



Short communication

Column chromatographic separation of uranium(VI) and other elements using poly(dibenzo-18-crown-6) and ascorbic acid medium

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Abstract

A selective and very effective separation method for uranium(VI) has been developed by using poly(dibenzo-18-crown-6) and column chromatography. The separations are carried out from ascorbic acid medium. The adsorption of uranium(VI) was quantitative from 0.00002 to 0.006 M ascorbic acid. The elution of uranium(VI) was quantitative with 2.0–8.0 M HCl and 2.0–5.0 M H₂SO₄. The capacity of poly(dibenzo-18-crown-6) for uranium(VI) was found to be 0.92 ± 0.01 mmol g⁻¹ of crown polymer. Uranium(VI) was separated from a number of cations in binary as well as in multicomponent mixtures. The method was extended to the determination of uranium in geological samples. It is possible to separate and determine 5 ppm of uranium(VI) by this method. The method is very simple, rapid, selective and has good reproducibility (approximately $\pm 2\%$).

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1. Introduction

Since the discovery, crown ethers have been used extensively in extraction analysis studies of various metal ions. By polymerization or immobilization of crown ethers on inert support materials they have been used as stationary phases for chromatographic separations. Polymeric crown ethers possess special features such as high resistance to chemicals, to temperature, to radiolysis and also to polar solvents. Because of the special features shown by poly(dibenzo-18-crown-6) it has been used for selec-

tive cation separations from strong acid matrices [1–3]. The use of other polymeric crown ethers for the sorption studies of uranium have been reported [4–10]. But no attempts have been made for the separation of uranium(VI) from associated elements using organic acid media and column chromatography. This paper describes in detail the separation studies of uranium(VI) using poly(dibenzo-18-crown-6) in ascorbic acid medium. The advantages of this method over the reported methods are that ascorbic acid is not hazardous, that the concentration of ascorbic acid required for the quantitative adsorption of uranium(VI) is very low and that a clean cut separation of uranium from thorium, cerium and other associated metal ions in geological samples

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have been achieved. The method was extended to the analysis of uranium in geological samples such as monazite sand and syenite rock sample.

2. Experimental

2.1. Apparatus and reagents

A Zeiss (Germany) spectrophotometer, a digital pH meter (Model LI-120, Elico, India) with glass and calomel electrodes, and a digital flame photometer (PEI, Model No. 041, India) were used.

A stock solution of uranium(VI) was prepared by dissolving 2.166 g of uranyl nitrate hexahydrate (AnalaR grade, BDH, Poole, UK) in 1000 ml of distilled deionised water and standardized gravimetrically [11]. A solution containing 100 $\mu\text{g ml}^{-1}$ of uranium(VI) was prepared by appropriate dilution of the standard stock solution. Ascorbic acid solution (0.5 M) was prepared by dissolving 8.8 g of ascorbic acid (Fluka, Buchs, Switzerland) in distilled deionised water and diluted to 100 ml.

A crown ether polymer poly(dibenzo-18-crown-6) from Merck (Darmstadt, Germany) was used after screening to 100–200 mesh. A total of 0.5 g of polymer was slurred with distilled deionized water and poured in to a Pyrex glass chromatographic column (20 \times 0.8 cm I.D.). The column was used after preconditioning with ascorbic acid solution.

2.2. General procedure

A total of 100 μg of uranium(VI) was mixed with ascorbic acid in the concentration range of 0.00001–0.1 M in a total volume of 10 ml. The solution was then passed through a poly(dibenzo-18-crown-6) column preconditioned with the same concentration of ascorbic acid as that of the sample solution, at a flow-rate of 0.5 ml min^{-1} . The column was then washed with the same concentration of ascorbic acid. The adsorbed uranium(VI) was then eluted with different eluting agents (described later) at a flow-rate of 0.5 ml min^{-1} . A total of 5.0 ml fractions were collected and the uranium content was determined spectrophotometrically with PAR at 530 nm [12]. The concentration of uranium(VI) was calculated from a calibration graph.

3. Results and discussion

3.1. Adsorption of uranium(VI) on poly(dibenzo-18-crown-6) as a function of ascorbic acid concentration

Adsorption studies of uranium(VI) were carried out from ascorbic acid medium. The concentration of ascorbic acid was varied from 0.00001 to 0.1 M. After adsorption uranium(VI) was eluted with 4.0 M hydrochloric acid. It was found that there was quantitative (100%) adsorption of uranium(VI) from 0.00002 to 0.006 M ascorbic acid. With increase in ascorbic acid concentration there was decrease in adsorption of uranium. The subsequent adsorption studies on uranium(VI) were carried out with 0.005 M ascorbic acid.

3.2. Elution studies of uranium(VI) with various eluting agents

A total of 100 μg of uranium(VI) was adsorbed on the poly(dibenzo-18-crown-6) column at 0.005 M ascorbic acid concentration. After adsorption, uranium(VI) was eluted from the column with various eluents such as hydrochloric, hydrobromic, sulfuric, perchloric and acetic acid. The concentrations of eluting agents were varied from 0.1 to 8.0 M. The results are shown in Fig. 1. Various elution studies revealed that there was quantitative elution of uranium(VI) with 25 ml of 2.0–8.0 M HCl and 2.0–5.0 M H_2SO_4 where as hydrobromic, perchloric and acetic acid were found to be inefficient eluents for quantitative elution of uranium(VI). Further elution studies of uranium(VI) in this work were carried out with 4.0 M hydrochloric acid. The elution profile of uranium(VI) with hydrochloric acid is shown in Fig. 2. The elution studies revealed that V_i was 25 ml and V_{max} 5 ml.

3.3. Effect of varying concentration of uranium(VI)

The capacity of poly(dibenzo-18-crown-6) for uranium(VI) was evaluated using 1.0 g of poly(dibenzo-18-crown-6) and adsorption studies were carried out from 0.005 M ascorbic acid using 4.0 M hydrochloric acid as eluent. The volume of uranium(VI) sample solution used was 10.0 ml. The

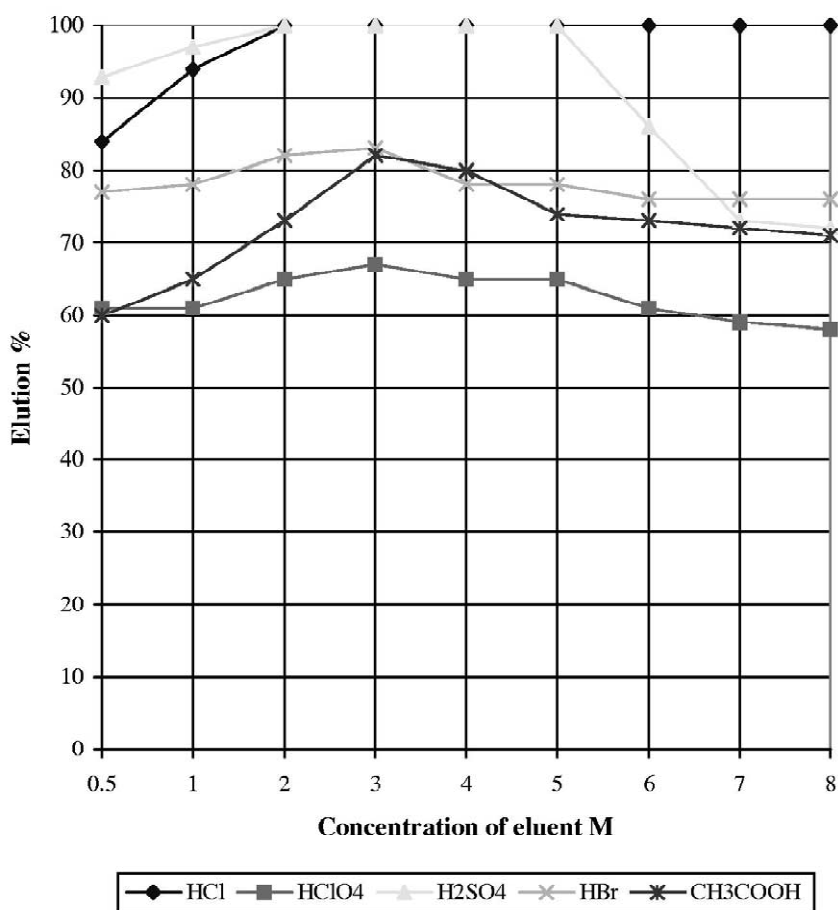


Fig. 1. Elution studies of uranium(VI) with various eluting agents.

concentration of uranium(VI) was varied from 200 to 3000 μg of uranium(VI)/10 ml of solution. The results showed that the adsorption of uranium(VI) was quantitative up to 2200 μg –10 ml. The extent of adsorption of uranium(VI) decreased with increasing concentration of uranium(VI). The capacity of poly(dibenzo-18-crown-6) for uranium(VI) was found to be $0.92 \pm 0.01 \text{ mmol g}^{-1}$ of crown polymer.

3.4. Separation of uranium(VI) from binary mixtures

An aliquot of solution containing 100 μg uranium(VI) and the foreign ions to be tested was taken and ascorbic acid was added so that its concentration was 0.005 M in a total volume of 10.0

ml. The tolerance limit was set as the amount of foreign ions required to cause $\pm 2\%$ deviation in the recovery of uranium(VI). The column was equilibrated with 0.005 M ascorbic acid and the binary mixture solution was passed through a poly(dibenzo-18-crown-6) column at a flow-rate of 0.5 ml min^{-1} . Subsequently the column was washed with 15 ml of 0.005 M ascorbic acid to remove unadsorbed metal ions. Various foreign ions were not adsorbed and so passed through the column. The effluent was collected and analyzed for foreign ion content. It was found that uranium(VI) was not contaminated with most of the cations except potassium(I) and rubidium(I) from the alkali metals, barium(II) from the alkaline earths, which were adsorbed quantitatively. Most of the p-block and d-block cations were

Elution of U(VI) by HCl

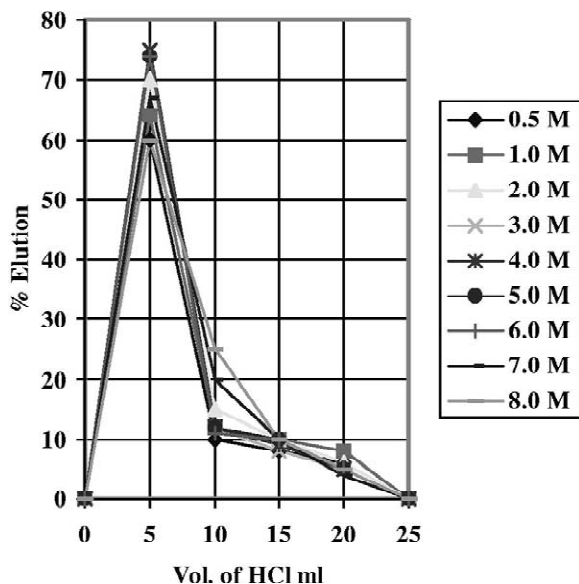


Fig. 2. Elution profile of uranium(VI) with hydrochloric acid.

not adsorbed and showed high tolerance limits. Amongst the inner transition elements, uranium(VI), lanthanum(III) and cerium(III) were adsorbed quantitatively and their separation from uranium has been described in multicomponent mixtures. The anions of the inorganic and organic acids showed very high tolerance limits. The tolerance limit of various foreign ions is shown in Table 1.

3.5. Separation of uranium(VI) from multicomponent mixtures

When a mixture containing iron(III)/molybdenum(VI)/lithium(I), uranium(VI), cerium(III) and thorium(IV) was passed through the poly(dibenzo-18-crown-6) column at 0.005 M ascorbic acid concentration, iron(III)/molybdenum(VI)/lithium(I) were not adsorbed (hence passed through the column), whereas uranium(VI), cerium(III) and thorium(IV) were adsorbed. The adsorbed uranium(VI) was first eluted with 25 ml of 0.2 M lithium hydroxide. Under these conditions, cerium(III) and thorium(IV) were not eluted from

Table 1

Separation of uranium(VI) from binary mixtures U(VI) 100 µg, adsorption 0.005 M ascorbic acid, eluent 4.0 M HCl

Ion	Added as	Tol. limit (mg)	Ion	Added as	Tol. limit (mg)
Li ⁺	LiCl	10	In ³⁺	InCl ₃	0.5
Na ⁺	NaCl	5	Tl ³⁺	Tl(NO ₃) ₃ ·3H ₂ O	0.5
K ⁺	KCl	0.5	La ³⁺	La(NO ₃) ₃ ·6H ₂ O	5
Rb ⁺	RbCl	0.5	Ce ³⁺	CeCl ₃ ·6H ₂ O	8
Cs ⁺	CsCl	0.5	Sb ³⁺	SbCl ₃	10
NH ₄ ⁺	NH ₄ Cl	0.8	Y ³⁺	Y(NO ₃) ₃	0.5
Be ²⁺	Be(NO ₃) ₂ ·4H ₂ O	5	Zr ⁴⁺	Zr(NO ₃) ₄ ·4H ₂ O	0.5
Mg ²⁺	MgCl ₂ ·6H ₂ O	20	V ⁴⁺	VO ₂ SO ₄ ·4H ₂ O	2
Ca ²⁺	CaCl ₂	15	Th ⁴⁺	Th(NO ₃) ₄	3
Sr ²⁺	Sr(NO ₃) ₂	10	Cr ⁶⁺	K ₂ Cr ₂ O ₇	3
Ba ²⁺	Ba(NO ₃) ₂	2	Mo ⁶⁺	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	5
Co ²⁺	CoCl ₂ ·6H ₂ O	3	W ⁶⁺	Na ₂ WO ₄ ·4H ₂ O	3
Ni ²⁺	NiCl ₂ ·6H ₂ O	4	Cl ⁻	HCl	10
Mn ²⁺	MnCl ₂ ·4H ₂ O	3	Br ⁻	HBr	8
Zn ²⁺	ZnCl ₂	10	I ⁻	HI	5
Cd ²⁺	CdCl ₂	5	SCN ⁻	NaSCN	3
Pb ²⁺	Pb(NO ₃) ₂	1	ClO ₄ ⁻	HClO ₄	5
Cr ³⁺	Cr(NO ₃) ₃ ·9H ₂ O	10	CH ₃ COO ⁻	CH ₃ COOH	10
Fe ³⁺	FeCl ₃ ·6H ₂ O	5	SO ₄ ²⁻	H ₂ SO ₄	3
Al ³⁺	Al(NO ₃) ₃ ·9H ₂ O	5	BO ₃ ³⁻	H ₃ BO ₃	2
Ga ³⁺	GaCl ₃	0.5	Tartrate	Tartaric acid	2

the column. The adsorbed cerium(III) was eluted with 25 ml of 0.05 M perchloric acid and finally thorium(IV) was eluted with 25 ml of 4.0 M hydrochloric acid.

3.6. Determination of uranium in geological samples

Monazite sand and syenite rock samples were brought into solution as per the procedure described elsewhere [13,14]. An aliquot of sample solution was subjected for the determination uranium as per the above procedure. The amount of uranium found in monazite sand was 0.295% (0.30%) and in syenite rock it was 278 ppm (280 ppm). The certified values are shown in parenthesis. The standard deviation for monazite sand sample was found to be 0.002 and for syenite rock it was 2.0. The RSD for monazite sand was 0.6779 and that for syenite rock 0.7194.

4. Conclusions

The important feature of this method is that using column chromatographic method and poly(dibenzo-18-crown-6) the separation of uranium(VI) from associated elements in ascorbic acid medium has been achieved. The capacity of poly(dibenzo-18-crown-6) for uranium(VI) was found to be 0.92 ± 0.01 mmol g⁻¹ of crown polymer. Uranium(VI) was separated from a number of cations in binary as well as in multicomponent mixtures. The method was extended to the determination of uranium in geological samples. The method is

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