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Preconcentration of Trace Uranium from Natural Water with Solid-Phase Extraction

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In the present study, an effective method was used for the preconcentration and determination of uranium(VI) by solid-phase extraction (SPE). For this purpose, a microcolumn of alumina modified with sodium dodecyl sulfate (SDS) and 1-(2-pyridylazo)-2-naphthol (PAN) was prepared for the preconcentration of trace uranyl(VI) from water samples. The uranium(VI) was completely eluted with 6.0 mol dm^{-3} HCl and determined by a spectrophotometric method with Arsenazo III. The SPE conditions were optimized by evaluating the effective factors such as pH, flow rate and masking agent. By the proposed method a preconcentration factor more than 150 was achieved. The average recovery of uranium(VI) was 99.8%. The relative standard deviation was 2.6% for ten replicate determinations of uranyl(VI) ion in a solution with a concentration of 50 ng cm^{-3}. Some concomitant ions such as Cd^{2+}, Ni^{2+}, $MoO_4{}^{2-}$, Cu^{2+}, Th^{4+} and Ce^{3+}, which interfere in the determination process of uranium(VI), were masked with EDTA in the aqueous phase during the extraction process. The proposed method was successfully used for the determination of uranium in natural water.

The toxicology of uranium is complicated by the dual nature of the biological effects of uranium on organisms. The initial biological effects produced by uranium are the result of its toxicity, whereas the effects are due to the radioactivity of delayed uranium.[1] The importance of uranium has grown manifold due to the increasing applications of atomic energy. Therefore, there is an analytical requirement for the trace determination of uranium in various types of samples ranging from geological and seawater to industrial effluents. The determination of uranium by flame atomic absorption spectrometry requires a full rich luminous flame to provide suitable reducing conditions to obtain a sufficiently large population of atoms.[2] It has a poor sensitivity (50 ppm for 1% absorbance).[3] However, a dinitrogen oxide-acetylene flame for 1000 ppm uranium gives an absorbance reading of about 0.09 if sufficient alkali has been added to suppress ionization.

Although ICP–AES has been used in fields as the method of choice for the determination of uranium, prior solvent extraction is necessary.[4,5] Numerous methods have been reported for the microanalysis of uranium although most of them are nonselective.[6] As a result, various separation and preconcentration techniques are often employed prior to analysis.[7,8]

The liquid–liquid extraction of uranium with organic solutions of tri-*n*-octylphosphine oxide,[9,10] tri-*n*-butyl phosphate,[11,12] crown ethers,[13,14] tri-*n*-octylamine,[15] or bis(2-ethylhexyl) sulfoxide[16] has attracted considerable attention. However, these classical extraction methods are usually time-consuming and labor-intensive and require large volumes of highly pure 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(VI) complex; hence, the Arsenazo III method requires that the uranyl ion be back-extracted into an aqueous phase.[13,15]

Solid-phase extraction (SPE) is an attractive technique that reduces the consumption of and exposure to solvents, disposal costs and extraction time.[17,18] Recently, surfactant-coated alumina as an absorbent was successfully utilized for the preconcentration and determination of chromium.[19,20]

Ionic or nonionic surfactant molecules form self-aggregate structures called “micelles” in aqueous solutions above the critical micelle concentration. The hydrocarbon cores of the micelles give them the ability to solubilize hydrophobic organic compounds. Similar surfactant aggregates can be formed on solid surfaces such as alumina[21,22] and iron(III) oxide hydrate.[23] They are called “hemi-micelles,” whose interiors tend to incorporate sparingly soluble organic substances.

Also water-insoluble chelating agents such as 1-nitroso-2-naphthol,[24] 1-(2-pyridylazo)-2-naphthol (PAN),[25] and pyrrolidinedithiocarbamate[26] were introduced into the hemimicelles of SDS-coated alumina for the preconcentration of trace elements.

Compared with the recent development in the preconcentration, separation and determination of uranium (VI), the proposed method is simple and very sensitive.[27–32]

In the present work, an efficient method for the preconcentration of uranium from a large volume of the aqueous solutions, through the immobilization of PAN on a surfactant-coated alumina and the determination of uranium with Arsenazo III as a chromogenic reagent is proposed.

Experimental

Reagents. Analytical reagent-grade chemicals and doubly distilled water were used. All of the glassware was soaked in 0.7 mol dm^{-3} nitric acid for at least 24 h, washed with deionized water and dried in a dust-free environment.

Alumina powder (γ-alumina (particle size, 10–50 μm; chromatographic grade; Darmstadt, Germany)) was purified prior to use by shaking with 4 mol dm^{-3} nitric acid, and washing three times with water.

Sodium dodecyl sulfate (SDS): the analytical-grade reagent (Schuchardt; Germany) was used without further purification.

To prepare a PAN solution, 0.01 mol dm^{-3}, 0.25 g of PAN was dissolved in 100 cm^3 of 95% ethanol.

A stock of uranyl(VI) ion was prepared by dissolving an appropriate amount of $UO_2(NO_3)_2 \cdot 6H_2O$ in 0.5 mol dm^{-3} nitric acid. Working solutions were prepared from the stock solution by serial dilutions with distilled water.

To prepare a 7×10^{-4} mol dm^{-3} Arsenazo III solution, 0.5 g of Arsenazo III and 0.125 g sodium acetate were dissolved in 100 cm^3 of water. The solution was stored in an amberglass bottle.

SDS-coated alumina column: Purified alumina particles (1.5 g) were suspended in 50 cm^3 of water and mixed with 100 mg of SDS and 2 cm^3 PAN solution (0.01 mol dm^{-3}). The suspension was then acidified to pH 2–2.5 with 3 mol dm^{-3} nitric acid and mixed for 15 min with a mechanical shaker. After the supernatant solution was discarded, the PAN-coated alumina was packed into a column (9 mm × 13 mm i.d.).

Apparatus. A methrom 713 pH meter was used for measuring the pH of the solutions.

The absorbance measurements were carried out with a shimadzu UV–Vis 265 spectrophotometer.

Recommended Procedure. A given volume of aqueous sample up to 1500 cm^3 uranium(VI), after an adjustment to pH 9.0 with NH_3, was passed through the microcolumn at a flow rate of 5 cm^3 min^{-1}. The adsorbed metal was eluted with 7 cm^3 of 6.0 mol dm^{-3} HCl at an elution rate of 2 cm^3 min^{-1}. The eluent was then transferred into a 10 cm^3 volumetric flask containing 2 cm^3 of 0.05% Arsenazo III solution and diluted to 10 cm^3 with deionized water. The uranyl(VI) concentration was then determined at 655 nm against a blank solution (external linear calibration range 0.06–20 µg mL^{-1}, $r = 0.9994$).[33]

Result and Discussion

Effect of the pH. The adsorption of SDS on alumina is highly dependent on the solution pH. Negatively charged SDS was more effectively adsorbed on positively charged alumina surfaces at lower pH values. Almost complete adsorption was achieved at pH values of 1–4 by shaking SDS solution with alumina for 15 min.[19,34]

When the SDS and PAN solutions were acidified, SDS would form hemimicelles on alumina by strong adsorption. The micelles could trap PAN molecules homogeneously, which caused alumina to change color from white to orange.

By mixing 1.5 g of alumina with 0.1 g of SDS and 2 cm^3 of PAN solution at pH 2–2.5, 5 mg of PAN was approximately immobilized on the alumina.

The effect of the pH of solution containing microgram quantities of uranium(VI) was examined over the pH range of 1–12 and the percentage retention of metal on the absorbent was calculated. The results are shown in Fig. 1. Uranium(VI) was absorbed quantitatively over the pH range of 8.5–9.8.

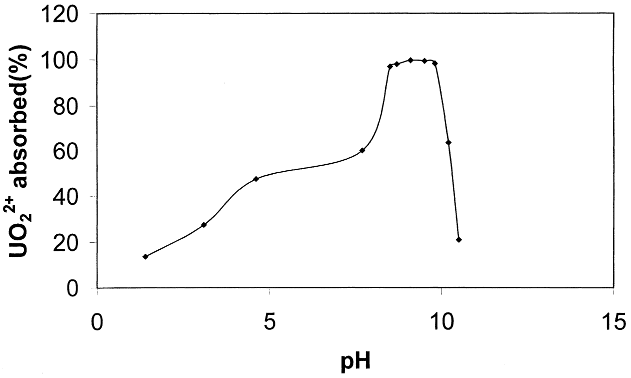

Fig. 1. Effect of pH on the adsorption of uranyl on PAN-coated alumina. Concentration of standard solution UO_2^{2+} 200 ng mL^{-1}, flow rate: 5 mL min^{-1}.

Effect of the Flow Rate. The effect of the flow rate of the solution through the microcolumn on the retention behavior of uranium was studied over the range of 1–15 cm^3 min^{-1}. The adsorption began to decrease with an increase in the flow rate when it was greater than 6 cm^3 min^{-1}. The metal was absorbed quantitatively at a flow rate of 5 cm^3 min^{-1} and subsequently eluted with 6.0 mol dm^{-3} HCl at an elution rate of 2 cm^3 min^{-1}.

Effect of the Volume of the Sample Solution. The volume of the sample solution containing 0.01 mg uranyl(VI) was varied over the range of 25–1500 cm^3 under the optimum conditions, while keeping all other variables constant. It was observed that the signal height was almost constant up to 1500 cm^3. However, for convenience, all of the experiments were carried out with 50 cm^3 of the aqueous phase. In the present work, because the elution volume was 10 cm^3, a preconcentration factor of 150 could be achieved by the column.

Capacity of the Sorbent. In order to study the adsorptive capacity of PAN-coated alumina for uranyl(VI) a batch method was used. To 1.5 g PAN-coated alumina was added 50 cm^3 of a solution containing 5 mg of uranium(VI) at pH 9.0. After shaking for 1 h, the mixture was filtered. Then 10 cm^3 of the supernatant solution was diluted to 100 cm^3 and determined by a spectrophotometric method using Arsenazo III. The capacity of the sorbent was found to be 3070 µg g^{-1}.

Desorption of Uranium(VI) from the Column. The desorption of uranium(VI) from the PAN-coated alumina was studied by using different eluents such as HCl and HNO_3. The elution volume was 5, 10 and 15 cm^3. As can be seen from Table 1. 10 cm^3 of 2 mol dm^{-3} HNO_3 or 6 mol dm^{-3} HCl were found to be satisfactory for quantitative elution (recovery $> 98.5\%$) and 10 cm^3 of 6 mol dm^{-3} HCl at an elution rate of 5 cm^3 min^{-1} was selected for subsequent experiments. The eluted uranium(VI) was determined by a spectrophotometric method using Arsenazo III complexation.

It has been reported that Arsenazo III is the most sensitive reagent[35] for the determination of uranyl(VI) ions and quantitative work is best carried out at pH 7–8. However serious interferences are caused by Th^{4+}, Zr^{4+}, Fe^{3+}, rare earths, etc.[36–38] It is also known that in HCl medium, Arsenazo III, reacts selectively with uranyl(VI) ions even in the presence of iron and rare earths. Since the reaction of uranyl ions with Arsenazo III in acid solutions gives rise to the formation of two complexes of type ML (M is metal ion and L is ligand), their proportions being dependent upon the acidity,[39] the determination was carried out in 4 mol dm^{-3} HCl using Arsenazo III.

Interference Effects. The influence of several cations and anions on the adsorption and determination of uranyl(VI) ion (200 ng mL^{-1}) was studied. A relative error of twice the stan-

Table 1. Effect of Type and Volume of Solution on Recovery of Uranium(VI)

Type of elution solution	Volume/cm^3	Concentration /mol dm^{-3}	Recovery/%
HCl	5	2	70
	10		76
	15		81
	5	4	75
	10		82
	15		86
	5	6	91
	10		98.8
	15		98.7
	5	8	95.3
	10		98.6
	15		98.9
HNO_3	5	0.5	75.3
	10		77.4
	15		81.5
	5	1	85.3
	10		87.4
	15		91.5
	5	2	94.6
	10		98.6
	15		98.9
	5	3	94.5
	10		98.9
	15		99

Table 2. Tolerance Limits for Coexisting Ions in the Adsorption of 200 ng mL^{-1} Uranyl(VI)

Coexisting ion	Concentration/ μg mL^{-1}
EDTA	3000
K^+, Cl^-, NO_3^-, NH_4^+, CH_3COO^-, F^-	1000
Ca^{2+}, Al^{3+}, Mg^{2+}	350
Ni^{2+}	80
Mn^{2+}, Co^{2+}, Ag^+	50*
Cu^{2+}	40
Fe^{3+}, Hg^{2+}, Zn^{2+}	32*
MoO_4^{2-}	20
Pb^{2+}	20*
Cd^{2+}	18
Ce^{3+}	16*
Th^{4+}	5*

*In the presence of EDTA (2×10^{-3} mol dm^{-3}).

Table 3. Analytical Determination of Uranyl(VI) in Water Samples

Water sample	U(VI) added/ ng mL^{-1}	Found/ ng mL^{-1}*	RSD/%
Tashk	0.0	2.3	3.2
	10.0	12.4	2.4
	12.0	14.2	2.3
Anarak	0.0	33.2	2.6

*Results Certified by Atomic Energy Organization of Iran

dard deviation of measurements was considered to be tolerable. The results are summarized in Table 2. Most of the cations and anions examined did not interfere with the extraction and determination of uranium. However, some of the species tried, such as Cd^{2+}, Ni^{2+}, MoO_4^{2-}, Cu^{2+}, and especially Th^{4+} and Ce^{3+} interfered with the determination of uranyl(VI) ion. These interferences were eliminated or reduced considerably in the presence of proper masking reagent such as EDTA. This reagent forms a stable complex with most metals ions, but doesn't interfere with the reaction between uranium(VI) and PAN.

Calibration, Precision and Detection Limit. The calibration graph for the determination of uranyl(VI) was linear up to 20 μg cm^{-3} of uranyl(VI). The repeatability of the measurement was tested with different amounts of uranyl(VI). At the 50 ng cm^{-3} level of uranyl(VI), the relative standard deviation (10 replicate analyses) was 2.6%.

The detection limit defined as three-times the standard deviation of a blank determination was 0.4 ng cm^{-3}, respectively, based on ten replicate determinations of the blank.

Application to Samples. The results for the analysis of water samples taken from two springs near uranium mines at Tashk (Bandar Abbass, Iran) and Anarak (Yazd, Iran) are given in Table 3. All samples were analyzed in triplicate.

The accuracy of the method was examined by recovery study of the spike samples. The quantitative recovery of the uranium spikes and the relative standard deviation confirm the good precision and accuracy of the proposed method for the preconcentration and determination of uranium.

Conclusion

The solid-phase extraction of uranyl ions combined with its spectrometric determination eluate, provides an accurate, precise and reliable technique for the preconcentration and determination of trace uranyl(VI) from 1500 cm^3 of natural water. Due to the accessible high concentration factor (150-fold), this method is very sensitive.

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