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SCIENCE DIRECT®

Talanta 69 (2006) 393–396

Talanta

www.elsevier.com/locate/talanta

Separation and preconcentration of U(VI) on XAD-4 modified with 8-hydroxy quinoline

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Received 31 August 2004; received in revised form 24 June 2005; accepted 24 June 2005

Abstract

Amberlite XAD-4 adsorber resin was modified with 8-hydroxy quinoline (Oxine) by equilibrating with methanol solution of the reagent and the modified resin was used as a support material for the solid phase extraction and preconcentration of UO_2^{2+} from aqueous solution at pH between 4 and 5.5. Ten micrograms of uranium from 300 ml of aqueous phase could be quantitatively extracted in to 1 g of the modified resin giving an enrichment of 200. Uranium collected in the column could be eluted out with methanol–HCl mixture and determined spectrophotometrically using arsenazo(III) as the chromogenic reagent. The preconcentration could be made selective to uranium by using EDTA as a masking agent for transition metal ions and Th(IV).

Keywords: Oxine; Uranium; Methanol

1. Introduction

Determination of metal ions at a very low concentration often needs preconcentration in order to meet the detection limit of a given analytical method. The preconcentration methods using solid adsorbents are simple, rapid and usually helps to eliminate the interference from the matrix elements. The enrichment is higher than the liquid–liquid extraction, the waste generation is minimal and the metal ions are collected on the solid support in a well-defined chemical form.

Various types of solid supports such as chelating resins [1–3], bonded silica membranes [4], silica gel [5,6] activated carbon [7,8] and polymers [9,10] have been tried as support material for the preconcentration of metal ions. XAD-4 has been successfully used for the separation and enrichment of Ga(III) as 4-(2-thiazolylazo) resorcinol complex [11]. Supported liquid membranes [12–14] and modified cation exchange membrane [15] have been used for the selective separation between monovalent and multivalent ions. Resins impregnated with tetra-butyl ammonium pyrazoles or diphosphonates have been used for the improvement of the selectivity of metal ions [16,17]. In a previous communication, we reported preconcentration and separation of uranium from thorium in aqueous solution using Amberlite XAD-4 modified with tri-*n*-octyl phosphine oxide (TOPO) as support material [18]. However, the application of the method for preconcentration and analysis of uranium could not be recommended due to unusually long elution time and large volume of eluent needed for the recovery of the metal ion from the support material.

Development of efficient method for the recovery and selective preconcentration of uranium from low grade source like seawater have attracted the attention of scientists primarily due to the application of the metal in nuclear industry. Determination of traces of uranium in environmental sites and in the facilities of nuclear industry is also important from safety considerations. The separation and preconcentration of uranium by solid phase extraction using naphthalene modified with 5,7-dichloro quinolinol have been recently reported [19]. In the present study, preconcentration and recovery of uranium from aqueous solution by solid phase extraction using XAD modified with 8-hydroxy quinoline (Oxine) as support material has been examined. The recovery of U(VI) in the presence of transition metal ions and thorium has been tested using EDTA as masking agent. The preconcentrated uranium could be eluted out with dilute acid in a small volume and determined

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0039-9140/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.talanta.2005.06.072

spectrophotometrically using arsenazo(III) as chromogenic reagent.

2. Experimental

2.1. Apparatus

Absorbances were measured using Shimadzu 120 UV–vis spectrophotometer (Shimadzu, Kyoto, Japan). A digital pH meter (ELICO, India) equipped with a combination electrode was used for pH measurements.

Concentrations of interfering ions were measured with atomic absorption spectrophotometer.

2.2. Reagents

XAD-4: Adsorber resin (polystyrene divinyl benzene) Amberlite XAD-4 (20–50 mesh ASTM) was obtained from Emerck, Germany.

Buffer solutions: Acetate and phosphate buffer solutions were prepared by mixing 1 M solutions of sodium acetate or sodium dihydrogen phosphate with their corresponding acids to get pH 4 and 6, respectively. Ammonium chloride buffer solution was prepared by mixing appropriate amounts of 0.1 M ammonia and 0.1 M ammonium chloride solutions for pH 8–10.

Stock solution of uranium was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ in dilute nitric acid.

Arsenazo(III) (Fluka, A.G., Switzerland) solution was prepared by dissolving 0.05 g of the reagent in 100 ml distilled water.

Oxine solution: A stock solution of 1×10^{-3} M was prepared by dissolving appropriate amount of the reagent (Emerck) in methanol.

All reagents and solvents used were of analytical grade.

2.3. Preparation of XAD-4 column loaded with Oxine

XAD-4 resin obtained from the supplier contained organic and inorganic impurities. To remove the contaminants, it was washed successively with methanol, water, 1.0 M HNO_3, water 1.0 M NaOH and water.

For the modification of the resin, methanol solution of Oxine (1.5 ml of 1×10^{-3} M) was taken in a glass beaker and diluted to 10 ml with methanol. Approximately 1 g of clean and dry XAD-4 resin beads were added to the solution and equilibrated with constant stirring for 2 h. Oxine penetrated into the resin bed and was held up strongly. The uptake of Oxine by the resin beds was studied as a function of time (Table 1). The amount of Oxine taken up by the resin was determined by measuring the increase in the weight of the resin after the equilibration followed by washing with methanol and deionized water and dried for an hour at 60 °C. There was marginal increase in the weight during the equilibration period of >2 h. The treated beads were loaded in a glass column (10 cm long and 1 cm i.d.) and washed successively with methanol and deionized water for removing unadsorbed reagent.

Table 1
Weight of the XAD-4 support after adsorbed 8-hydroxy quinoline (Oxine)

Time (h)	Initial support weight (mg)	Support weight after adsorption (mg)	Increase in weight (mg)
0.5	200	204	4
1.0	200	204	4
2.0	200	205	5
4.0	200	205	5
24.0	200	205	5

3. Procedure

An aliquot of uranium solution containing 10–150 μg of the metal ion was taken in a beaker and diluted to 20 ml with deionized water. The pH of the solution was adjusted to 4.5–5.0 with acetate buffer and the solution was allowed to pass through the modified column at the rate of 1.5–2.0 ml/min. The effluent from the column was collected in a volumetric flask. The column was then washed with three 5 ml portions of acetate buffer solution. The washings were also collected in the same flask and the uranium content in it was determined spectrophotometrically with arsenazo(III) at 650 nm [14]. The uranium retained in the column was eluted out with a mixture of acid and methanol. Solution of ammonium carbonate could also be used for the elution of uranium from the column. However, the rapid and quantitative elution of uranium from the column could be accomplished using a mixture of HCl and methanol. The uranium retained in the column was quantitatively eluted out with 10 ml of methanol containing 1 ml of 1 M HCl. The column was washed with deionized water. The eluted solution and the washings were collected in a flask, mixed with 2 ml of 1 M HCl and 1 ml of 0.05% arsenazo(III) solution. The volume was made up to 25 ml and the absorbance of the solution was measured at 650 nm against a corresponding reagent blank. The selective retention of uranium and the interference of transition metal ions and thorium were studied by carrying out the retention experiments in the presence of EDTA. It was necessary to modify the experimental procedure for the separation of uranium from a large excess of interfering metal ions for this XAD resin loaded with an excess concentration of Oxine was prepared. One gram of resin was equilibrated with 5 ml of 10^{-3} M Oxine diluted to 10 ml with methanol for 2 h. One milliliter of EDTA (0.01 M) was mixed with the sample solutions containing U(VI) and the interfering ion and the pH of the mixture was adjusted to 9 with ammonia buffer. The solution was allowed to pass through the column. Uranium was retained on the column and the interfering ions eluted out as their EDTA complex. The concentration of the interfering ions in the effluent and the washings were determined with an atomic absorption spectrometer. The column was repeatedly washed with water and the uranium retained in the column was eluted out and determined in the usual manner.

4. Results and discussuion

In order to obtain maximum recovery of uranium from aqueous solution, it was necessary to optimize the experimental

Table 2
Recovery of uranium from XAD column modified with Oxine

Uranium taken (μg)	Uranium recovered (μg)	Recovery (%)
10	10	100
25	24.8	98.2
40	39.6	98.0
50	49.2	99.0
100	99.0	99.0
150	145	96.5

Eluent: mixture of methanol and 1N HCl (9:1), flow rate: 1.5 ml/min.

parameters such as pH, modification of the adsorber, sample volume, eluents and effects of interfering ions, etc.

4.1. Adsorption of U(VI)

The amount of UO_2^{2+} adsorbed in the column was calculated from the difference between the concentration of uranium in the loading solution and the effluent coming out of the modified column. The percentage of uranium adsorbed in the column for solutions having uranium concentration ranging between 10 and 150 μg in 50 ml is given in Table 2. It can be seen from the Table 2 that the maximum uptake of uranium(VI) by 1 g of modified resin is 100 μg as above; this recovery is reduced (96.5% for 150 μg). It may be noted that there was practically no adsorption of the metal ion in the absence of the modifier. Oxine adsorbed in the resin bed formed a stable chelate with UO_2^{2+} and the quantitative removal of the metal ion was due to its complex formation with the adsorbed Oxine. Equilibration of XAD with Oxine solution for a long time (≈5 h) marginally increased the adsorption of the metal ion but in practice, the stationary phase prepared by equilibration of Oxine for 2 h was sufficient for the quantitative recovery of 100 μg of uranium.

4.2. Effect of pH

Another important factor that controlled the recovery was the pH of the loading solution. The modifying reagent Oxine is a versatile chelating agent that forms complex with many metal ions. It is often used as an extracting agent or as a gravimetric reagent for their determination. It has a nitrogen atom in the heterocyclic ring and a phenolic —OH group in the adjacent position. This makes it suitable for chelate formation with metal ions. As the complex formation is strongly pH dependent, careful adjustment of proper pH for the reagent was necessary. The nitrogen in the heterocyclic ring gets protonated at lower pH while the phenolic —OH dissociates in the alkaline region. On account of this, the reagent has sufficient solubility both in acidic and alkaline solution. The solubility is minimal in the aqueous phase between pH 4 and 9. It reacts with UO_2^{2+} under neutral or slightly alkaline condition to form a stable complex $UO_2(Oxine)_2$. Retention and preconcentration of uranium in the column is due to its complex formation with Oxine. The effect of pH on the adsorption of U(VI) on the modified XAD column is shown in Fig. 1. It is seen from the figure that the recovery of uranium is optimum between pH 4 and 6 and this corresponds to the pH of complex formation of Oxine with the metal ion. Hence, in all further experiments, the operative pH was normally adjusted between 4.5 and 5.5 using acetate buffer.

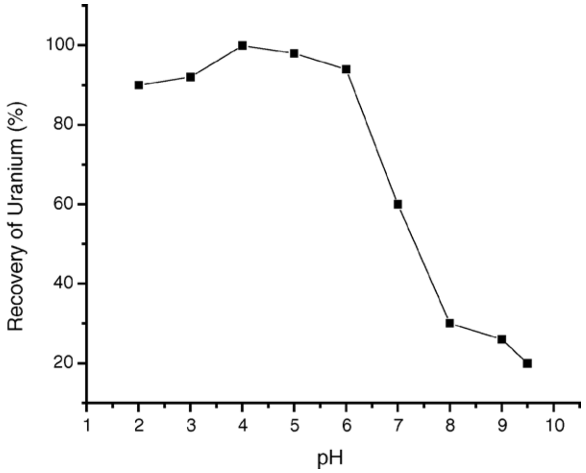

Fig. 1. Effect of pH on percentage recovery of uranium.

4.3. Effect of solution volume

The recovery of uranium from different volumes of aqueous solutions containing varying amounts of the metal ion is shown in Table 3. The results suggest a near quantitative recovery from a small volume of solution while more than 95% of uranium could be recovered from a solution volume of 300 ml. An enrichment factor of 200 could be accomplished during the recovery.

4.4. Desorption studies

Uranium retained in the column could be quantitatively eluted out with acidified methanol. However, the percentage recovery depended on the nature of the acid and its concentration. Quantitative recovery (>98%) of uranium could be accomplished using a mixture of methanol and 1N HCl or HNO_3 in the ratio of 9:1 but the recovery was reduced to 85% when 1N H_2SO_4 was used in place of 1N HCl or HNO_3. However, the use of nitric acid as elutant was avoided due to the high blank values in the spectrophotometric determination of uranium(VI) using arsenazo(III). Ammonium carbonate could also be used successfully for desorption of uranium from the column but a large volume (90 ml of 0.1 M) of the reagent solution was necessary for the

Table 3
Recovery of 25 μg of uranium from various sample volumes pH of feed solution = 5, flow rate of loading: 2 ml/min

Solution volume (ml)	Uranium recovered (μg)	Recovery (%)
50	25	100
75	24.9	99.8
100	24.7	99
150	24.6	99
200	24.5	98
250	24.2	97
300	23.7	95
500	23	93
1000	22.5	90

Table 4
Effect of eluents on the elution of uranium (20 μg) from XAD column

Eluent	Volume of eluent (ml)	Uranium recovered (μg)	Recovery (%)
Methanol	10	1	5
Methanol + 1N HCl (9:1)	10	19.8	99
Methanol + 1N HNO_3 (9:1)	10	19.9	99.5
Methanol + 1N H_2SO_4 (9:1)	10	16.8	84
Ammonium bicarbonate (1 M)	90	19.9	99

quantitative elution of the metal ion from the column. The results are shown in Table 4.

4.5. *Effect of diverse ions on the recovery*

In order to assess the possible analytical application of the recommended procedure, the effect of foreign ions on the separation and preconcentration was studied. Alkali and alkaline earth metal ions did not show any interference in the preconcentration and separation of uranium. Oxine being a versatile chelating agent for metal ions, most of the transition metal ions and thorium(IV) simultaneously was separated on the column and preconcentrated along with U(VI). It was, therefore, necessary to add a suitable masking agent like EDTA to eliminate the interference of these ions. Synthetic binary mixtures were prepared by mixing uranium solution containing 50 μg of uranium and known quantities (milligrams) of various ions and EDTA. The pH was adjusted to 5.5 and the mixture was allowed to pass through the column. The concentration of the interfering ion in the effluent was determined by atomic absorption spectrometry. The stability constants of the EDTA complexes of transition metal ions and Th(IV) is much higher than that of UO_2^{2+} whereas uranyl oxinate is more stable than the Oxine complex of other metal ions particularly in the presence of EDTA. This enabled preferential retention of UO_2^{2+} in the column. Although UO_2^{2+}–EDTA complex is rather weak, it was observed that uranium partially eluted out from the column if the operational pH was maintained at 5.5 or less. In these studies about 40% of uranium co-eluted with other metal ions. The partial retention of UO_2^{2+} is presumably due to the lowering of the conditional stability of UO_2^{2+}–Oxine complex in the presence of EDTA. Similar observation was also made by Venkatesh and Maiti [18]. Use of a XAD-4 treated with excess of Oxine in ensured the stable and quantitative complex formation of UO_2^{2+} with Oxine at pH 9, while EDTA could effectively mask transition metal ions and thorium [20] at this pH. However, the recovery of uranium was poor in the presence of Cu^{2+}. The results of the interference studies have been summarized in Table 5.

Table 5
Recovery of uranium (50 μg) from binary mixture with other ions

Interfering ion	Added as	Amount (μg)	Recovery (%)
Fe^{2+}	$FeSO_4$	500	100
Ca^{2+}	$CaCl_2$	1000	98.9
Cu^{2+}	$CuSO_4$	1600	57.2
Al^{3+}	$Al_2(SO_4)_3$	1350	97.5
Mg^{2+}	$MgCl_2$	4800	95.8
Na^+	Na_2SO_4	5000	98
Th^{4+}	$Th(NO_3)_4$	100	96.5

Masking agent EDTA, pH 9.

5. Conclusion

Adsorber resin XAD-4 could be modified with 8-hydroxy quinoline (Oxine) and the modified resin could be used as support material for separation and preconcentration of UO_2^{2+} from aqueous solution. Nearly 200-fold enrichment of uranium could be obtained. The preconcentration method could be applied to the determination of uranium in the presence of transition metal ions and thorium(IV). The interference of various cations could be effectively eliminated by EDTA.

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