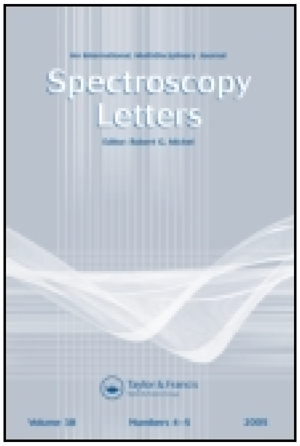

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Solid-Phase Extraction Using Polymer-Based Cartridge Modified with 2-(2-benzothiazolylazo)-3-hydroxyphenol for Preconcentration of Uranium(VI) Ions from Water and Real Samples

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ABSTRACT A highly sensitive, selective, and rapid method for the determination of ng mL^{-1} level of U(VI) based on the rapid reaction of U(VI) with 2-(2-benzothiazolylazo)-3-hydroxyphenol (BTAHP) and the solid-phase extraction of the colored complex with a reversed-phase polymer-based C18 cartridge was developed. The BTAHP reacted with U(VI) to form a violet complex of molar ratio 2:1 [BTAHP to U(VI)] in the presence of 4.0 M of phosphoric acid solution and Triton X-114 medium. This complex was enriched by the solid-phase extraction with a polymer-based C18 cartridge. The enrichment factor of 200 was achieved. The molar absorptivity of the complex is 2.73×10^6 L mol^{-1} cm^{-1} at 639 nm in the measured solution. The system obeys Beer's law in the range of 2.0–125 ng mL^{-1}, whereas the optimum concentration range obtained from Ringbom plot was 8.0–115 ng mL^{-1}. The relative standard deviation for 10-replicates sample of 100 ng mL^{-1} level is 1.05%. The detection and quantification limits are 0.6 and 1.98 ng mL^{-1} in the original sample. This method was applied to the determination of uranium(VI) in sea, tap, and waste waters, ore standard reference material, soil and sediment samples with good results comparing to the graphite furnace atomic absorption spectroscopy (GFAAS) method.

KEYWORDS solid-phase extraction, spectrophotometry, thiazolylazo dyes, uranium determination, water and ores analysis

INTRODUCTION

There is high interest in new separation techniques that selectively extract metal ions from dilute and waste-water samples. Although a variety of methods such as precipitation, solvent extraction, electrolysis, and ion exchange can be used to remove dissolved metals from aqueous samples, most of them have disadvantages of noneconomic character, poor removal efficiency, high

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cost, generation of secondary pollution, and ineffectiveness for low metal concentrations.[1]

Solid-phase extraction (SPE) has commonly been used as a technique for preconcentration/separation of various inorganic and organic species. SPE is used to enhance the selectivity and sensitivity of the method as it allows for discriminatory binding of analyte to a solid support where it will be accumulated and subsequently eluted with a small volume of solvent. This technique has advantages of higher enrichment factor, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of reagent, being environment friendly, flexibility, and having easier incorporation into automated analytical techniques.[2–5] Selectivity of the solid-phase sorbent toward an analyte depends on the structure of the immobilized organic ligands.

Uranium is extensively used in the nuclear industry and is highly radioactive. It is present in low quantities in wash streams coming out of nuclear reactors in both aqueous and nonaqueous media, and monitoring of these streams for the presence of uranium in high activity content is essential. The maximum uranium concentration in drinking water and seawater also is reported as less than 9.0 and 1.0–3.0 ng mL^{-1}, respectively.[6] This extreme dilution in the presence of relatively high concentrations of other ions makes it difficult to determine directly uranium ions, and refined analytical methods must be employed to detect small concentrations.

Since the 1950s, great efforts have been focused on new materials and technologies for separation of uranium(VI) from aqueous solution. Although liquid–liquid extraction (LLE) has been widely used in separation and/or recovery of uranium(IV) from U-containing aqueous solution so far,[7–9] this technology is being applied with its insurmountable limitations due to heavy use of organic extractants and solvents and so on.[10–12] The researches on SPE have steadily increased over recent years. In the field of separation of nuclides including uranium, the technology based on SPE can lead to superior application properties such as high volume reduction ratio, larger cost-effectiveness, more reliable safety in practice, and, more importantly, environmental friendliness.[11–14]

Several methods for determination of uranium based on the preconcentration techniques have been reported. Solid sorbents such as neutral polymer-Amberlite XAD series,[15–18] silica[19,20] octadecyl silica membrane discs,[21] activated silica gel,[22] controlled pore glass,[23] polyurethane foam,[24] and cationic or anionic exchange resins[25–29] have been reported for the enrichment of uranium(VI) from dilute solutions prior to determination by a variety of analytical techniques.

In this paper, the SPE of U(VI)–BTAHP complex with a reversed-phase polymer-based C18 cartridge was studied. The polymer-based C18 is manufactured from a hydrophilic methacrylate polymer, which is functionalized with C18 ligands. It is a reversed-phase solid-phase cartridge that provides a broad range of solvent choices and a pH range from 0.0 to 14. By using the polymer-based C18 cartridge, the U(VI)–BTAHP complex was enriched by SPE in phosphoric acid medium, and the enrichment factor of 200 was achieved. Based on this, a highly sensitive, selective, and rapid method for the determination of U(VI) ions in water samples was developed.

MATERIALS AND METHODS

Apparatus

A Perkin Elmer Lambda 12 UV-Visible spectrophotometer (USA) with a 10 mm quartz cell was used for all spectral measurements. The extraction was performed on a Waters SPE device (that can prepare 20 samples simultaneously), and a reversed-phase polymer C18 TM cartridge (methacrylate polymer functionalized with C18 ligands, 10 mm i.d., 15 mm, 30 μm particle) was obtained from Beijing Genosys Technologies, P. R. China. A Perkin Elmer atomic absorption spectrometry model AAnalyst 300 (USA) was used for all GFAAS measurements. An Orion research model 601 A/digital ion analyzer pH meter (Japan) was used for checking the pH of solutions.

Reagent

Analytical reagent grade chemicals and doubly distilled water were used throughout. 2-(2-Benzothiazolylazo)-3-hydroxyphenol (BTAHP) used in the present investigation was prepared according to the procedure described previously.[30] An appropriate weight was dissolved in 100 mL of absolute ethanol (2×10^{-3} M). The solution was stable for more than 1 month.

A stock solution of 100 μg mL^{-1} solution of hexavalent uranium solution was prepared by dissolving

0.0223 g of uranyl nitrate $UO_2(NO_3).6H_2O$ (Johnson and Matthey, New York, USA, www.matthey.com) in 100 mL deionized water. We added 5.0 mL concentrated HNO_3 to the solution to suppress hydrolysis. A working solution containing 100 ng mL^{-1} was prepared by appropriate dilution with distilled water. A 4.0 M solution of phosphoric acid was used. Triton X-114 (Sigma Company, USA) solution (5.0%, v/v) was prepared by dissolving Triton X-114 with water.

General Procedure

To a standard or sample solution containing no more than 125 ng of U(VI) in 100 mL of measuring flask, 6.0 mL of 4.0 M of phosphoric acid solution, 3.0 mL of 2×10^{-3} M BTAHP solution, and 4.0 mL of 5.0% Triton X-114 solution were added. The mixture was diluted to volume of 100 mL and mixed well. After 5.0 min, the solution was passed through the polymer-based C18 cartridge at a flow rate of 20 mL min^{-1}. After the enrichment was finished, the retained complex is eluted from the cartridge at a flow rate of 5.0 mL min^{-1} with 0.5 mL of acetonitrile in the reverse direction. The absorbance of this solution was measured at 639 nm in a 10 mm cell against a reagent blank prepared in a similar way without U(VI).

Determination of Uranium in Sea Water Samples

We filtered 50 mL sea water sample and then treated it with 5.0 mL concentrated nitric acid, boiled it for 15 min—in order to oxidize any trace organic matter and to expel dissolved carbon dioxide—and diluted it to 100 mL. Solution was filtered, and the recovered uranium was estimated using the above general procedure. The results obtained were compared with the results of the standard addition technique and results obtained from GFAAS method.

Determination of Uranium in Various Water Samples

An aqueous solution of tap or industrial wastewater samples (100 mL) spiked with uranyl ions at a total concentration $\leq$50 ng mL^{-1} was first filtered through 0.45 μm cellulose membrane filters and stored in sample bottles (200 mL). The test solution at the optimum experimental conditions of uranyl ion complexation and sorption described above in the general procedure was applied.

Procedure for the Recovery Studies to Water Sample by Standard Addition

Two 50 mL portions of water sample were filtered and then treated with 5.0 mL concentrated nitric acid and boiled for 15 min, in order to oxidize any trace organic matter and to expel dissolved carbon dioxide, and diluted to 100 mL. One of the solutions was doped with different nanogram of the standard uranium solution (to apply the standard addition techniques). Solutions were filtered, and the uranium content in both the solutions were estimated after SPE spectrophotometrically as described above in the general procedure.

Procedure for Soil and Standard Uranium Ore Samples

About 0.10–0.50 g of sample was treated with 5.0 mL concentrated HF and 1.0 mL concentrated HNO_3 at 160°C on sand bath until the mixture became dry. The mixture was cooled and treated with 10 mL nitrohydrochloric acid (aqua regia) on sand bath until the mixture was dry. The residue was then cooled and dissolved in 50 mL of deionized water. The amount of uranium in the sample was determined using the general procedure described above.

RESULTS AND DISCUSSION

Absorption Spectra

Our previous studies[30] on the complexation of U(VI) using BTAHP in the presence of sodium lauryl sulphate showed an absorption band with $\lambda_{max} =$ 599 nm. This method was modified through SPE using the polymer-based C18 cartridge at variable conditions. The absorption bands of BTAHP and its complex in acetonitrile medium after SPE are located at 547 nm and 639 nm, respectively (Fig. 1).

Effect of Acidity

Results showed that the optimal conditions for the reaction of U(VI) with BTAHP are in acid medium. Therefore, the effects of hydrochloric, nitric,

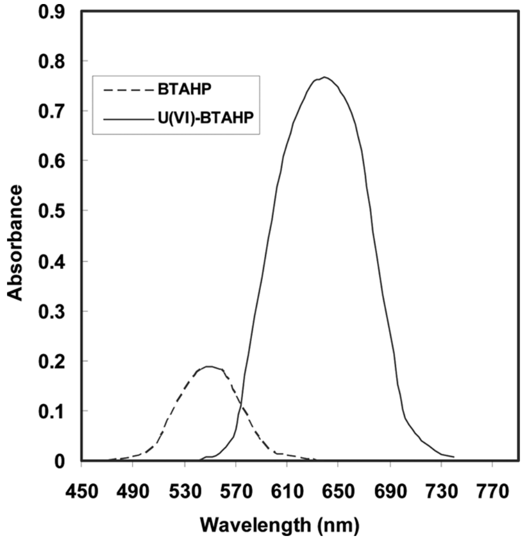

FIGURE 1 Absorption spectra for 5×10^{-5} M BTAHP and its complexes with 100 ng mL^{-1} U(VI) after SPE at the optimum conditions.

perchloric, phosphoric, and sulfuric acids on the color reaction of U(VI) with BTAHP were studied, because the anion of each acid can have some effect on the complex formation. Moreover, experiments have showed that 4.0 M phosphoric acid has the best effect, and the amount of 5.5–7.0 mL was found to give a maximum and constant absorbance (Fig. 2), so 6.0 mL of 4.0 M phosphoric acid was recommended.

Effect of Surfactants

The effects of surfactants on the U(VI)–BTAHP system were investigated. The results showed that, in the present or absence of anionic or cationic surfactants, the U(VI)–BTAHP chromogenic system gives low absorption, whereas in the presence of nonionic surfactants, the absorption of the chromogenic system increases markedly due to the nonionic nature of the formed complex. Various nonionic surfactants enhance the absorbance in the following sequence: Triton X-114 > Triton X-100 > emulsifier-OP > Tween-80 > Tween-60 > Tween-20. Accordingly, the Triton X-114 was the best additive, and the use of 3.0–4.5 mL of 5.0% Triton X-114 solution gave constant and maximum absorbance (Fig. 3). Consequently, the use of 4.0 mL was recommended.

Effect of BTAHP Concentration

For up to 1.8 μg of U(VI), the use of 3.0 mL of 2×10^{-3} M of BTAHP solution was found to be sufficient for a complete reaction. Accordingly, 3.0 mL of BTAHP solution were added in all further measurements.

Stability of the Chromogenic System

After the components are mixed, the absorbance reaches its maximum within 5.0 min at room temperature and remains stable for at least 9.0 hr. After having been extracted into the acetonitrile medium, the complex was stable for at least 18 hr.

SPE

Both the enrichment and the elution were carried out on a Waters SPE device. The flow rate was set to

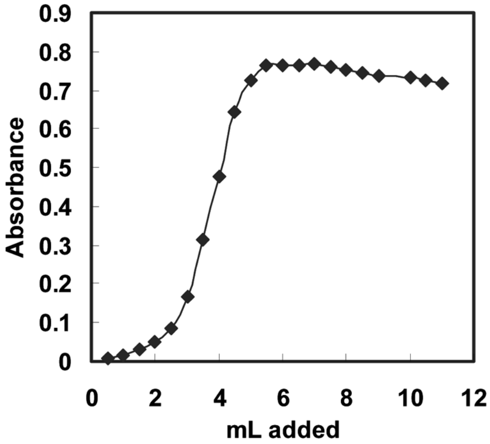

FIGURE 2 Effect of 4.0 M H_3PO_4 volume on the SPE of 100 ng ml^{-1} U(VI) under the optimum conditions.

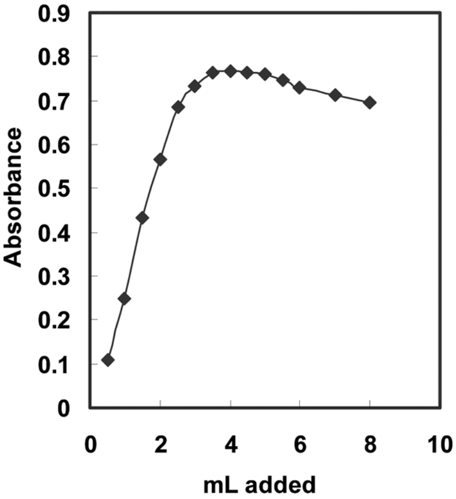

FIGURE 3 Effect of 5.0% Triton X-114 on the SPE of 100 ng mL^{-1} U(VI) at the optimum conditions.

$20\,\mathrm{mL\,min^{-1}}$ for enrichment and $5.0\,\mathrm{mL\,min^{-1}}$ for elution.

Some experiments were carried out in order to investigate the retention of BTAHP and its U(VI) complex on the cartridge. It was found that the BTAHP and its U(VI) complex are retained on the cartridge quantitatively when they pass the cartridge as phosphoric acid medium. The adsorption capacity of the sorbent was 100 mg, whereas the capacity of the cartridge was determined as 46 mg for U(VI)–BTAHP complex in 100 mL of solution. In this experiment, the maximum amount of uranium is only 1.8 μg. Therefore, the cartridge has adequate capacity to enrich the U(VI)–BTAHP complex.

In order to choose a proper eluent for the retained BTAHP and its U(VI) complex, we studied various organic solvents. For eluting the U(VI)–BTAHP complex from the cartridge, the volume of the solvent needed is 0.5 mL for acetonitrile, 1.2 mL for acetone, 1.5 mL for isopentyl alcohol, 1.8 mL for DMF, 2.2 mL for ethanol, and 2.5 mL for methanol. The maximum enrichment was achieved when acetonitrile was selected as eluent. The experiment shows that it was easier to elute the retained BTAHP and its U(VI) complex in reverse direction than in forward direction, so it is necessary to reverse the cartridge during elution. Since 0.5 mL of acetonitrile was sufficient to elute the BTAHP and its U(VI) complex from cartridge at a flow rate of $5.0\,\mathrm{mL\,min^{-1}}$, the volume of 0.5 mL was selected.

Calibration Curve and Sensitivity

The calibration curve showed that the system obeys Beer's law in the concentration range of 2.0–125 ng U(VI) per mL in the measured solution. For more accurate results, Ringbom optimum concentration range was found to be 8.0–115 ng U(VI) per mL in the measured solution. The linear regression equation obtained was $A = 7.677\ C\ (\mu\mathrm{g\,mL^{-1}}) - 0.008$ ($r = 0.9996$). The molar absorptivity was calculated to be $2.73 \times 10^6\ \mathrm{L\,mol^{-1}\,cm^{-1}}$ at 639 nm, whereas Sandell sensitivity was found as $0.076\ \mathrm{ng\ cm^{-2}}$.

The standard deviations of the absorbance measurements were calculated from a series of 13 blank solutions. The limits of detection ($K = 3$) and of quantification ($K = 10$) of the method were established[31] and recorded in Table 1, according to the IUPAC definitions ($C_1 = KS_o/s$, where C_1 is the limit of detection, S_o is the standard error of blank, s is the slope of the standard curve, and K is the constant related to the confidence interval. The relative standard deviation was 1.05% obtained from a series of 10 standards, each containing $100\,\mathrm{ng\,mL^{-1}}$ of U(VI).

A comparison of the proposed method with the previously reported methods for preconcentration and spectrophotometric determination of uranium[11,13,17,19,32–41] in addition to that using molecularly imprinted polymers[42–45] and cloud point extraction[46,47] (Table 2) indicates that the proposed method is faster and simpler than the existing methods and that it provides a lower limit of detection. Although the procedures for xylenol orange[36] using laser fluorimetry or pyrocatechol violet[37] using spectrophotometry have lower detection limits, the proposed method has more advantages through the sensitivity and interference point of view. To the best of our knowledge, this is the first report of using a reversed-phase polymer-based C18 cartridge for SPE of uranium.

Stoichiometric Ratio

The nature of the complex was established at the optimum conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of BTAHP to

TABLE 1 **Analytical Parameters**

Parameter	Value	Parameter	Value
Beer's law limit ($\mathrm{ng\,mL^{-1}}$)	2.0–125	Regression equation[a]	
Ringbom optimum range ($\mathrm{ng\,mL^{-1}}$)	8.0–115	Slope (b)	7.677
Molar absorptivity ($\mathrm{L\,mol^{-1}\,cm^{-1}}$)	2.73×10^6	Intercept (a)	−0.008
Sandell sensitivity ($\mathrm{ng\,cm^{-2}}$)	0.076	Correlation coefficient (r)	0.9996
Detection limit ($\mathrm{ng\,mL^{-1}}$)	0.60	RSD (%)	1.05
Quantification limit ($\mathrm{ng\,mL^{-1}}$)	1.97	S Stoichiometric ratio (L:M)	2:1

[a] $A = a + b\ C$, where C is the concentration of U(VI) in $\mu\mathrm{g\,mL^{-1}}$.

TABLE 2 **Comparison of the Proposed Method with Some Preconcentration Methods**

Chelating agent	Sorbent or micellar media	Analytical method	D.L. ng mL^{-1}	Ref.
Quinoline-8-ol	chloromethylated polymeric resin	FT-IR spectroscopy	5.0	[11]
Quinoline-8-ol	Amberlite XAD-4	Spectrophotometry	2.0	[17]
Quinoline-8-ol	Silica	ICP-AES	1.0	[19]
5,7-Dichloroquinoline-8-ol	Naphthalene	Spectrophotometry	5.0	[32]
1,2-(Pyridylazo)-2-naphthol	Benzophenone	Spectrophotometry	5.0	[33]
1,2-(Pyridylazo)-2-naphthol	TritonX-114	Spectrophotometry	1.1	[34]
Arsenazo III	silica gel	Spectrophotometry	10	[35]
arsenazo(III)	Silica	Spectrophotometry	4.0	[13]
xylenol orange	Silica	Laser fluorimetric	0.05	[36]
pyrocatechol violet	TritonX-114	Spectrophotometry	0.06	[37]
Dibenzoylmethane	TritonX-114	Spectrophotometry	11	[38]
Dibromosuccinic acid	Amberlite XAD-4	Spectrophotometry	2.0	[39]
Diarylazobisphenol	Activated carbon	Spectrophotometry	5.0	[40]
o-Vanillin semicarbazone	Amberlite XAD-4	ICP-AES and GFAAS	100	[41]
polymer imprinting		AAS	1.5	[42]
Molecularly imprinted	ion exchange resin	Spectrophotometry and mass spectra	2.2	[42]
Molecularly imprinted	—	Spectrophotometry and plasma spectra	1.7	[43]
imprinted polymer particles	—	MS, ICPS	1.2	[44]
polymer imprinting	porogen type	Spectrophotometry	2.0	[45]
cloud point extraction	—	FAAS, ETAAS, ICP-OES, ICPMS	1.4	[46]
mixed micelle-mediated extraction	—	Spectrophotometry	3.2	[47]
BTAHP	polymer-based C18 cartridge	Spectrophotometry	0.6	This work

U(VI), obtained by varying the BTAHP concentration, showed inflection at molar ratio 2.0, indicating presence of two BTAHP molecules in the formed complex. Moreover, the Job method showed a ratio of BTAHP to U(VI) = 2.0 (Fig. 4). Consequently, the results indicated that the stoichiometric ratio was (2:1) [BTAHP to U(VI)]. The conditional formation constant (log K), calculated using Harvey and Manning equation, applying the data obtained from the above two methods, was found to be 6.56, whereas the true constant was 6.40.

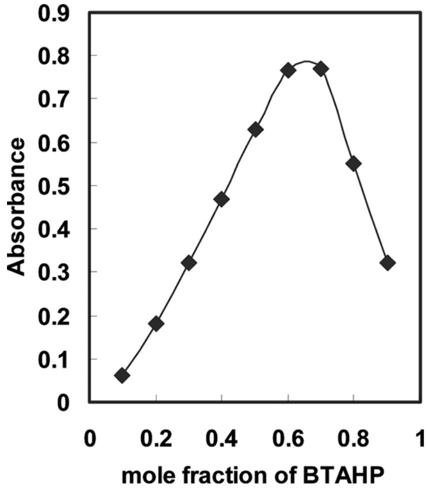

FIGURE 4 **Continuous variation method for U(VI) complexed with BTAHP.**

For ion-associate complexes of U(VI)–BTAHP–Triton X-114, the stoichiometric ratio as obtained from molar ratio indicated the formation of 1:2 for [U–BTAHP$_2$]: Triton X-114. So we conjectured that an ion-association complex {[U–BTAHP$_2$][Triton X-114]$_2$} is formed in the system, the structure of which is probably as follows:

$$\mathrm{U(VI)} + 2\mathrm{BTAHP} \leftrightarrows [\mathrm{U} - \mathrm{BTAHP}_2][\mathrm{U} - \mathrm{BTAHP}_2] + 2[\mathrm{Triton\ X} - 114]\{[\mathrm{U} - \mathrm{BTAHP}_2] \leftrightarrows [\mathrm{Triton\ X} - 114]_2\}$$

Interference

As NaCl, KCl, and KNO$_3$ are the main electrolytes present in nuclear fuel waters and environmental samples,[48] their influences on the quantitative extraction of U(VI) were studied in the concentration

TABLE 3 Tolerance Limits of Some Cations and Anions on the SPE and Determination of U(VI) at Optimum Conditions

Foreign ion	Tolerance limit[a]
K^+, Na^+, Cl^-, NO_3^-, PO_4^{3-}	18000
Tl^+, Mg^{2+}, Ca^{2+}, CH_3COO^-	12500
Cd^{2+}, Ni^{2+}, Cu^{2+}, I^-, SO_4^{2-}	8000
Pb^{2+}, Zn^{2+}, F^-, $S_2O_3^{2-}$	5000
La^{3+}, Ce^{3+}, $Cr_2O_7^{2-}$	2500
Al^{3+}, MoO_4^{2-}, $C_2O_4^{2-}$	1000
Cs^+, Fe^{3+}, Co^{2+}, Zn^{2+}	700
VO_3^-, Cr^{3+},	450
EDTA, Ag^+	250
Pb^{2+}, Pd^{2+}	100
Th^{4+}, Zr^{4+}	25

[a] The concentration ratio of the foreign ions to the U(VI) ions.

range of 0.001–0.200 M. The results showed that the alkaline ions had no significant effect on sorption of U(VI) at the studied concentrations.

Effect of alkaline, alkaline earth, transition metal ions, and some anions on sorption of 100 ng mL^{-1} U(VI) ions was investigated in binary solution of U(VI) accompanying interfering ions. The tolerance limit for a foreign ion was taken as the largest amount of the ions that could be present with the U(VI) and gives the adsorption within 5.0% of that of the U(VI) ions alone. The degrees of tolerance for some alkaline, alkaline earth, and transition metal ions are presented in Table 3. From the tolerance data, it can be seen that except thorium and zirconium, other ions have no significant effects on preconcentration of U(VI).

Analytical Applications

In order to confirm the applicability of the proposed method, it has been applied to the determination of nanogram amounts of U(VI) in water and in real samples.

TABLE 5 Recovery of 100 ng mL^{-1} of Uranium Spiked in Seawater

No. of samples	Mediterranean sea (Alexandria) (%)	Red Sea (Safaga) (%)
1	99.4	99.7
2	99.5	99.6
3	99.2	99.0
	RSD% = 1.65	RSD% = 1.40

Seawater Analysis

Results for the analysis of two seawater samples (Mediterranean Sea and Red Sea) are given in Table 4. Since a standard method for the determination of uranium in seawater has not been reported in literature, and inductively coupled plasma mass spectrometry (ICP-MS) as accepted independent method is not available, the accuracy of the method was examined by recovery study of the spiked samples. The recovery of the spikes added to seawater samples is given in Table 5. The quantitative recovery of the uranium spikes and relative standard deviation of 1.65% confirm the good precision and accuracy of the proposed method for the determination of U(VI) at SPE conditions.

The performance of the proposed method was assessed by calculation of the t value (for accuracy) and F test (for precision)[49] compared with GFAAS method. The mean values were obtained in Student's t and F tests at 95% confidence limits for five degrees of freedom. The results showed that the calculated values (Table 4) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability, and being less time consuming show the advantage of the proposed method over other method.

TABLE 4 U(VI) Contents of Seawater Samples

	Uranium Contents[a] (ng mL^{-1})			
No. of samples	Mediterranean sea (Alexandria)	GFAAS method	Red Sea (Safaga)	GFAAS method
1 (t and F test)[b]	2.33 ± 0.05 (0.54 and 1.61)	2.37 ± 0.13	2.45 ± 0.04 (0.73 and 2.07)	2.47 ± 0.13
2 (t and F test)[b]	2.30 ± 0.05 (0.84 and 2.09)	2.29 ± 0.09	2.40 ± 0.04 (0.95 and 2.55)	2.39 ± 0.09
3 (t and F test)[b]	2.38 ± 0.04 (0.95 and 2.55)	2.36 ± 0.11	2.44 ± 0.06 (0.87 and 2.13)	2.49 ± 0.11
	C = 2.34 RSD % = 1.2	C = 2.34 RSD % = 2.3	C = 2.43 RSD % = 1.65	C = 2.45 RSD % = 2.90

[a] Mean ±SD (n = 6).

[b] Theoretical value for t and F values for five degrees of freedom and 95% confidence limits are 2.57 and 5.05, respectively.

TABLE 6 **Analysis of Water Samples**

Name of sample source of collection	Method adopted	Concentration of U(VI) (μg L^{-1})	R.S.D. (%)[a]
Tap water, Benha	Proposed	2.85 ± 0.05	1.54
	GFAAS	2.90 ± 0.05	2.22
Tap water, Enshase	Proposed	3.44 ± 0.05	1.65
	GAAS	3.40 ± 0.05	2.45
Waste water, Benha	Proposed	3.05 ± 0.05	1.40
	GAAS	3.10 ± 0.05	2.25
Waste water, Enshase	Proposed	4.21 ± 0.05	1.55
	GAAS	4.14 ± 0.05	2.50

[a]Based on values obtained on triplicate analysis.

TABLE 8 **Determination of Uranium(VI) in Soil and Sediment Samples**

No.	Description of the sample	Uranium/(μg g^{-1}) Added	Found[a]	Recovery/ (%)
1	Soil sample from farmland nearby the Enshase City	—	6.85 ± 0.30	—
		8.0	14.8 ± 0.20	101.9
		16.0	22.85 ± 0.25	101.3
2	Sediment from Nile River nearby the Enshase City	—	4.75 ± 0.15	—
		4	8.80 ± 0.25	101.5
		8	12.65 ± 0.20	100.5

[a]Average and standard deviation from triplicate run.

Analysis of Tap Water Samples

The tap water samples were subjected to uranium(VI) analysis by employing the developed general procedure described above. The results obtained based on direct and standard addition methods agree well (Table 6). These results indicate the usefulness of the developed SPE procedure for monitoring U(VI) levels in drinking and sea water samples with a simple instrument like spectrophotometer.

Analysis of Soil and Standard Uranium Ore Samples

To verify applications and validations of the proposed method, one standard reference material, soil collected from farmland, and sediment collected from the Nile River were subjected to dissolution, preconcentration and determination. The results obtained for the standard reference material are shown in Table 7, and those for the soil sample and the sediment sample are shown in Table 8. The results obtained are in good agreement with the certified values, and the recoveries of spiked uranium were quantitative. Thus, these results indicated that the SPE preconcentration method developed in the present work is accurate, simple, and low in cost for analyzing ore, soil, and sediment samples containing traces of uranium.

TABLE 7 **Analysis of Uranium Ore Standard Reference Material (GBW04108)**

No.	U(VI) added/ (μg g^{-1})	Uranium found/(μg g^{-1}) Present method	Certified[a]	Recovery/ (%)
1	None	80.5 ± 0.50	79	—
2	60	140 ± 0.30		99.64
3	120	202 ± 0.30		100.75

[a]Average and standard deviation from triplicate runs carried.
[b]Certified values reported by Centre of China Reference Materials.

CONCLUSION

In this paper, a new, simple, sensitive, selective, and inexpensive method with the U(VI)–BTAHP complex was developed for the determination of uranium in sea, tap, and waste waters, ore standard reference material, soil, and sediment samples with good results in comparison to the GFAAS method. The new method offers also a very efficient procedure for speciation analysis. Although many sophisticated techniques such as HPLC, AAS, FAAS, GF-AAS, ICP-AES, and ICP-MS are available for the determination of uranium at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables, and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories of developing countries with limited budgets. The sensitivity in terms of molar absorptivity and precision in terms of relative standard deviation of the present method is very reliable for the determination of uranium in real samples down to ng g^{-1} levels in aqueous medium at room temperature (25 ± 5°C).

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