PRECONCENTRATION OF URANIUM(VI) ON MODIFIED AND UNMODIFIED AMBERLITE XAD 4 SORBENT

Jan VÁCHA and Lumír SOMMER

Department of Analytical Chemistry, Masaryk University, 611 37 Brno, The Czech Republic

Received August 19, 1992
Accepted January 9, 1993

The sorption of uranyl ions on columns with the macroporous hydrophobic sorbent Amberlite XAD 4 modified with 1-(2-pyridylazo)-2-naphthol, 1-(2-thiazolylazo)-2-naphthol and sodium diethyldithiocarbamate was examined. Following elution of the uranyl ion with HNO_3 (2 – 4 mol l^{-1}) or of the diethyldithiocarbamate UO_2^{2+}-chelate with a methanolic solution of HCl (0.1 mol l^{-1}), uranium was determined spectrophotometrically with 4-(2-pyridylazo)resorcinol or with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. The preconcentration of uranium on Amberlite XAD 4 type sorbents is convenient for its spectrophotometric determination in waters.

Macroporous hydrophobic sorbents of the Amberlite XAD type are increasingly finding application to the preconcentration of minority elements. For this purpose, the sorbents are modified with surface-bonded organic reagents, or alternatively, neutral chelates and ionic associates prepared before the treatment are sorbed on them[1 – 13]. Sorbents whose surface is modified with organic reagents are more easy to prepare than chelating sorbents with chemically bonded groups in their molecules[14]. Trace concentrations of transition metals can conveniently be trapped with N-heterocyclic azo-dyes immobilized on various sorbents, particularly on silica gel or on nonpolar sorbents of the polystyrene-divinylbenzene type[1, 15 – 17].

In the present work, uranium was preconcentrated on Amberlite XAD 4 sorbent (A) of various particle size, modified with 1-(2-pyridylazo)-2-naphthol (A-PAN), 1-(2-thiazolylazo)-2-naphthol (A-TAN), and diethyldithiocarbamate (A-DDC). Unmodified sorbent was also employed for the sorption of neutral uranyl chelates. The analytical finish was spectrophotometric, using 4-(2-pyridylazo)resorcinol (PAR)[18 – 20] or 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP)[21,22] as the reagents. The procedures are well suited to the determination of uranium in any kind of water.

EXPERIMENTAL

Amberlite XAD 4 (Merck, Darmstadt), grain size 0.3 – 0.9 mm, was dried at 30 °C and ground, and fractions 0.16 – 0.32 mm and 0.10 – 0.20 mm grain size were obtained using standardized sieves. The sorbent was wetted with ethanol for 24 h, filtered out, rinsed with water and placed in a column

90 × 6 mm (0.5 g of sorbent, column height 55 mm) or 65 × 16 mm (3 g of sorbent, column height 65 mm). The column was eluted with methanol to remove air bubbles and modified with 5 or 30 ml, respectively, of a 0.5 wt.% solution of the organic reagent of choice in methanol (flow rate 0.5 to 1.0 ml min^{-1}). Metal impurities that could be present in the reagents were removed by washing with 5 or 15 ml, respectively, of nitric acid (4 mol l^{-1}). Finally, the column was eluted with water to a negative reaction. In the same manner the column was prepared for the next experiment after each elution of uranium. The modified sorbent was stored in water. To desorb any reagent prior to a next activation, the sorbent was eluted with 10 to 20 ml of an acetone–concentrated HNO_3 (9 : 1) mixture at a flow rate of 0.5 to 1.0 ml min^{-1}. For sorbent whose grain size was below 0.2 mm, the reduced flow rate was made up for by increasing the pressure of nitrogen, fed to above the column from a pressure vessel.

The standard solution of UO_2Cl_2 (0.115 mol l^{-1}) in HCl (0.1 mol l^{-1}) was standardized gravimetrically via 8-hydroxyquinoline and was invariably diluted with HCl (0.1 mol l^{-1}). Solutions containing UO_2^{2+} in a concentration of 10^{-4} mol l^{-1} were used for no longer than 4 weeks.

1-(2-Pyridylazo)-2-naphthol (PAN), 1-(2-thiazolylazo)-2-naphthol (TAN), sodium diethyldithiocarbamate (DDC) and 4-(2-pyridylazo)resorcinol (PAR) were chemicals obtained from Lachema, Brno. PAN was purified with activated carbon in a methanolic solution and recrystallized. TAN was recrystallized from ethanol. DDC was used as a 0.5 wt.% solution in methanol or in water. PAR was recrystallized from aqueous ethanol and used as a 0.2% solution in water.

2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP), obtained from Sigma, U.S.A., was used as a solution in 99.5 wt.% dimethylformamide in a concentration of 5 . 10^{-4} mol l^{-1}. Solutions no older than 7 days were employed.

Borate (0.5 mol l^{-1}, pH 8.00), hexamethylenetetramine (1 mol l^{-1}, pH 5.0) and triethanolamine (1 mol l^{-1}, pH 8.0) buffers were used.

Masking mixture for interfering ions was prepared by dissolving cyclohexanediaminetetraacetic acid (CDTA, 5.0 g), NaF (0.5 g) and 5-sulfosalicylic acid (13 g) in water, adjusting to pH 8.0 and diluting to 100 ml with water.

Sodium hydroxide of reagent grade purity (Lachema, Brno) was dissolved to obtain a 30% aqueous solution. The solution was allowed to stand for 7 days in a closed polyethylene bottle, filtered rapidly through a glass filter funnel and protected against atmospheric CO_2. The solution was diluted as required. Dimethylformamide (Reakhim, C.I.S.), 99.5 wt.%, was chemically pure. All the other chemicals used were of reagent grade purity or were recrystallized. Water was redistilled in a quartz still (Heraeus, Germany).

Apparatus

A Spekol 211 single-beam digital spectrophotometer (Zeiss, Jena), equipped with 10 mm glass cells. A 208/1 digital pH-meter (Radelkis, Budapest) fitted with an OP-0808 P combined electrode.

Determination of Uranium in Eluate

After sorption on the column and elution, uranyl was determined spectrophotometrically with PAR at pH 8 in a medium containing triethanolamine or borate buffer and masking mixture (analytical wavelength 530 nm, ref.[18]), or with Br-PADAP at pH 7.3 in 30% dimethylformamide in the presence of Triton X-100, triethanolamine buffer and masking mixture (analytical wavelength 579 nm, ref.[22]).

Model of Mineral Water

The model solution contained, in mg l^{-1}: Na^+ 2 070 (as NaCl), K^+ 1 560 (as K_2SO_4), Ca^{2+} 151 (as $CaCl_2$), Mg^{2+} 50.5 (as $MgCl_2$), Fe^{3+} 1.3 (as $FeCl_3$), Al^{3+} 0.1 (as $Al(NO_3)_3 . 9 H_2O$), SO_4^{2-} 1 920, NO_3^- 0.7, and standard additions of UO_2Cl_2.

Model of Sea Water

The model solution contained, in mg l^{-1}: Na^+ 11 850, K^+ 625, Ca^{2+} 320, Mg^{2+} 400, Al^{3+} 0.01, Fe^{3+} 0.01 (cf. ref.[23]), Cl^- 18 520, SO_4^{2-} 770, CO_3^{2-} 30, and standard additions of U (9.4 – 14.5 μg).

Drinking and Surface Water

500 or 1 000 ml of drinking water with standard additions of UO_2Cl_2 was made acidic with concentrated HNO_3 to pH 1.5 – 1.8 and stored for 24 h in a polyethylene bottle at a temperature not exceeding 10 °C.

River water, taken 10 – 15 cm below the level, was not filtered; instead, it was conserved with a small amount of HNO_3 (pH < 2) and stored for 24 h in a polyethylene bottle at 10 °C.

RESULTS AND DISCUSSION

Sorption of Uranyl Ions on A-PAN

The sorption efficiency is inversely proportional to the sorbent particle size. For 41 μg U in 25 ml of the urotropine buffer (0.05 mol l^{-1}) at pH 5.1 – 5.2, the sorption was 100% for the grain size fraction of 0.10 – 0.20 mm and 82% for the grain size fraction of 0.16 – 0.32 mm (flow rate 8 ml min^{-1}). The maximum sorption efficiency for 16.4 – 41.0 μg U in 25 ml, on 0.5 g of sorbent with a grain size of 0.10 – 0.20 mm, was attained at pH 5 to 6 (0.05 mol l^{-1} urotropine buffer) even if the flow rate was 11.0 – 16 ml min^{-1}; the recovery was 95 – 100%. Uranium (41.0 μg) did not wash out of the column even if volumes as large as 25 – 1 000 ml were used, uranium breakthrough being only observed for 380 – 410 μg U.

The uranium elution was quantitative with the use of 6 ml of HCl (6 mol l^{-1}) or HNO_3 (4 mol l^{-1}) at flow rates of 0.5 – 1.0 ml min^{-1}. The reagent itself usually was not eluted from the modified sorbent under such conditions. The eluate in HNO_3 was collected in a 50 ml quartz beaker, the sorbent after elution was washed with 5 ml of water, and the combined fractions were evaporated under an infrared lamp just to dryness. Taken up in water, the residue was transferred quantitatively into a volumetric flask for spectrophotometric quantitation of uranium.

Effect of associate ions and compounds. Increase in the ionic strength of the solution which contained 41.0 μg U in 25 ml of urotropine buffer (0.05 mol l^{-1}) at pH 5.1 – 5.2 had a positive effect on the uranium sorption efficiency; for 0.1 mol l^{-1} KCl and NaCl it remained quantitative even at a flow rate of 16 ml min^{-1}. The limiting amounts of some associate ions for a 96 to 100% sorption of uranium are given in Table I. Their effect diminishes if a larger amount of sorbent in the column is used and if the fixed reagent content is higher. Nitric acid (5 mol l^{-1}) elutes such ions together with UO_2^{2+}, and therefore the interferents must be masked with the masking solution for the spectrophotometric determination of uranium with PAR or Br-PADAP. Triton X-100 has no effect if present in a concentration of 0.05 wt.%, higher concentrations, however, reduce the sorption efficiency. Acetate, succinate, malonate or tartrate (all 0.05 ml l^{-1}), as well as fluoride, sulfosalicylate and CDTA (all 0.002 mol l^{-1}), decrease appreciably the uranium sorption efficiency even at flow rates not exceeding 7 ml min^{-1}.

Sorption of UO_2^{2+} Chelate with PAN on Unmodified Sorbent

The sorption was accomplished from 10 vol.% methanol containing 0.05 wt.% PAN, because both the reagent and the UO_2L_2 or UO_2LCl chelates[24,25] are low soluble in water. The sorption of 41.0 μg U from 25 ml of solution was optimum at pH 7.0 – 8.0 (0.05 mol l^{-1} borate buffer), it did not, however, exceed 97% at low flow rates (3 – 4 ml min^{-1}) and decreased rapidly as the flow rate was increased. The in situ methanol itself is responsible for the reduced sorption efficiency. Inert salts such as NaCl at concentrations ≥ 0.5 mol l^{-1} also had an adverse effect. The elution of uranium from the column, on the other hand, was quantitative with 2 ml of HNO_3 (4 mol l^{-1}) due to the fact that the uranyl ion from the decomposed chelate, which is all sorbed in the upper part of the column, passes through the low-sorbing sorbent A only.

Sorption of Uranyl Ions on A-TAN

Sorption of 41.0 μg U from 20 – 25 ml of solution was quantitative over the wide region of pH 5.0 – 8.5 (0.05 mol l^{-1} urotropine or borate buffer) also at high flow rates

TABLE I
Effect of some ions on the sorption of uranyl (41.0 μg U) on A-PAN sorbent at pH 5.1 – 5.2[a]

Ion	Limiting quantity in 25 ml mg	Sorption, %
Ca^{2+}	5.0	100
Mg^{2+}	5.7	100
Fe^{3+}	$8.9 \cdot 10^{-3}$	96
Al^{3+}	$14.8 \cdot 10^{-3}$	96
SO_4^{2-}	24.0	100
CO_3^{2-}	15	100

[a] Urotropine buffer (0.05 ml l^{-1}), sample flow rate 5 – 20 ml min^{-1}.

(15 – 18 ml min^{-1}) from aqueous solutions as well as from 0.5 mol l^{-1} NaCl using sorbent of 0.10 – 0.20 mm grain size. The recovery was 94 – 100% for 8.2 – 41 μg U in 25 ml of solution at pH 6.1 – 6.2 (0.05 mol l^{-1} urotropine buffer) and the elution was quantitative with 2.5 – 3.0 ml of HNO_3 (4 mol l^{-1}) at flow rates of 0.5 – 1.0 ml min^{-1}.

Sorption of UO_2^{2+}–DDC Chelate on Sorbent A

Sorption of 41.0 μg U in the form of the UO_2L_2 chelate[26] on sorbent A (grain size 0.10 – 0.20 mm) from 25 ml of solution containing 0.05 wt.% DDC and 0.05 mol l^{-1} urotropine or borate buffer at pH 5.5 – 8.0 was quantitative even at flow rates as high as 20 ml min^{-1}, both from aqueous solution and from the medium of 0.5 mol l^{-1} NaCl. Three ml of methanolic solution of HCl (0.1 ml l^{-1}) were sufficient for the quantitative elution of uranium from the column at flow rates of 0.5 – 1.0 ml min^{-1}. After the elution the column was washed with 5 ml of water, the two portions being collected in a 25 ml volumetric flask. Uranium was then determined spectrophotometrically with PAR or Br-PADAP. The DDC present did not interfere even at the molar concentration ratio c(DDC)/c(PAR) or c(DDC)/c(Br-PADAP) = 14. Elution with 5 ml of Na_2CO_3 at flow rates of 0.7 – 1.0 ml min^{-1} is also feasible if the excess carbonate is eliminated, prior to the uranium determination, by short heating of the solution which has been made acidic with HCl (4 mol l^{-1}).

Using the A-DDC sorbent (0.10 – 0.20 mm particle size), the uranium sorption was also quantitative at pH 6.5 – 7.5 (0.05 ml l^{-1} urotropine buffer) or at pH 7.1 – 7.0 (0.05 mol l^{-1} borate buffer) at flow rates as high as 21 ml min^{-1}, and from solutions of NaCl (0.5 ml l^{-1}) at flow rates as high as 14 ml min^{-1}. The partial deactivation of the modified sorbent during the elution with HCl (2 ml l^{-1}) is a drawback: re-activation is necessary after the elution of uranium and complete removal of DDC with the acetone–concentrated HNO_3 9 : 1 mixture.

Determination of Uranium in Waters Following Preconcentration on Modified or Unmodified Sorbent A, 0.10 – 0.20 mm Grain Size

Mineral waters. Sorption of UO_2^{2+} on A-PAN sorbent from 25 ml of model water was conducted at pH 5.1 – 5.2 (0.1 ml l^{-1} urotropine buffer) at a flow rate of 15 ml min^{-1}, and 6 ml of HNO_3 (4 mol l^{-1}) were used for elution. Using A-TAN sorbent, pH was adjusted to 6.2 with 0.05 mol l^{-1} urotropine buffer, flow rate was 10 ml min^{-1}, and 4 ml of HNO_3 (4 mol l^{-1}) were employed for elution. UO_2L_2 chelate was sorbed on unmodified sorbent A at pH 6.2 as above applying flow rates as high as 11 ml min^{-1}, and 5 ml of HNO_3 (4 mol l^{-1}) were used for elution. The recovery, using 41.0 μg U, was 95 – 101% in the three cases. The eluate was evaporated just to dryness, the warm residue was taken up in a small volume of water and transferred into a volumetric flask, and uranium was determined spectrophotometrically with PAR. Aluminium(III) ions (0.2 mg l^{-1}) or iron(III) ions (2.6 mg l^{-1}) did not interfere.

TABLE II
Spectrophotometric determination of uranium in drinking water using the PAR reagent after preconcentration on Amberlite XAD 4 sorbents[a]

Sorbent	pH	U, µg		Recovery, %
		added	found	
A-PAN	5.2	49.2	48.2[b]	98.0
			50.2[c]	102.0
		Mean RSD = ±0.020 for U		
A-TAN	6.2	41.0	39.4[b]	96.0
			41.0[b]	100
			41.7[c]	101.5
		27.3	28.5[b,d,e]	104.5
			28.1[b,d,e]	103.5
		13.7	13.5[b,d,e]	98.5
			14.0[b,d,e]	102.5
		19.1	20.2[c,d,e]	106.0
			20.0[c,d,e]	104.0
		Mean RSD = ±0.030 for U		
		Mean recovery: (101.8 ± 2.5)%		
modified sorbent A[f]	6.2	13.7	13.5	98.5
			13.3	97.0
		19.1	19.5	102.0
			18.8	98.5
		24.6	23.1	94.5
		27.3	27.1	99.5
			27.7	101.5
		32.8	32.5	99.0
		Mean RSD = ±0.022 for U		
		Mean recovery: (98.8 ± 1.7)%		

[a] Sorption on columns containing 3 g of sorbent (0.10 – 0.20 mm grain size); [b] sorption from 500 ml of water; [c] sorption from 1 000 ml of water; [d] uranium in eluate determined with Br-PADAP; [e] sorption on columns containing 0.5 g of sorbent; [f] sorption of UO_2^{2+}–DDC chelate.

Sea water. The recovery was 98 – 101% for 9.4 – 14.5 µg U in 25 ml of model water, passed at flow rates of 10 – 14 ml min^{-1}, and eluted with 6 or 4 ml of HNO_3 (4 mol l^{-1}) from the A-PAN, or A-TAN sorbent or from the unmodified sorbent A onto which uranium was sorbed in the uranyl chelate form with DDC. For the last mentioned, the chelate prior formed in water had to be sorbed on sorbent A because only in this case the chelate is also formed in the presence of uranium carbonate complexes $[UO_2(CO_3)_n]^{n-2}$ at pH 7.1 – 7.2 (0.05 mol l^{-1} borate buffer).

Drinking and surface waters. Using small columns containing 0.5 g of sorbent or larger columns with 3 g of modified or unmodified sorbent A for the sorption of uranium from 500 or 1 000 ml volumes, respectively, and applying flow rates of 16 – 20 ml min^{-1}, the sorption of UO_2^{2+} (14 – 50 µg U) was also quantitative and the recovery was 96.5 – 101.0%. The optimum pH was 5.1 – 5.2 (0.04 mol l^{-1} urotropine buffer) for A-PAN sorbent and 6.1 – 6.3 (0.04 mol l^{-1} urotropine buffer) for A-TAN sorbent as well as for the unmodified sorbent onto which the DDC chelate was sorbed. In the last-mentioned case, 4 to 8 ml of 0.5 wt.% aqueous sodium diethyldithiocarbamate was added to the solution prior to sorption. Uranium was eluted with 15 ml of HNO_3 (4 mol l^{-1}) for the sorbed DDC chelate, 15 ml of HNO_3 (2 mol l^{-1}) when using 3 g of sorbent, and 4 ml of HNO_3 (4 mol l^{-1}) or 5 ml of HNO_3 (2 mol l^{-1}) when using 0.5 g of sorbent. The column was additionally washed with water (up to 5 ml), the combined eluates were collected in a quartz beaker, the solution was evaporated under an

TABLE III
Spectrophotometric determination of uranium in surface water using the PAR reagent after preconcentration on Amberlite XAD 4 sorbents[a]

Sorbent	pH[b]	U, µg		Recovery, %
		added	found	
A-PAN	5.1	49.2	51.1	104.0
			47.8	98
A-TAN	6.2	41.0	42.1	102.5
			42.8	101.5
Unmodified sorbent A[c]	6.2	32.8	32.8	100
			33.0	100.5

Mean RSD = ±0.024 for U
Mean recovery: (101.1 ± 1.6)%

[a] Sorption from 500 ml of water on columns containing 3 g of sorbent (0.10 – 0.20 mm grain size); [b] urotropine buffer (0.04 mol l^{-1}); [c] sorption of UO_2^{2+}–DDC chelate.

infrared lamp nearly to dryness, and the residue was taken up in 5 ml of water and transferred into a volumetric flask for spectroscopic quantitation of uranium.

The results of spectrophotometric determination of uranium in drinking water using PAR and Br-PADAP, applying sample flow rates through the columns of 12 – 20 ml min^{-1} and the optimum pH, are given in Table II, the results of determination of uranium in surface water using the PAR reagent are given in Table III.

REFERENCES

1. Chwastowska J., Mozer E.: Talanta *32*, 574 (1985).
2. Yang X. G., Jackwerth E.: Fresenius Z. Anal. Chem. *331*, 588 (1988).
3. Yang X. G., Jackwerth E.: Fresenius Z. Anal. Chem. *327*, 179 (1987).
4. Yang X. G., Jackwerth E.: Fresenius Z. Anal. Chem. *335*, 483 (1989).
5. Cheng K. L., Guh K. H.: Mikrochim. Acta *1978*, 55 (I).
6. Brajter K., Olbrach-Szleszynska E., Stankiewicz M.: Talanta *35*, 65 (1988).
7. Nevoral V.: Chem. Listy *75*, 102 (1981).
8. Nevoral V.: Hydrochémia *85*, 89 (1985).
9. Willis R. B., Saugster D.: Anal. Chem. *48*, 59 (1976).
10. Singh A. K., Kumar T. G. S.: Microchem. J. *40*, 197 (1989).
11. Osaki S., Osaki T., Takashima Y.: Talanta *30*, 683 (1983).
12. Jambor J., Javorek T.: Collect. Czech. Chem. Commun., in press.
13. Persand G., Cantwell F. F.: Anal. Chem. *64*, 89 (1992).
14. Marina M. L., Gonzales V., Rodriguez A. R.: Microchem. J. *33*, 275 (1986).
15. Ide Sh., Takagi M., Ueno K.: Bunseki Kagaku *31*, 651 (1982); Anal. Abstr. *44*, No. 6, 6B10 (1983).
16. Shvoeva O. P., Savvin S. B., Trutneva L. M.: Zh. Anal. Khim. *45*, 476 (1990).
17. Porta V., Sarzanini C., Abolino O., Mentasti E., Carlini E.: J. Anal. At. Spectrosc. *7*, 19 (1992).
18. Florence T. M., Farrar Y.: Anal. Chem. *35*, 1613 (1963).
19. Sommer L., Ivanov V. M.: Talanta *14*, 171 (1967).
20. Sommer L., Ivanov V. M., Novotná H.: Talanta *14*, 329 (1967).
21. Johnson D. H., Florence T. M.: Anal. Chim. Acta *53*, 73 (1971).
22. Sommer L., Šamlotová E.: Can. J. Chem. *60*, 401 (1988).
23. Wayne Meinke W., Taylor J. K. (Eds): *Analytical Chemistry: Key to Progress in National Problems*, p. 403. NBS Special Publication 351, Washington, D. C. 1972.
24. Cheng K. L.: Anal. Chem. *30*, 1072 (1958).
25. Hayes M. R., Wright J. S.: Talanta *11*, 607 (1964).
26. Byrko V. M.: *Ditiokarbamaty* (*Seriya Analiticheskie Reagenty*), p. 150. Nauka, Moscow 1984.

Translated by P. Adámek.