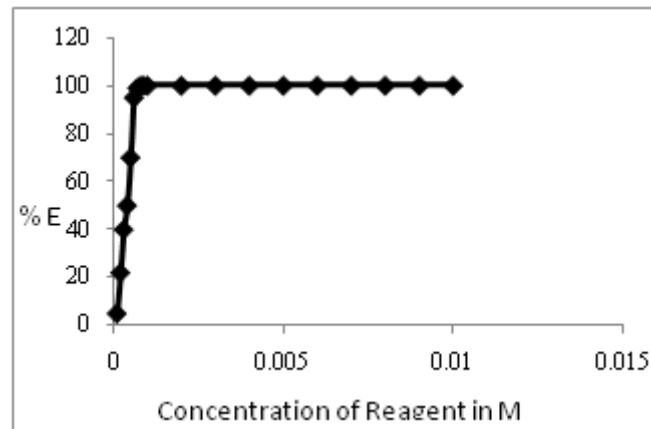


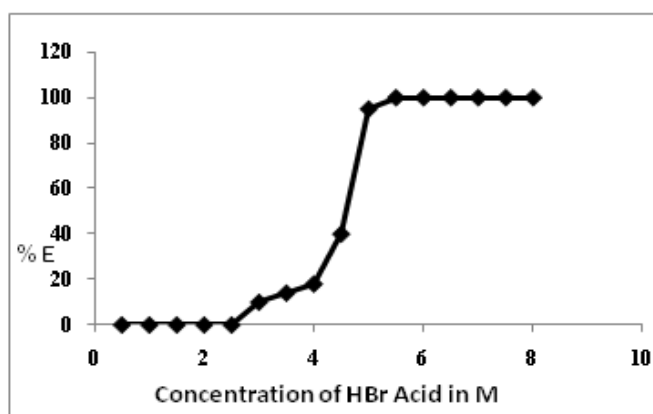
Figure 1: Effect of varying Concentration of Dicyclohexano-18-crown-6

3.3 Effect of hydrobromic acid Concentration

The effect of hydrobromic acid concentration on the extraction of Uranium (VI), extractions were performed with 0.001M DC-18-Crown-6 in nitrobenzene by varying the concentration of hydrobromic acid in the range of 0.05-8M. The results of extraction studies are shown in Table- 3 and fig-2. It was found that the extraction of Uranium (VI) was 98 % at 6M hydrobromic acid and was quantitative from 6.5M-8 M hydrobromic acid. Further extraction studies of Uranium (VI) were carried out with 6.5 M hydrobromic acid.

Table 3: Effect of hydrobromic acid Concentration Uranium (VI -100 µg, Strippant-0.5M HCl Crown Ether-0.001M in Nitrobenzene

HBr acid Concentration M	% Extraction E	Distribution Ratio D	HBr acid Concentration M	% Extraction E	Distribution Ratio D
0.5	0	0	4.5	40	0.500
1	0	0	5	95	24.15
1.5	0	0	5.5	100	∞
2	0	0	6	100	∞
2.5	0	0	6.5	100	∞
3	10	0.0999	7	100	∞
3.5	14	3.545	7.5	100	∞
4	18	0.195	8	100	∞

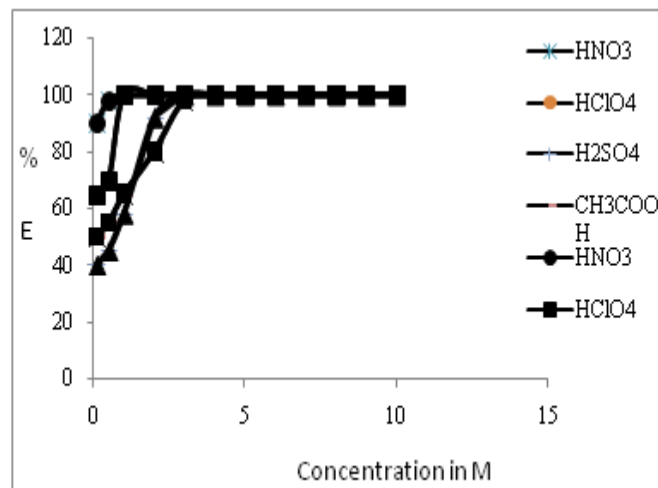
**Figure 2:** Effect of hydrobromic acid Concentration

3.4 Effect of Several of Stripping Agents

After extraction of Uranium (VI) from 6.5 M hydrobromic acid with 0.001M DC-18- Crown-6 in nitrobenzene, it was stripped from the organic phase with various stripping agents such as nitric acid, hydrochloric acid, sulphuric acid, perchloric acid, acetic acid in the concentration range of 0.1-10 M. The stripping of Uranium (VI) was quantitative with 2.0-10M nitric, perchloric acid and 4.0-10.0M sulphuric acid and acetic acid and hydrochloric acid was found to be an insufficient strippant for Uranium (VI) in the concentration range of 0.1 -10M. Further stripping studies of Uranium (VI) were carried out with 0.5M Hydrochloric acid. The results of stripping of Uranium (VI) are shown in table-4 and fig-3

Table 4: Effects of Several of Stripping Agents Uranium (VI -100 µg, Crown Ether-0.001M in Nitrobenzene, 6.5M HBr Acid

Conc Molar	% Stripping				
	HNO ₃	HClO ₄	H ₂ SO ₄	CH ₃ COOH	HCl
0.1	90	65	40	50	100
0.5	98	70	45	55	100
1	100	100	58	65	100
2	100	100	92	80	85
3	100	100	100	98	70
4	100	100	100	100	45
5	100	100	100	100	10
6	100	100	100	100	00
7	100	100	100	100	00
8	100	100	100	100	00
9	100	100	100	100	00
10	100	100	100	100	00

**Figure 3:** Effects of Several of Stripping Agents

3.5 Effect of various Diluents

To study the effect of diluents on the extraction of Uranium (VI), extractions were performed from 6.5 M hydrobromic acid by using 0.001M DC-18- Crown-6 in various solvents such as benzene, toluene, xylene, carbon tetrachloride, chloroform, and nitrobenzene. The phase volume ratio was maintained at unity. It was observed that the extraction of Uranium (VI) was 0% with benzene, toluene, xylene, carbon tetrachloride, and chloroform, and was quantitative only with nitrobenzene. Therefore studies of Uranium (VI) were carried out from nitrobenzene as diluent. The results of extraction studies are shown in Table-5

Table 5: Effect of various Diluents Uranium (VI)-100 µg, DC-18C-6 0.001M, 6.5 M HBr Acid, Strippant 0. 5M HCl

Diluent	Dielectric Constant	Extraction %	Distribution Ratio D
Benzene	2.28	0	0
Toluene	2.38	0	0
xylene	2.3	0	0
Carbon Tetrachloride	2.24	0	0
Chloroform	4.8	0	0
Tetrachloroethane	8.2	0	0
Tetra chloromethane	9.08	0	0
Dichloromethane	10.5	0	0
Nitrobenzene	34.8	100	∞

3.6 Effect of varying Concentration of Uranium (VI)

Uranium (VI) was extracted with 10 ml of 0.001M dicyclohexano-18-crown-6 from 6.5M hydrobromic acid by using nitrobenzene as a diluent. The Uranium (VI) was varied from 100- 1500µg per 10 ml. It was found that 10ml of 0.001M DC18C6 solution was adequate to extract Uranium (VI) quantitatively up to 1200µg per 10 ml of sample solution. The results are shown in table-6 and fig-4

Table 6: Effect of varying Concentration of Uranium (VI) DC-18C-6 0.001M, 6.5M HBr Acid, Strippant 0. 5M HCl

Uranium (VI)µg	Extraction %	Distribution Ratio D
100	100	∞
200	100	∞
300	100	∞

400	100	∞
500	100	∞
600	100	∞
700	100	∞
800	100	∞
900	100	∞
1000	100	∞
1100	100	∞
1200	100	∞
1300	97	49.01
1400	90	8.09
1500	85	5.67

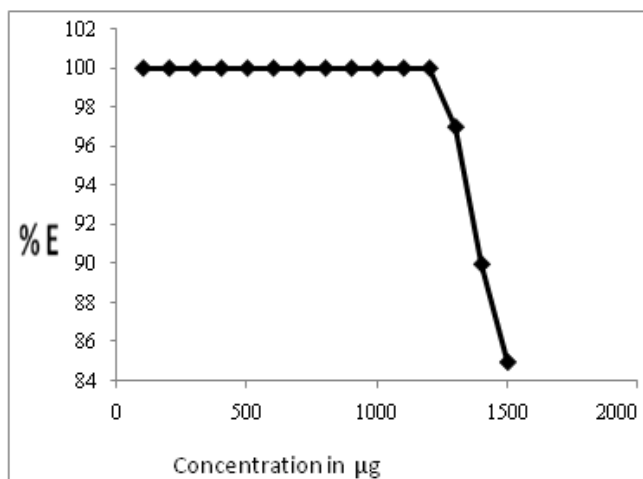


Figure 4: Effect of varying Concentration of Uranium (VI)

3.7 Period of Equilibration

Table 7: Separation of Uranium (VI) from Binary Mixtures

Ions	Added as	Tolerance Limit(mg)	Ions	Added as	Tolerance Limit (mg)
Na ⁺	NaCl	25	Ce ³⁺	CeCl ₃ .6H ₂ O	0.1
Rb ⁺	RbCl	0.5	Sb ³⁺	SbCl ₃	0.1
Cs ⁺	CsCl	0.1	Y ³⁺	Y(NO ₃) ₃	0.5
Be ²⁺	BeSO ₄ .4H ₂ O	0.3	Zr ⁴⁺	Zr(NO ₃) ₄ .4H ₂ O	0.3
Mg ²⁺	MgCl ₂ .6H ₂ O	30	V ⁴⁺	VO ₂ SO ₄ .4H ₂ O	0.5
Ca ²⁺	CaCl ₂	15	Th ⁴⁺	Th(NO ₃) ₄	0.5
Sr ²⁺	Sr(NO ₃) ₂	20	Cr ⁶⁺	K ₂ Cr ₂ O ₇	0.5
Ba ²⁺	Ba(NO ₃) ₂	20	Mo ⁶⁺	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O	0.5
Cu ²⁺	CuCl ₂ .2H ₂ O	0.5	W ⁶⁺	Na ₂ WO ₄ .4H ₂ O	30
Ni ²⁺	NiCl ₂ .6H ₂ O	0.1	La ³⁺	LaCl ₃	0.1
Mn ²⁺	MnCl ₂ .4H ₂ O	0.3	Al ³⁺	Al(NO ₃) ₃ .9H ₂ O	0.5
Zn ²⁺	ZnCl ₂	30	SCN ⁻	NaSCN	75
Pb ²⁺	Pb(NO ₃) ₂	15	ClO ₄ ⁻	ClO ₄	10
Fe ³⁺	FeCl ₃ .6H ₂ O	20	CH ₃ COO ⁻	CH ₃ COOH	35
Cr ³⁺	Cr(NO ₃) ₃ .9H ₂ O	20	Tartrate	Tartaric acid	25

3.9 Separation of Uranium (VI) from multicomponent Mixtures

When mixture containing uranium (VI) Iron (III) Potassium (I) and Lithium was extracted with 0.001M DC18C in dichloroethane from 6.5M hydrobromic acid. Under these set conditions there was no extraction of U (VI), K (I) and Li (I) at 6.5 M hydrobromic acid. There was quantitative extraction of iron (III) with dicyclohexano-18-crown-6. Unextracted Uranium (VI) Potassium (I) and Lithium was extracted with 0.001M DC18C in nitrobenzene from 6.5M

hydrobromic acid while Uranium (VI) was quantitatively extracted with 0.001M DC18C in nitrobenzene from 6.5M hydrobromic acid whereas potassium(I) and Lithium (I) was not extracted. Again potassium (I) and Lithium (I) was extracted with 0.001M DC18C in nitrobenzene from 0.001M Picric acid whereas Lithium (I) remains in aqueous phase and determined by Flame photometrically. The separation of Uranium from iron and other cations was accomplished by following similar methodology table-8

3.8 Separation of Uranium (VI) from Binary Mixtures

Uranium (VI) was extracted with 10 ml of 0.001M dicyclohexano-18-crown-6 in nitrobenzene from 6.5M hydrobromic acid in the presence of various diverse ions. The tolerance limit was set at the amount of foreign ions required to cause a $\pm 2\%$ error in the recovery of Uranium (VI). Amongst s-block cations, rubidium(I), cesium(I), strontium (II), and barium(II) were co-extracted along with potassium (I), strontium (II), and barium(II) showed low tolerance limit. All the s-block cations showed high tolerance limit. Amongst d-block cations, showed high tolerance limit. All the s-block cations showed high tolerance limit. Most of the p-block cations showed high tolerance limit except lead (II) which showed low tolerance limit. The results of separation of potassium (I) from binary mixtures are shown in Table 7

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Table 8: Separation of Uranium (VI) from multicomponent Mixtures

Sr.No	Mixture	Taken μg	Found μg	Recovery %	Extractants	Stripping agents
1	U(VI)	100	100	100	DC18C6,6.5MHBBr	0.5M HCl
	Fe(III)	100	100	100	DC18C6,6.5MHBBr	2M HNO ₃
	K(I)	100	100	100	DC18C6,0.01MPicric acid	2M HNO ₃
	Li(I)	100	100	100	Aqueous Phase	-----
2	U(VI)	100	100	100	DC18C6,6.5MHBBr	0.5M HCl
	Fe(III)	100	100	100	DC18C6, 6.5MHBBr	2M HNO ₃
	K(I)	100	100	100	DC18C6,0.01MPicric acid	2M HNO ₃
	Be(II)	100	100	100	Aqueous Phase	-----
3	U(VI)	100	100	100	DC18C6,6.5MHBBr	0.5M HCl
	Fe(III)	100	100	100	DC18C6, 6.5MHBBr	2M HNO ₃
	K(I)	100	100	100	DC18C6,0.01MPicric acid	2M HNO ₃
	Mg(II)	100	100	100	Aqueous Phase	-----
4	U(VI)	100	100	100	DC18C6,6.5MHBBr	0.5M HCl
	Fe(III)	100	100	100	DC18C6, 6.5MHBBr	2M HNO ₃
	K(I)	100	100	100	DC18C6,0.01MPicric acid	2M HNO ₃
	Ca(II)	100	100	100	Aqueous Phase	-----
5	U(VI)	100	100	100	DC18C6,6.5MHBBr	0.5M HCl
	Fe(III)	100	100	100	DC18C6, 6.5MHBBr	2M HNO ₃
	K(I)	100	100	100	DC18C6,0.01MPicric acid	2M HNO ₃
	Th(IV)	100	100	100	Aqueous Phase	-----
6	U(VI)	100	100	100	DC18C6,6.5MHBBr	0.5M HCl
	Fe(III)	100	100	100	DC18C6, 6.5MHBBr	2M HNO ₃
	K(I)	100	100	100	DC18C6,0.01MPicric acid	2M HNO ₃
	Ce(III)	100	100	100	Aqueous Phase	-----

3.10 Application to the Analysis of Uranium (VI) from various Samples

The method has been applied to the determination of uranium (VI) in monazite sand. The monazite was decomposed by fusion with sodium peroxide [11]. Uranium (VI) was separated from interfering ions by liquid extraction with DC-18 Crown -6 methods in nitrobenzene as diluents. The experiment was repeated 5 times and the results obtained as 0.3 to 0.33 % to the certified values.

4. Conclusion

The important feature of the developed method is that it permits the separation of Uranium (VI) at trace level concentration. The concentration of crown ether required is very low. It is possible to separate uranium (VI) from iron(III), potassium (I), lithium(I), beryllium(II), calcium(II), magnesium(II), thorium(IV), effectively. The method was extended to the analysis of uranium (VI) in various standard rock samples yielding excellent results. The method is simple, rapid, selective, and reproducible and adds significantly to the use of crown ethers as extractants for the separation of Uranium (VI).

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Author Profile

Dr. Shivaji H. Burungale is working as Associate Professor. He started his career as lecturer in Yashwantrao Chavan College of Science Karad for UG and PG students. He has published 22 research papers in International and National scientific journals, successfully guided 15 research students for MSc in analytical chemistry