Synthesis of a Novel Chelating Resin for the Separation and Preconcentration of Uranium(VI) and Its Spectrophotometric Determination

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A novel chelating polymer including three different functional groups, such as amidoxime (–C(NH₂)=NOH), azo (–N=N–) and carboxylic acid (–COOH), was synthesized.   The poly(acrylamidoxime-co-(1-(2-pirydylazo)-2-naphtyl-2-methacrylate)-co-methacrylicacid) (APM) polymer, prepared in three steps, was characterized by FT-IR and elemental analyses.   The resin was used for solid-phase extractive separation and the preconcentration of trace amounts of uranium(VI).   The determination of U(VI) was performed by a spectrophotometric method using Arsenazo III as a complexing agent.   The optimum conditions were found for the quantitative recovery of U(VI) (pH 5; eluent, 3 mol L^{-1} HClO$_4$; sample and eluent flow rates, 1 mL min^{-1} *etc.*).   The capacity of the APM resin for U(VI) was found to be 24.2 mg g^{-1}.   A preconcentration factor of 37.5 and the three sigma detection limit of 1.6 µg L^{-1} ($n = 20$) were achieved for U(VI) ions.   The polymer was used for separating and preconcentrating the uranyl ion existing in seawater samples and a certified reference material (TMDA 70; fortified lake water sample).

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Introduction

The determination of traces of uranium in environmental sites and in facilities of the nuclear industry is important from safety considerations.   Atomic power plants continuously require uranium resources; therefore, 4.5 billion tons of total uranium in seawater can be recovered for atomic power utilization.[1]   Uranium is dissolved in seawater at a concentration of about 3 µg L^{-1} in the ionic form of uranyl tricarbonate ions.[1]   The World Health Organization (WHO), Health Canada and Australian drinking water guidelines have fixed the maximum uranium concentration in drinking water to be less than 9, 20 and 20 µg L^{-1}, respectively.[2,3]   On the other hand, uranium and its compounds, like lead, are highly toxic, which result in progressive or irreversible renal injury, and in acute cases may lead to kidney failure and death.   The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 µg kg^{-1} of body weight per day.[2-5]

Solid-phase extraction (SPE) has been increasingly used for the separation and preconcentration of trace and ultra-trace amounts of inorganic and organic species from complex matrices.[6-9]   SPE is being replaced by liquid–liquid extraction (LLE) due to the following merits: (i) high enrichment factors, (ii) absence of an emulsion, (iii) low intrinsic costs, (iv) low solvent consumption, (v) shorter processing times, (vi) simpler processing procedures, (vii) ease of automation, and (viii) more importantly, environmentally friendlier.[10]

Chelating resins are superior in selectivity to solvent extraction and ion exchange, owing to their triple functions, including ion exchange, chelate formation and physical adsorption.   By selecting a combination of a polydentate ligand and a polymeric support with moderate cross-linking, highly sought chelating resins of high capacity may be designed.[11-14]   Different types of solid resins have been used for the separation and preconcentration of various trace metal ions.[15-19]   The choice of the ligand introduced into the resin plays an important role in achieving selectivity.   In the literature, a variety of chelating resins including amidoxime groups (–C(=NOH)NH₂),[1,20] azo groups (–N=N–)[21] and carboxylic acid groups (–COOH)[22] have been synthesized and used for the separation/preconcentration of uranium(VI) ions.   It is well known that resins or adsorbents containing amidoxime groups as a functional group adsorb U(VI) species in seawater.[23]   U(VI) in seawater exists mainly in the form of $UO_2(CO_3)_3{}^{4-}$.   The adsorption mechanism of U(VI) by amidoxime resin has been revealed as a complex formation between $UO_2{}^{2+}$ and an amidoxime functional group.[24,25]

In addition to the nature of the chromogenic reagent, the role of the medium of determination is also very important.   Various lengthy and complicated procedures have been reported for the determination of uranium in organic and mineral acid media.   Nitric acid, being an oxidizing agent, can easily decompose azo-dyes at room temperature.   Arsenazo III was found to be more stable in perchloric acid than in nitric acid, which can cause oxidation.   It has wide applications in analytical work, particularly for the elimination of organic interferences.[26]   In the present work, the polymer has been synthesized and characterized by incorporating three functional groups for the separation and preconcentration of U(VI).   The modified chelating resins are capable of separating trace levels of uranium with solid-phase extraction from seawater.   The preconcentrated uranium was determined spectrophotometrically in a perchloric acid medium using Arsenazo III as a chromogenic reagent.[26]

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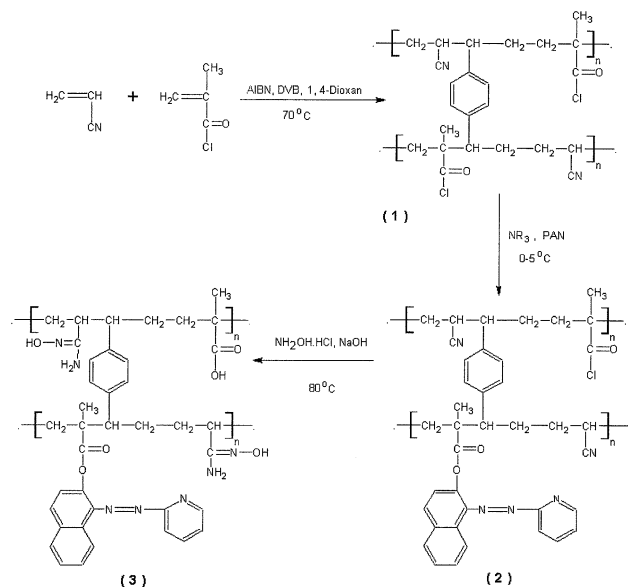
Scheme 1   Preparation of the APM resin.

Experimental

Reagents and chemicals

A stock solution of uranium(VI) was prepared by dissolving an appropriate amount of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (Merck, Darmstadt, Germany) in deionized water. Concentrated HNO_3 (5 mL) was added to 100 mL of the solution to suppress hydrolysis. Then, a 0.1% (w/v) Arsenazo III (Aldrich, MO) solution was prepared by dissolving 0.1 g of the reagent in 100 mL of deionized water. The following buffer solutions were used for solid-phase extraction procedures: $CH_3COOH/$ CH_3COONa buffer for pH 3 – 6, Na_2HPO_4/NaH_2PO_4 buffer for pH 7, and NH_3/NH_4Cl buffer for pH 9 – 11. These different buffer solutions were used to maintain the pH of the aqueous phase during the preconcentration process. Other reagents used were also of analytical reagent grade. Distilled-deionized water was used in all experiments.

Instruments

FT-IR spectra of the resins were recorded with a Jasco 460 Plus Fourier-transform IR spectrometer using a KBr disc in the range of 4000 – 700 cm^{-1}. Elemental analyses were carried out on a Leco CHNS-932 elemental analyzer. A Shimadzu UV-1208 Model UV-Vis spectrophotometer was used to determine U(VI) as a U(VI)-Arsenazo III complex at 653 nm. The pH measurements were made with a Consort C931 Model digital pH-meter.

Synthesis of the chelating polymer

Poly(acrylamidoxime-co-(1-(2-pirydylazo)-2-naphtyl-2-methacrylate)-co-methacrylic acid) (APM) polymer was synthesized in three steps (Scheme 1).

In the first step (radicalic polymerization), methacryloil chloride (MCl) (1.96 mL, 0.03 mol), acrylonitrile (AN) (3.46 mL, 0.03 mol) and divinylbenzene (0.87 mL, 8 mol %) were dissolved in 30 mL of 1,4-dioxane, and 1 mol (%) 2,2′-azoisobutyronitrile (AIBN) (0.068 g) was added as an initiator. A polymerization mixture was purged with argon for 10 min and then heated at 70°C for 24 h. The resulting viscous solution was cooled, poured into 250 mL of agitated hexane to precipitate the polymer (**1**) as a white solid, and dried under a vacuum.

In the second step (ester reaction), PAN (5 g, 0.01 mol), triethylamine (1 mL, 7.5 mmol), and acetone were placed in a flask equipped with a magnetic stirrer and a drooping funnel, and the contents were cooled to approximately 0°C; the AN/MCl crosslinked copolymer (**1**) was dissolved in acetone, and was then added dropwise from a dropping funnel with constant stirring. This mixture was stirred for 3 h at approximately 0°C in an ice bath. The product was filtered off for removing quaternary ammonium salt, and the polymer (**2**) was precipitated in hexane.

In the third step (amidoximation), the obtained polymer was reacted with a methanol–water (5:1, v/v) solution containing hydroxylamine·HCl (1:1 in $NH_2OH \cdot HCl$–NaOH) at 80°C. After completion of the amidoximation reaction, the amidoximated polymer (**3**) was taken from the reaction vessel, washed with distilled water and then dried in a vacuum oven.

Column dynamic method

A glass column (Vensil, size: 7 mm diameter and 12 cm length) was packed with 0.3 g of APM resin and then washed three to four times with deionized water. The pH of sample solutions (50 mL) containing 5 – 200 μg of uranium(VI) was adjusted to ~5 by the addition of acetate buffer, and was passed trough the column at a flow rate of 1 mL min^{-1}. Uranium ions were stripped from the resin bed by using 20 mL of 3 mol L^{-1} $HClO_4$, and determined spectrophotometrically after the addition of 1 mL of 0.1% (w/v) Arsenazo III. The absorbance of the U(VI)–Arsenazo III complex was measured at 653 nm.[26]

Procedure for the analysis

Seawater samples were collected from Aegean Sea, İzmir. Polyethylene bottles were cleaned with a detergent, water, diluted nitric acid and water in this sequence. The samples were immediately filtered through a cellulose membrane filter (pore size 0.45 μm), and then acidified to pH 2 for storage. A 750-mL portion of a seawater sample was taken into a 1000-mL beaker (n = 4). Fifty milliliters of the TMDA-70 standard reference material sample were taken into a 100-mL of beaker (n = 3), and 5 mL of acetate buffer (pH 5) was added to these sample solutions. The uranyl ion contents in the seawater samples were determined by the standard addition method using 13.3 and 26.7 μg L^{-1} of U(VI) ion. The preconcentration of uranium onto the APM resin and its determination by the Arsenazo III procedure were carried out as described in the above section (*Column dynamic method*).

Results and Discussion

Chracterization of the resins

The FT-IR spectra of resins (**1**, **2** and **3**) are shown in Fig. 1. In the FT-IR spectrum of poly(acrylonitrile-co-methacryloilchloride) (**1**) a sharp band at 2240 cm^{-1} for the C≡N group can be clearly seen. In the FT-IR spectrum of methacryloil chloride, there is a strong band due to stretching vibration of halide attached to C=O groups at 1792 cm^{-1}. In the FT-IR spectrum of poly(acrylamide-co-(1-(2-pyridylazo)-2-naphtyl-2-methacrylate)-co-methacryloil chloride) (**2**) a sharp band at 1221 cm^{-1} for the C–O ester group is assignable. Two strong peaks at 1758 and 1807 cm^{-1} are assignable to the C=O of two kinds of carbonyl groups. In the FT-IR spectrum of poly(acrylamidoxime-co-(1-(2-pyridylazo)-2-naphtyl-2-methacrylate)-co-methacrylic acid) (**3**), after a treatment with hydroxylamine, the C≡N band disappeared and a new band of

N–H and O–H appeared at 3200 and 3380 cm⁻¹, respectively. On the other hand, methacryloil chloride was hydrolyzed. Molar ratios of the resins, as calculated by C/H/N stoichiometry based on the elemental analysis data, are given in Table 1.
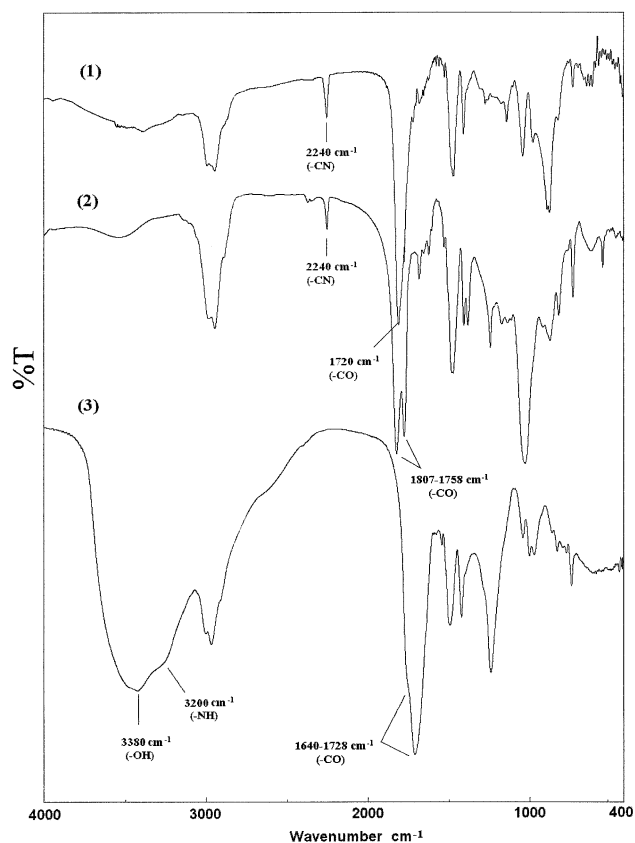

Fig. 1   FT-IR spectra of the resins.

Effect of pH

The effect of the pH on the sorption of uranium ion was investigated by the column method; 50 mL of solutions containing 0.4 μg mL⁻¹ of uranium ion was passed at various pH values while changing from 3 to 9. The percent recovery of U(VI) slowly increased with increasing pH from 86.9 (pH 3) to 95.9 (pH 5), and then decreased at pH values higher than 5 from 75.7 (pH 6) to 62.4 (pH 9). The maximum retention of the U(VI) ions on the APM resin was observed at pH 5. The sorption behavior can be explained based on the equilibriums: (1) At pHs < 5 the competition equilibria between cations and protons for occupying the resin active sites occur; (2) At higher pH values (pH > 5) precipitation of the salt occurs.[21] Considering these results, the selected pH was 5. The retained U(VI) ions on the resin were desorbed with 20 mL of 3 mol L⁻¹ HClO₄, and then determined spectrophotometrically. Therefore, for all subsequent work, pH 5 was fixed as the optimum value for the quantitative separation and preconcentration of U(VI) ions.

Choi *et al.* has reported that the adsorption rate of U(VI) ion by resins with amidoxime and carboxylic acid groups was higher than that of resins with the amidoxime group at room temperature.[1]   Especially, adsorbents containing amidoxime groups, which make chelate complexes with uranyl ions, are notable for the recovery of uranium from seawater.[1] Consequently, the dominant site of the APM resin for the adsorption of U(VI) is the amidoxime functional group, but the azo and/or carboxylic acid groups may probably cause an increase in the adsorption capacity of the resin for the adsorption of uranyl ions. On the other hand, an isomeric change of the amidoxime chelating functional group in different acidic solutions is an important impact factor on the adsorption of U(VI) on the resin.[20]

Optimization of sorption and elution of uranium(VI)

The optimum pH was found to be 5. Other optimal conditions were ascertained in a similar fashion as given in Table 2. For the sorption of uranium(VI) onto the APM resin, a flow rate of 1.0 mL min⁻¹ was found to be suitable for optimum loading onto

Table 1   Molar ratios of the resins

Resin	AN, %	MCl, %	MA, %	PAN-M, %	Aox, %	DVB, %
Poly(acrylonitrile-co-methacryloilchloride) (**1**)	22.90	71.35	—	—	—	5.75
Poly(acrylamide-co-(1-(2-pyridylazo)-2-naphtyl-2-methacrylate)-co-methacryloil chloride) (**2**)	26.67	58.51	—	8.12	—	6.70
Poly(acrylamidoxime-co-(1-(2-pyridylazo)-2-naphtyl-2-methacrylate)-co-methacrylic acid) (**3**)	—	—	58.51	8.12	26.67	6.70

AN, Acrylonitrile; MCl, methacryloil chloride; MA, methacrylic acid; PAN-M, 1-(2-pyridylazo)-2-naphtyl-2-methacrylate; Aox, acrylamidoxime; DVB, divinyl benzene.

Table 2   Optimization of the experimental parameters for the SPE of uranium(VI) (pH 5, *n* = 4)

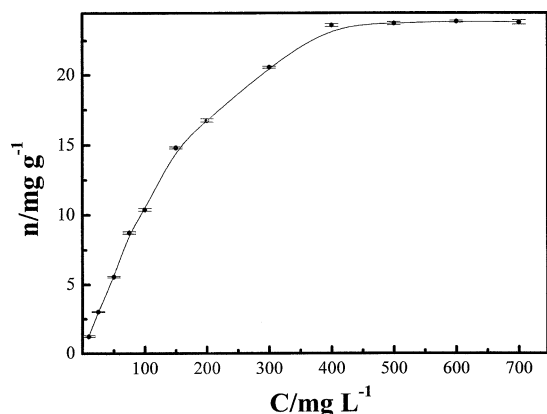| Parameter						
Preconcentration flow rate/mL min⁻¹	0.5	1.0	2.0	3.0		
Recovery, %	97.2 ± 6.4	95.9 ± 0.7	90.7 ± 5.4	81.1 ± 1.0		
Elution flow rate/mL min⁻¹	0.5	1.0	2.0	3.0		
Recovery, %	97.9 ± 1.0	96.3 ± 1.5	88.2 ± 1.1	84.1 ± 1.0		
Eluent volume/mL	10	20	30			
Recovery, %	75.1 ± 0.5	95.9 ± 0.7	96.5 ± 1.7			
Aqueous phase volume/mL	50	100	250	500	750	1000
Recovery, %	97.9 ± 1.0	96.6 ± 1.1	97.3 ± 1.6	97.8 ± 1.1	95.1 ± 1.0	90.1 ± 0.3

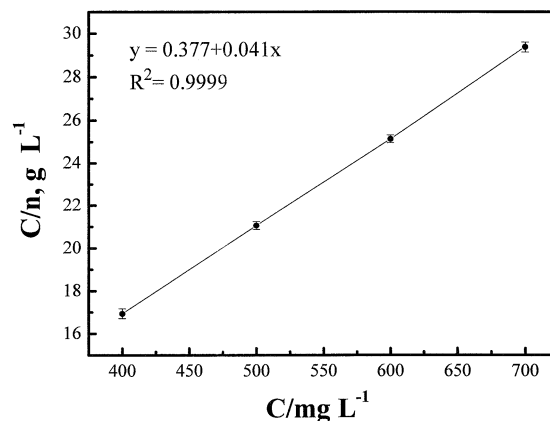Fig. 2   Adsorption isotherm of the chelating resin for uranium(VI).

Fig. 3   Langmuir plot for the adsorption of uranium(VI) on the resin.

the resin.   Flow rates higher than 1.0 mL min^{-1} were not adequate for the quantitative recovery of U(VI) ions.   Similarly, the variation of elution flow rates from 0.5 to 1.0 mL min^{-1} show that the elution of sorbed U(VI) is quantitative over the entire range.   Elution flow rates higher than 1.0 mL min^{-1} could not be attained under our experimental conditions.   Further, as low as 20 mL of 3 mol L^{-1} HClO$_4$ was sufficient for the quantitative elution of sorbed U(VI).   Therefore, for complete desorption, 20 mL of 3 mol L^{-1} HClO$_4$ was used for convenience.   The sorption and desorption of U(VI) were found to be quantitative by changing the volume of the sample solution in the range of 50 – 750 mL while keeping the total amount of loaded U(VI) at 20 μg.

Matrix effect

The influence of possible matrix ions in the seawater samples was also examined.   The effect of potential interfering ions on the determination of U(VI) was investigated by using a synthetic seawater sample (SSW).[27]   These results show that the proposed preconcentration and separation method could be applied to seawater samples at the ratios of SSW/3, SSW/2 and SSW.   The recoveries (%) of U(VI) for these samples were found to be 98.8 ± 1.7, 96.9 ± 1.5, 95.8 ± 2.6, respectively (n = 3).

Adsorption isotherm and adsorption capacity

The adsorption capacity of the APM resin was determined for U(VI) by using the column technique.   Therefore, portions of 50 mL of model solutions containing 10 – 700 mg L^{-1} U(VI) at pH 5 were passed through a column filled with 0.3 g of the APM resin at a flow rate of 1.0 mL min^{-1}.   The retained uranium ions were eluted from the resin with 3 mol L^{-1} HClO$_4$.   The concentrations of U(VI) in the eluate were determined spectrophotometrically.   The concentration of the adsorbed metal ion (n) in mg g^{-1} was studied as a function of the metal ion concentration (C, mg L^{-1}) in the initial solution.   Figures 2 and 3 show the adsorption isotherms for U(VI) ions, which conforms to the Langmuir equation.[28]   The adsorption capacity (n_m) of the resin for uranium was calculated from the Langmuir equation.   The equation is as follows:

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right) \cdot C \qquad (1)$$

The adsorption capacity (n_m) and the binding equilibrium constant (K) were calculated from the slope and the intercept of the regression plot obtained by the least-squares method,

respectively.   The adsorption capacity of the chelating resin for uranium was found to be 24.2 mg g^{-1} (0.102 mmol g^{-1}), and the binding equilibrium constant was found to be 0.110 L mg^{-1}.   As can be seen in Table 3, the adsorption capacity of the resin for U(VI) ions using the column method is higher than chelate modified and/or imprinted SPE procedures reported in the literature up to now.[6,29-31]   However, even higher adsorption capacities (>0.102 mmol g^{-1}) have been reported in the literature in similar studies using the batch method.[10,18,22]   On the other hand, the resin can be successfully regenerated in over 250 operating cycles by the column method without any loss in its sorption capacity.

Validation and application of the proposed method

The proposed method was applied to seawater samples.   For validation of the method, the certified reference material (TMDA 70; fortified lake water sample) was analyzed, and recovery studies were performed in which the analyte was added to the seawater sample at known concentrations.   The uranium(VI) ions were added to seawater samples at concentrations of 13.3 and 26.7 μg L^{-1}.   The results of the analysis are given in Table 4.   A good agreement was obtained between the added and the found analyte contents.   While the recovery values for the uranium ion were 98.5 and 99.3%, the relative standard deviation values for the samples were 1.6 and 0.9%, respectively.   Analyzing the CRM (included 55.8 ± 0.8 μg L^{-1}) for the U(VI) ion gave a result of 54.4 ± 1.4 μg L^{-1} with a relative error of –2.5% (n = 3, at 95% confidence interval).   The found and the certified values were in good agreement for validating the method.

Conclusion

In the present work, a novel polyfunctional resin was synthesized and characterized by FT-IR and elemental analyses.   The SPE procedure was then developed by using this resin.   This SPE method has good potential for the separation of uranium(VI) from a host of coexisting alkali and alkaline earth ions.   The proposed method is simple, and the sorption capacity of the APM resin is much higher than that of other similar SPE materials, as can be seen in Table 3.   The APM resin has high mechanical and chemical strength, and the reusability was as high as 250 cycles without any loss in its sorption behavior.   The applied method provided good precision with relative standard deviations lower than 2%, and high accuracy was obtained with

Table 3   Comparison of the adsorption capacity of SPE materials prepared by using various sorbents for uranium(VI)

SPE material	Adsorption capacity for U(VI)/ mmol g^{-1}	Ref.
Succinic acid, Amberlite XAD-4	0.052[a]	6
5,7-Dichloroquinoline-8-ol-4-vinylpyridine, PS-DVB	0.143[b]	10
(Bis-3,4-dihydroxy benzyl)-*p*-phenylene diamine, Amberlite XAD-16	0.666[b]	18
o-Phenylene dioxydiacetic acid, Amberlite XAD-2000	0.121[a]	22
Quinoline-8-ol, Amberlite XAD-4	0.012[a]	29
PAN-benzophenone	0.010[a]	30
Diarylazobisphenol modified activated carbon	0.077[a]	31
APM resin	0.102[a]	Present method

a. Column method.
b. Batch method.

Table 4   Results for tests of addition/recovery for uranium determinations in a seawater sample from Aegean Sea (sample volume, 750 mL; final volume, 20 mL, $n = 4$)

	Added/μg L^{-1}	Seawater from Aegean Sea	
		Found/μg L^{-1}	Recovery, %
U(VI)	0	4.14 ± 0.30	—
	13.3	17.3 ± 0.3	98.5 ± 2.1
	26.7	30.6 ± 0.3	99.3 ± 1.0

the quantitative recovery of U(VI). Thus, the resin offers a reliable analysis of U(VI) in water samples, even if it has high salt matrices, like seawater samples.

Acknowledgements

References

1. S. H. Choi, M. S. Choi, Y. T. Park, K. P. Lee, and H. D. Kang, *Radiat. Phys. Chem.*, **2003**, *67*, 387.
2. A. P. Gilman, D. C. Villenuve, V. E. Secours, A. P. Yagminas, B. L. Tracy, J. M. Quinn, V. E. Valli, R. J. Willes, and M. A. Moss, *Toxicol. Sci.*, **1998**, *41*, 117.
3. WHO, "*Guidelines for Drinking Water Quality*", 3rd ed., **2003**, WHO.
4. WHO, "*Guidelines for Drinking Water Quality*", 2nd ed., WHO, **1998**, Addendum to Vol. 2. Health Criteria and other supporting information, WHO/EOS/98.1, Geneva, 283.
5. P. Metilda, K. Prasad, R. Kala, J. M. Gladis, T. Prasada Rao, and G. R. K. Naidu, *Anal. Chim. Acta*, **2007**, *582*, 147.
6. P. Metilda, K. Sanghamitra, J. M. Gladis, G. R. K. Naidu, and T. Prasada Rao, *Talanta*, **2005**, *65*, 192.
7. S. Saraçoğlu and L. Elçi, *Anal. Chim. Acta*, **2002**, *452*, 77.
8. Ş. Tokalıoğlu, Ş. Kartal, and L. Elçi, *Bull. Korean Chem. Soc.*, **2002**, *23*, 693.
9. I. M. M. Kenawy, M. A. H. Hafez, M. A. Akl, and R. R. Lashein, *Anal. Sci.*, **2000**, *16*, 493.
10. P. Metilda, J. M. Gladis, and T. Prasada Rao, *Anal. Chim. Acta*, **2004**, *512*, 63.
11. S. Pramanik, S. Dhara, S. S. Bhattacharyya, and P. Chattopadhyay, *Anal. Chim. Acta*, **2006**, *556*, 430.
12. M. J. Zohuriaan-Mehr, A. Pourjavadi, and M. Salehi-Rad, *React. Funct. Polym.*, **2004**, *61*, 23.
13. B. C. Mondal, D. Das, and A. K. Das, *Talanta*, **2002**, *56*, 145.
14. N. Tokman, S. Akman, and C. Özeroğlu, *Talanta*, **2004**, *63*, 699.
15. Ş. Tokalıoğlu, T. Oymak, and Ş. Kartal, *Anal. Chim. Acta*, **2004**, *511*, 255.
16. H. Bağ, A. R. Türker, R. Coşkun, M. Saçak, and M. Yiğitoğlu, *Spectrochim. Acta, Part B*, **2000**, *55*, 1101.
17. Ş. Tokalıoğlu, Ş. Kartal, and L. Elçi, *Anal. Sci.*, **2000**, *16*, 1169.
18. D. Prabhakaran and M. S. Subramanian, *Talanta*, **2003**, *61*, 423.
19. X. Chang, N. Jiang, H. Zheng, Q. He, Z. Hu, Y. Zhai, and Y. Cui, *Talanta*, **2007**, *71*, 38.
20. A. Zhang, T. Asakura, and G. Uchiyama, *React. Funct. Polym.*, **2003**, *57*, 67.
21. N. Bahramifar and Y. Yamini, *Anal. Chim. Acta*, **2005**, *540*, 325.
22. S. Seyhan, M. Merdivan, and N. Demirel, *J. Hazard. Mater.*, **2008**, *152*, 79.
23. M. Nogami, S. Y. Kim, N. Asanuma, and Y. Ikeda, *J. Alloy. Compd.*, **2004**, *374*, 269.
24. K. Saito, T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *Ind. Eng. Chem. Res.*, **1987**, *26*, 1977.
25. T. Hirotsu, S. Katoh, K. Sugasaka, M. Seno, and T. Itagaki, *J. Chem. Soc. Dalton Trans.*, **1986**, *9*, 1983.
26. M. H. Khan, P. Warwick, and N. Evans, *Chemosphere*, **2006**, *63*, 1165.
27. U. Şahin, Ş. Tokalıoğlu, Ş. Kartal, and A. Ülgen, *Chem. Anal.* [Warsaw], **2005**, *50*, 529.
28. S. Baytak, A. Balaban, A. R. Türker, and B. Erk, *J. Anal. Chem.*, **2006**, *61*, 476.
29. J. M. Gladis and T. Prasada Rao, *Anal. Bioanal. Chem.*, **2002**, *373*, 867.
30. C. R. Preetha and T. Prasada Rao, *Radiochim. Acta*, **2003**, *91*, 247.
31. A. M. Starvin and T. Prasada Rao, *Talanta*, **2004**, *63*, 225.