Solid-Phase Extraction of Ultratrace Uranium(VI) in Natural Waters Using Octadecyl Silica Membrane Disks Modified by Tri-*n*-octylphosphine Oxide and Its Spectrophotometric Determination with Dibenzoylmethane

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A simple and reliable method for rapid extraction and determination of uranium in natural waters using octadecyl-bonded silica membrane disks modified with tri-*n*-octylphosphine oxide (TOPO) and spectrophotometry with dibenzoylmethane is presented. Extraction efficiency and the influence of sample matrix, type, and optimum amount of extractant, flow rates, and type and minimum amount of organic eluent were evaluated. The maximal capacity of the membrane disks modified by 50 mg of TOPO was found to be 4033 μg of uranium. The limit of detection of the proposed method is 100 ng/1000 mL. The method was applied to the extraction and determination of uranium in natural waters.

Because uranium is a relatively mobile element in many surface or near-surface environments, its geochemical exploration methods require the measurement of the trace quantities of the metal ion in water samples,[1,2] along with that in plants, soils, and rocks. The uranium concentration of seawaters is about 3.3 μg/L,[2,3] in freshwaters even lower. Thus, highly sensitive methods are required for preconcentration and determination of uranium in water samples collected for prospecting purposes. It should be noted that uranium is a chemical toxin as well as being radioactive; the safety profiles for uranium compounds are well established.[4,5]

The measurement of the fluorescence of the uranyl ion in an alkali metal fluoride flux is one of the most common methods for determining trace amounts of uranium.[6,7] This method is of low accuracy and generally requires enrichment and separation of uranium from the matrix.[7,8] Several organic and inorganic reagents

have also been used for the spectrophotometric determination of uranium,[2,9−16] among which Arsenazo III and dibenzoylmethane allow UO_2^{2+} to be quantified at very low concentrations.[1,13,16] However, because of the low concentration of uranium in water, the formation of complexes with these reagents by other trace elements, and the similarity of the absorption curve of the uranium complex with the curves of the complexes formed by other trace elements, most spectrophotometric determinations of uranyl ion must be preceded by a separation and preconcentration step.

Liquid−liquid extraction of uranium with organic solutions of tri-*n*-octylphosphine oxide,[17,18] tri-*n*-butyl phosphate,[19,20] crown ethers,[21,22] tri-*n*-octylamine,[23,24] or bis(2-ethylhexyl) sulfoxide[25] has attracted considerable attention. However, these classical extraction methods are usually time-consuming and labor-intensive and require large volumes of high-purity solvents. Ligands such as tri-*n*-octylphosphine oxide, tri-*n*-butyl phosphate, or dicyclohexyl-18-crown-6 prevent the formation of the colored Arsenazo III−uranyl complex; hence, the Arsenazo III method requires that the uranyl ion is back-extracted into an aqueous phase.[22,24]

Solid-phase extraction (SPE) is an attractive technique that reduces consumption of and exposure to solvent, disposal costs, and extraction time.[26−29] Recently, SPE disks were successfully

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utilized for the extraction of several organic and inorganic analytes from different matrixes.[30-35] We recently modified octadecyl silica membrane disks with crown ethers for the extraction and determination of barium[34] and mercury[35] by flame AAS and CVAAS, respectively. We now report a rapid and efficient method for the selective extraction and concentration of uranyl ions by octadecyl silica membrane disks modified with tri-n-octylphosphine oxide (TOPO) from aqueous solutions and the determination of UO_2^{2+} with dibenzoylmethane (DBM) as a chromogenic reagent. To the best of our knowledge, modified octadecyl silica membrane disks have not been employed previously for the separation and concentration of uranyl ion from aqueous samples.

EXPERIMENTAL SECTION

Reagents. 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, triphenylphosphine oxide (TPPO), tri-n-butyl phosphate (TBP), dicyclohexyl-18-crown-6 (DC18C6) (all from Merck), and DBM (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 a 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 concentration was determined gravimetrically by precipitation of uranyl oxinate. The stock solution was diluted with water or appropriate acid solutions, as needed.

Instruments. The absorbance measurements were carried out with a Shimadzu UV-2100 spectrophotometer. The pH was determined with a model 691 Digital Metrohm pH meter with a combined glass–calomel electrode. Extractions were performed with 47 mm diameter × 0.5 mm thickness Empore membrane disks containing octadecyl-bonded silica (8-μm particle, 60-Å pore size, 3M Co., St. Paul, MN) with a standard Millipore 47-mm filtration apparatus.

Preparation of the SPE Membrane Disks. 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 of methanol was poured onto the disk and immediately drawn through the disk by applying a slight vacuum. After all of the solvent has passed through the disk, it was dried by passing air through it for few minutes. The disk conditioning was then began by pouring 10 mL of methanol onto disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk until the solvent surface almost reached

the surface of the disk. The disk should not be allowed to soak without vacuum, and air should not be allowed to make contact with 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. Immediately, 10 mL of water was introduced onto 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 50 mg of TOPO dissolved in 1 mL of methanol was introduced onto 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 of about 1 min, the filtration funnel containing the modified disk was transferred into an oven and the solvent was completely evaporated at 65 °C.

Solid-Phase Extraction and Quantification of UO_2^{2+}. 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 ion were passed through the membrane at 5–10 mL/min. The disk was dried completely by passing air through it. A 25 × 200 mm test tube was then placed under the extraction funnel. The uranyl–TOPO complex was eluted from the disk with methanol (3 × 2 mL) at a flow rate of 1–2 mL/min. This process ensured complete elution of the UO_2^{2+}–TOPO adduct. Then the eluent was transferred into a 10-mL volumetric flask containing 1 mL of DBM solution (2% w/v DBM in pyridine–methanol (1 + 1) 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 0.2–6.0 μg/mL, $r = 0.9999$).[17]

Uranyl Ions in Natural Waters. A 50-mL aliquot of the water was first passed through a 45-μm (Millipore) Nylon filter to remove particles. Then the filtrate was passed through a octadecyl silica membrane disk without TOPO to remove organic compounds that may be present in the water. Enough HNO_3 (12 M) was added to achieve a concentration of 0.5 M and enough $Na_2EDTA \cdot 2H_2O$ (0.0194 g) to reach a concentration of 1.0×10^{-3} M. The uranyl ions were extracted from the thus treated aliquot and then quantified as described above.

RESULTS AND DISCUSSION

Organic phosphorus compounds possess high extractive properties and have frequently been used as reagents in liquid–liquid extractions.[36] The extractive properties of these ligands depend on the number of ester oxygen atoms and the nature of substituents present in the molecule. Usually, elements in their highest oxidation state (e.g., U(VI)) yield the most extractable complexes with these ligands.[17-20,36] Thus, in preliminary experiments we used three different organic phosphorus compounds and the crown ether DC18C6 to modify the membrane disks for the SPE of the uranyl ion. It is noteworthy that the primary disk conditioning is necessary, since it not only removes all contaminants arising from the manufacturing process and environment but also provides a good interface between the solvent and sample matrix. Failure to condition the extraction disks properly will result in erratic and low recoveries. The results obtained with the ligands and with mixtures of crown ether with TOPO or TBP are

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Table 1. Recovery of Uranyl Ion from the Membrane Disks Modified with Ligands[a]

ligand	mass of ligand on disk (mg)	recovery of uranyl ion (%)[b]
TOPO	20	85 (2)
TPPO	20	52 (3)
TBP	20	25 (3)
DC18C6	20	40 (3)
TOPO + DC18C6	10 + 10	89 (2)
TBP + DC18C6	10 + 10	29 (2)

[a] 50 mL of 0.5 M HNO_3 containing 10 μg of uranium. [b] Values in parentheses are ±SD based on three replicate analyses.
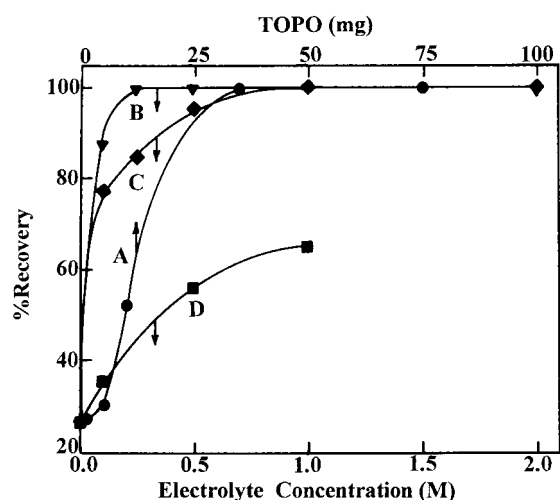

Figure 1. Recovery of 10 μg of uranium from a 50-mL 0.5 M HNO_3 solution by the membrane disks modified with varying amount of TOPO (A), and from 50-mL solutions containing different electrolytes of varying concentrations by the membrane disks modified with 50 μg of TOPO: (B) HNO_3, (C) HCl, and (D) $NaNO_3$.

summarized in Table 1. TOPO with 85% recovery is the most promising ligand for the quantitative SPE of UO_2^{2+} ion. Although the crown ether achieves a recovery of 40%, the mixture of crown ether with TOPO recovers 89% of the UO_2^{2+} ion. However, for the sake of simplicity and lower cost, TOPO was chosen as the ligand for further studies.

To investigate the influence of the matrix on the extraction of uranyl ion, the electrolytes HCl, HNO_3, and $NaNO_3$ were tested. Solutions (50 mL) containing UO_2^{2+} equivalent to 10 μg of uranium and varying concentrations of the electrolytes were passed through the membrane disks modified with 50 mg of TOPO. Uranyl ion is quantitatively extracted by 1.0−2.0 M HCl and 0.25−2.0 M HNO_3 (Figure 1B−D). A 0.5 M 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 coextracted with uranium by the membrane disk in the presence of high concentrations of Cl^- ion.[17]

The optimal amount of TOPO required for the proper modification of the membrane disks was investigated (Figure 1A). The membrane disks modified with 35−100 mg of TOPO retain 10 μg of uranium quantitatively. Thus, 50 mg of TOPO was used for further studies.

Organic solvents such as methanol, ethanol, cyclohexane, and chloroform were tested as eluents for the extracted uranyl−TOPO

Table 2. Tolerance Limits of Diverse Ions on the Recovery of 10 μg of U(VI) from 50 mL of 0.5 M HNO_3 Solutions by the Modified Membrane Disks

foreign ion	tolerated ratio of foreign ion to uranyl ion
K^+, NO_3^-, EDTA	30000[a]
F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, $NH_2OH-HCl$	20000[a]
Na^+, NH_4^+, CH_3COO^-	10000[a]
Ca^{2+}, Cd^{2+}	3500[a]
Mg^{2+}	2000[a]
Pb^{2+}, SCN^-	1000[a]
Cr^{3+}, citrate	1000
Mn^{2+}	400[a]
Ag^+, Zn^{2+}	200[a]
Co^{2+}	130
Ni^{2+}	120
Hg^{2+}, Al^{3+}	100[a]
Ce^{3+}	50[a]
Cu^{2+}	50
La^{3+}	30
Ce^{4+}, $Cr_2O_7^{2-}$	10[a]
Fe^{3+}, Bi^{3+}	5
VO_3^-	3
MoO_4^{2-}	2
Th^{4+}, ZrO^{2+}	1

[a] Above of which was not tested.

Table 3. Influence of Masking Agents on the Errors Produced by Interfering Ions Associated with the Recovery of 10 μg of U(VI) from the Modified Membrane Disks

interfering ion (mg)	masking agent (M)	% error
Th^{4+} (0.1)		+100
	EDTA (5.0 × 10^{-4})	−1
Th^{4+} (1.0)		+100
	F^- (1.0 × 10^{-2})	−3
ZrO^{2+} (0.1)		+100
	EDTA (5.0 × 10^{-4})	−4
	F^- (5.0 × 10^{-3})	+30
VO_3^- (0.1)		+100
	F^- (1.0 × 10^{-2})	+36
	$NH_2OH.HCl$ (1.0 × 10^{-2})	+2
MoO_4^{2-} (0.1)		+100
	F^- (1.0 × 10^{-2})	+83
	$NH_2OH.HCl$ (1.0 × 10^{-2})	+27
MoO_4^{2-} (0.05)	$NH_2OH.HCl$ (5.0 × 10^{-3})	+1
$Cr_2O_7^{2-}$ (0.1)		+100
	$NH_2OH.HCl$ (5.0 × 10^{-3})	+1
Fe^{3+} (0.2)		+100
	EDTA (5.0 × 10^{-4})	−3

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 but also because of the faster color development and improved spectrophotometric measurement of uranyl ion with DBM in the presence of pyridine.[13,17]

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_2^{2+} by the disk was not significantly affected by the flow rate in the range of 1−40 mL/min. However, the uranyl−TOPO was washed only at flow rates from 1 to 4 mL/min.

When solutions of 10 μg of uranium in 10, 25, 50, 100, 250, 400, and 1000 mL of 0.5 M HNO_3 were passed through the disks, the UO_2^{2+} was quantitatively retained in all cases. Thus, the

Table 4. Determination of Uranium in Water Samples

| | | uranium determined (ng/mL) | |
water sample	uranium added (ng/mL)	proposed method	α-spectrometry[a]
tap		2.3 (1.5)[b]	
tap	200	202.1 (4.6)	
Tashk		116.2 (3.1)	115.0
Anarak		33.6 (1.6)	34.0

[a] Results reported by Atomic Energy Organization of Iran. [b] RSD of three replicate experiments.

breakthrough volume for the method should be greater than 1000 mL. The limit of detection (LOD) of the method for the determination of U(VI) was studied under the optimal experimental conditions. The LOD obtained from 3σ of blank is 100 ng/1000 mL. It is interesting to note that the limit of detection obtained is similar to that achievable by the kinetic phosphorus analysis (KPA; Chemcheck Inc., Richland, WA), which is also a rapid quantitation method. However, the KPA method does suffer from potential interferences that could be resolved by the proposed method, and also the KPA is not field-rugged. The reproducibility of the procedure is at the most 1.5%.

The maximal capacity of the modified disks (50 mg of TOPO) was determined by passing 50-mL portions of 0.5 M HNO_3 solutions containing 6000 μg of uranium, followed by spectrophotometric determination of the retained cation. The maximal capacity of the disk obtained from three replicate measurements was 4033 ± 51 μg of uranium on the disk.

The influence of several cations and anions on the SPE and determination of uranyl ion (10 μg of uranium in 50 mL of 0.5 M HNO_3 solution) was studied. A relative error of twice the standard deviation of measurements (i.e., 3% concentration) was considered tolerable. The results are summarized in Table 2. 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 MoO_4^{2}, VO_3^-, Fe^{3+}, and especially Th^{4+} and ZrO^{2+} interfere with the determination of uranyl ion. These interferences were eliminated or reduced considerably in the presence of proper masking agents such as fluoride, EDTA, or $NH_2OH-HCl$ (Table 3).

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 two springs near the uranium mines at Tashk (Bandar Abbass, Iran) and Anarak (Yazd, Iran) were analyzed (Table 4). Satisfactory agreement exists between the results obtained by the proposed method and those reported by α-spectrometry.[37,38]

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