

## Synergistic Solid Phase Extraction of Ultra Trace Uranium by Mixtures of Dicyclohexyl-18-crown-6 and Tri-*n*-octylphosphine Oxide

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Ultra trace amount of uranium was extracted selectively by a simple and reliable method using C<sub>18</sub> membrane disks modified with mixtures of tri-*n*-octylphosphine oxide and dicyclohexyl-18-crown-6 and determined sensitively with dibenzoylmethane (DBM) as a chromogenic reagent. Synergistic solid phase extraction of uranium with different ligands such as tri-*n*-octylphosphine oxide (TOPO), tri-*n*-butylphosphate (TBP), bis(2-ethylhexyl) phosphoric acid (HDEHP), tri-*n*-octylamine (TOA), 1,10-phenanthroline (Phen), 8-hydroxyquinoline (HOx), methyl isobutyl ketone (MIBK) and dicyclohexyl-18-crown-6 (DC18C6), was studied. Extraction efficiency and the influence of sample matrix, type and optimum amount of extractant and synergist, flow rates, and type and minimum amount of organic eluent were evaluated. In this method, most of the cations and anions have no interfering effect on the extraction and determination of uranium. However, effects of some interfering species such as Th(IV), Zr(VI), Mo(VI) and Cr(VI) were eliminated in the presence of proper masking and reducing agents such as EDTA, NH<sub>2</sub>OH·HCl and F<sup>-</sup> or rinsing of membrane disk before elution. The limit of detection of the proposed method is 0.003 µg/mL. Maximum capacity of the membrane disks modified by 40 mg of TOPO and 5 mg of DC18C6 was found to be 4563 ± 42 µg of U(VI). The method was applied to the extraction and determination of uranium in natural waters.

**Key Words:** Synergistic, Solid Phase Extraction, Uranium, Spectrophotometric Determination, Dibenzoylmethane.

### INTRODUCTION

It is well known that the equilibrium extraction or extraction rate of metal ions can be strongly enhanced by employing a combination of appropriate extractants. This is called the synergistic effect in a liquid-liquid extraction system<sup>1–5</sup>. Valdo *et al.*<sup>6</sup> reported that copper(II) mixed ligand complexes show a synergetic adsorption onto the octadecyl-bonded silica column. It has also been reported that, a mixture of TBP and a β-diketone show a synergetic effect in the extraction of uranium from solid matrices using supercritical carbine dioxide<sup>7</sup>. Recently, a synergetic effect in the supercritical fluid extraction (SFE) of uranium using TOPO and HDEHP in the presence of DC18C6 has been reported<sup>8</sup>.

Solid-phase extraction (SPE) is an attractive technique that reduces consumption and exposure to solvent, disposal costs, and extraction time<sup>9–12</sup>. Recently, SPE disks were successfully utilized for the extraction of several organic and inorganic analytes from different matrixes<sup>13–18</sup>. In the present paper, a rapid and

efficient method for the selective extraction and concentration of uranyl ions by octadecyl silica (ODS) membrane disks modified with mixture of TOPO and DC18C6 from aqueous solutions and the determination of uranyl ions with DBM as a chromogenic reagent has been reported.

## EXPERIMENTAL

All acids were of the highest purity available from Merck and were used as received. All organic solvents were of HPLC grade from Aldrich. Reagent grade TOPO, TBP, TOA, HDEHP and DBM (from Merck or Fluka) were used as received. Analytical grade uranyl nitrate and other salts (all from Merck) were of the highest purity available and were dried in vacuum over  $P_2O_5$ . Doubly distilled deionized water was used throughout. A stock solution of uranyl ion was prepared by dissolving an appropriate amount of  $UO_2(NO_3)_2 \cdot 6H_2O$  in 0.5 M nitric acid. The stock solution was diluted with water or appropriate acid solutions, as needed.

The absorbance measurements were carried out with a Spectronics 20D photometer. Extractions were performed with 47 mm diameter  $\times$  0.5 mm thickness Empore membrane disks containing octadecyl-bonded silica (8  $\mu$ m particle, 60  $^\circ$ A pore size, 3M Co., St. Paul, MN) with a standard Millipore 47 mm filtration apparatus.

**Preparation of the membrane disks:** In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be done before its use. Thus, after placing the membrane disk in the filtration apparatus, 10 mL methanol was poured on to the disk and immediately drawn through the disk by applying a slight vacuum. After all of the solvent had passed through the disk, it was dried by passing air through it for few minutes. The disk conditioning was then begun by pouring 10 mL methanol onto the disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk until a thin layer of methanol was left on the surface of the disk. It is preferable to leave extra methanol above the disk rather than to allow any air to make contact with the surface of the disk. This is to ensure complete wetting of the disk with the organic solvent. Immediately, 10 mL of water was introduced on to the disk and was drawn through the disk. The disk was then dried under vacuum for 5 min or longer, if necessary. This is especially important for the disks that are used for the first time. Finally, a solution of 40 mg of TOPO and 5 mg of DC18C6 dissolved in 1 mL of methanol was introduced on to the disk so that the solution was spread on the whole disk surface. The solution was allowed to penetrate inside the membrane completely without applying any vacuum. After about 1 min, the filtration funnel containing the modified disk was transferred into an oven and the solvent was completely evaporated at 65 $^\circ$ C.

**Solid phase extraction and determination of uranium:** After drying, the modified disk was washed with 10 mL of water. Then 50 mL of a 0.5 M  $HNO_3$  solution containing uranyl ions was passed through the membrane at 15 mL/min. The disk was dried completely by passing air through it. A proper test tube was then placed under the extraction funnel. The complex was eluted from the disk with methanol (4  $\times$  2 mL) at a flow rate of 4 mL/min. This process ensured complete

elution of the  $\text{UO}_2^{2+}$ -TOPO-DC18C6 adduct. Then the eluent was transferred into a 10 mL volumetric flask containing 1 mL of DBM solution (2% w/v DBM in 50% v/v pyridine-methanol solution) and diluted to 10 mL with methanol. The uranyl concentration was then determined at 405 nm against a reagent blank (external linear calibration range 0.2–5.0  $\mu\text{g}/\text{mL}$ ,  $r = 0.9997$ ).

**Determination of uranyl ions in natural waters:** A 500 mL aliquot of the water was first passed through a 45  $\mu\text{m}$  (Millipore) nylon filter to remove particles. Then the filtrate was passed through an octadecyl silica membrane disk without ligands to remove organic compounds that may be present in the water. Enough  $\text{HNO}_3$  (12 M) was added to achieve a concentration of 0.5 M and enough  $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$  to reach a concentration of  $1.0 \times 10^{-3}$  M. The uranyl ions were extracted from the thus treated aliquot and then quantified as described above.

## RESULTS AND DISCUSSION

Organophosphorus compounds are important for the extractive separation of metal ions. They are capable of competing with water molecules for the available sites in the first coordination shell of the cations, and thus capable of forming extractable coordination solvated salt complexes. The extractive properties of these ligands depend on the number of ester oxygen atoms and the nature of substituents present in the molecule<sup>19</sup>. Especially, the successful liquid-liquid extraction and separation of uranium from its interfering matrices have been reported in the presence of organophosphorus co-extractants such as TOPO, TBP and HDEHP, usually in the nitric acid media<sup>20–22</sup>.

On the other hand, crown ethers have been demonstrated to be highly selective complexing agents for many ions and can potentially be applied in separation of these ions<sup>23</sup>.

Our previous experiences showed that the recovery of uranium using ODS membrane disks modified with TOPO have been increased in the presence of DC18C6<sup>13</sup>. Thus, some preliminary experiments were carried out for solid phase extraction of uranium using binary mixtures of different ligands, especially TOPO and DC18C6. The results are summarized in Table-1. As the results show, a mixture of TOPO and DC18C6 reveals a synergistic effect in the extraction of uranium and is the most promising choice for the quantitative solid phase extraction of uranyl ions.

In order to investigate the influence of the matrix on the extraction of uranyl ion, the electrolytes  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$  and  $\text{NaNO}_3$  were tested. 50 mL solutions containing 10  $\mu\text{g}$  of uranium and varying concentrations of the electrolytes were passed through the membrane disks modified with 30 mg of TOPO and 5 mg of DC 18C6. Uranium is extracted over 96% by 0.5–2.0 M  $\text{HNO}_3$  and 1.0–2.0 M  $\text{HCl}$  (Fig. 1). Recovery per cent of uranium using 1 M  $\text{CH}_3\text{COOH}$  and 1 M  $\text{NaNO}_3$  was 47 and 52 respectively; thus greater concentrations of these two electrolytes were not tested. A 0.5 M  $\text{HNO}_3$  solution was chosen not only because of the relatively low concentration of the electrolyte but also because of the decreased interfering effect of other elements such as iron, which could be co-extracted with uranium by the membrane disk in the presence of high concentrations of  $\text{Cl}^-$  ion<sup>24</sup>. In addition to this concentration of nitric acid provided enough salting-out effect for the extraction of uranium into lipophilic  $\text{C}_{18}$  solid phase.

TABLE-1  
RECOVERY OF URANYL ION FROM THE MEMBRANE DISKS  
MODIFIED WITH DIFFERENT LIGANDS<sup>a</sup>

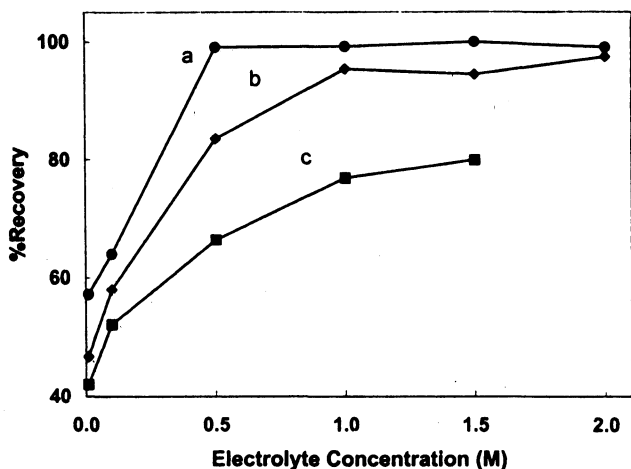
Ligand	Amount of Ligand (mg)	Recovery of uranium (%) <sup>b</sup>
TOPO	15	57 (1.3)
TOPO	30	86 (2.8)
TBP	30	60 (2.4)
TPPO	30	67 (3.1)
HDEHP	30	83 (2.8)
MIBK	30	81 (3.3)
Phen	30	55 (1.5)
HOx	30	51 (2.0)
DC18C6	30	37 (1.5)
TOPO + DC18C6	5 + 5	60 (1.6)
TOPO + DC18C6	10 + 5	71 (1.7)
TOPO + DC18C6	15 + 15	73 (1.9)
TOPO + DC18C6	30 + 5	96 (2.3)
TOPO + DC18C6	30 + 10	81 (2.5)
TOPO + TOA	15 + 15	76 (2.8)
DC18C6 + TOA	15 + 15	74 (2.1)
TBP + TOA	15 + 15	68 (1.9)
TPPO + TOA	15 + 15	86 (1.7)
HDEHP + TOA	15 + 15	69 (2.4)
MIBK + TOA	15 + 15	81 (1.5)
Phen + TOA	15 + 15	57 (1.8)

<sup>a</sup>50 mL of 0.5 M HNO<sub>3</sub> containing 10 µg of uranium.

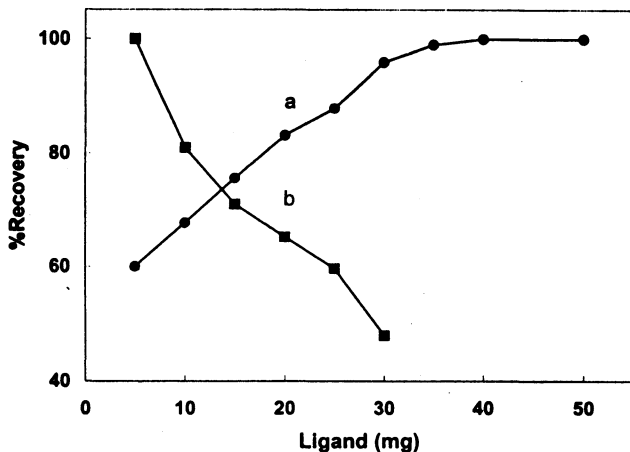
<sup>b</sup>Values in parentheses are ±SD based on three replicate analyses.

The optimal amounts of TOPO and DC18C6 required for the proper modification of the membrane disks were investigated (Fig. 2). The membrane disks modified with 5 mg of DC18C6 and 35–50 mg of TOPO retain 10 µg of uranium quantitatively. From the results, it is obvious that amounts of DC18C6 greater than 5 mg reduce the determined quantities of uranium, because of prevention of DBM colour development in the spectrophotometric determination step, but not because of decreasing the extraction yield. However, this is a limitation for the proposed simple determination method. Thus, 40 mg of TOPO and 5 mg of DC18C6 was used for further studies.

Different organic solvents, such as methanol, ethanol, chloroform and cyclohexane were tested as eluent for the extracted uranyl complex from the disks. Methanol was found to be the best extractant not only because of the improved recovery with the least amount of solvent (4 mL), but also because of the faster colour development and improved spectrophotometric measurement of uranyl ion with DBM in the presence of pyridine<sup>24</sup>.



**Fig. 1.** Recovery of 10 µg of uranium from 50 mL solutions containing different electrolytes of varying concentrations by the membrane disks modified with 30 mg of TOPO and 5 mg of DC18C6: (a) HNO<sub>3</sub>, (b) HCl, and (c) H<sub>2</sub>SO<sub>4</sub>



**Fig. 2.** Recovery of 10 µg of uranium from 50 mL 0.5 M HNO<sub>3</sub> solutions by the disks modified with TOPO and DC18C6: (a) 5 mg of DC18C6 and varying amounts of TOPO, (b) 40 mg of TOPO and varying amounts of DC18C6.

The influence of the flow rates of the aqueous solutions and methanol through the membrane disks on the retention and recovery of uranyl ion was investigated. The retention of UO<sub>2</sub><sup>2+</sup> by the disk was not significantly affected by the flow rate in the range of 1–60 mL/min. However, the complex was eluted at flow rate over the range of 1–8 mL/min.

#### Analytical performance

By dissolving 10 µg of uranium in 10, 50, 250, 1000, 2000 and 3000 mL of 0.5 M

HNO<sub>3</sub> solution, the breakthrough volume of the proposed method was tested and the recommended procedure was followed under optimal experimental conditions. The results showed that until 3000 mL, the extraction of uranium by the membrane disk was quantitative. Thus, the breakthrough volume for the method must be greater than 3000 mL, providing a concentration factor greater than 300.

The limit of detection (LOD) of the method for the determination of uranium was studied under the optimal experimental conditions. The LOD obtained from 3 $\sigma$  of blank is 0.003 ng/mL. The reproducibility of the procedure is at the most 2%.

When 50 mL solutions of 0.5 M HNO<sub>3</sub> containing 10–100  $\mu$ g of uranium were passed through the disks, the UO<sub>2</sub><sup>2+</sup> was quantitatively retained in all cases. The maximal capacity of the modified disks (40 mg of TOPO and 5 mg of DC18C6) was determined by passing 50 mL portions of 0.5 M HNO<sub>3</sub> solutions containing 6000  $\mu$ g of uranium, followed by spectrophotometric determination of the retained uranyl ion. The maximal capacity of the disk obtained from three replicate measurements was 4563  $\pm$  42  $\mu$ g of uranium on the disk.

In order to investigate the selective separation and determination of UO<sub>2</sub><sup>2+</sup> ions from its binary mixtures with various ions, an aliquot of aqueous solutions (50 mL of 0.5 M HNO<sub>3</sub>) containing 10  $\mu$ g uranium and amount of other ions (mg) was taken and the recommended procedure was followed. A relative error of twice the standard deviation of measurements (*i.e.*, 3% concentration) was considered tolerable. The results are summarized in Table-2.

TABLE 2  
TOLERANCE LIMITS OF DIVERSE IONS ON THE RECOVERY OF 10  $\mu$ g OF URANIUM FROM 50 mL OF 0.5 M HNO<sub>3</sub> SOLUTIONS BY THE MEMBRANE DISKS MODIFIED WITH TOPO (40 mg) AND DC18C6 (5 mg)

Diverse ion	Tolerated ratio of diverse ion to uranium
EDTA, Na <sup>+</sup> , NO <sub>3</sub> <sup>-</sup>	250000 <sup>a</sup>
NH <sub>2</sub> OH·HCl, Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>	20000 <sup>a</sup>
CH <sub>3</sub> COO <sup>-</sup> , Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	10000 <sup>a</sup>
Ca <sup>2+</sup> , Mg <sup>2+</sup>	3500
Cd <sup>2+</sup>	2000 <sup>a</sup>
Pb <sup>2+</sup>	800
Mn <sup>2+</sup>	400 <sup>a</sup>
Ag <sup>+</sup> , Zn <sup>2+</sup>	200 <sup>a</sup>
Ni <sup>2+</sup> , Al <sup>3+</sup> , Hg <sup>2+</sup>	100 <sup>a</sup>
Co <sup>2+</sup>	80
Cu <sup>2+</sup> , La <sup>3+</sup> , Bi <sup>3+</sup>	30
Cr(VI), Ce(IV), V(V), Fe(III)	10
Mo(IV)	2
Th(IV), Zr(VI)	1

<sup>a</sup>Above of which was not tested.

Most of the cations and anions examined do not interfere with the extraction and determination of uranium, and many of them are tolerated at very high levels. However, some of the species tried such as Cu(II), Co(II), Cr(VI), Mo(VI), Th(IV)

and Zr(VI) interfere with the determination of uranyl ions. These interferences were eliminated or reduced considerably in the presence of proper masking agents such as fluoride, EDTA,  $\text{NH}_2\text{OH}\cdot\text{HCl}$  or by rinsing the membrane disk with 50 mL 1.0 M  $\text{HNO}_3$  before elution of the complex (Table-3). Especially the interferences of Cu(II) and Co(II) were eliminated completely using rinsing method.

TABLE 3  
REDUCING OF THE ERRORS PRODUCED BY INTERFERING IONS IN THE RECOVERY OF 10  $\mu\text{g}$  OF URANIUM FROM THE MODIFIED MEMBRANE DISKS

Interfering ion	(mg)	Masking agent	(M)	% Error
Mo(VI)	(0.1)	–	–	100
	(0.1)	KF	$(5.0 \times 10^{-3})$	18
	(0.1)	$\text{NH}_2\text{OH}\cdot\text{HCl}$	$(5.0 \times 10^{-3})$	33
Th(IV)	(0.1)	–	–	100
	(0.1)	EDTA	$(5.0 \times 10^{-4})$	34
	(0.1)	KF	$(5.0 \times 10^{-3})$	5
Zr(VI)	(0.1)	–	–	100
	(0.1)	EDTA	$(5.0 \times 10^{-4})$	3
Cr(VI)	(0.1)	–	–	100
	(0.1)	KF	$(5.0 \times 10^{-3})$	–6
	(0.1)	$\text{NH}_2\text{OH}\cdot\text{HCl}$	$(5.0 \times 10^{-3})$	–2
Cu(II)	(0.1)	–	–	100
	(0.1)	EDTA	$(5.0 \times 10^{-4})$	7
	(0.1)	Rinsing <sup>a</sup>	–	4
Co(II)	(0.1)	–	–	100
	(0.1)	EDTA	$(5.0 \times 10^{-4})$	5
	(0.1)	Rinsing <sup>a</sup>	–	8

<sup>a</sup>The membrane disk was washed with 50 mL 1.0 M  $\text{HNO}_3$  before elution.

To assess the applicability of the method to real samples, it was applied to the extraction and determination of uranium from different water samples. Tap water and two water samples taken from the two springs near the uranium mines were analyzed (Table-4). Satisfactory agreement exists between the results obtained by the proposed method and those reported by  $\alpha$ -spectrometry<sup>25</sup>.

TABLE 4  
DETERMINATION OF URANIUM IN WATER SAMPLES<sup>a</sup>

Water samples	Uranium added (ng/mL)	Proposed Method (ng/mL)	$\alpha$ -Spectrometry <sup>b</sup> (ng/mL)
Tap (Khorram Abad, Iran)	–	3.4 (1.5) <sup>c</sup>	–
Tap (Khorram Abad, Iran)	200	200.5 (2.6)	–
Golastan spring (Khorram Abad, Iran)	200	204.3 (3.6)	–
Tashk (Bandar Abbass, Iran)	–	113.7 (2.1)	115.0
Anarak (Yazad, Iran)	–	35.4 (2.5)	34.0

<sup>a</sup>500 ml of each sample was taken.

<sup>b</sup>Results reported by Atomic Energy Organization of Iran.

<sup>c</sup>RSD of three replicate analyses.

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