Chelating ion-exchanger containing benzoylacetanilide moiety: Part II—Separation of beryllium(II) and uranium(VI) from other metal ions

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The sorption patterns of Na(I), K(I), Be(II), Ca(II), Mg(II), Cu(II), Co(II), Ni(II), Al(III), Fe(III), Ti(IV) and U(VI) on macroreticular polystyrene based chelating resin containing benzoylacetanilide functional group have been studied as a function of pH. The selective sorption of Be(II) and U(VI) at pH 4.0 and 3.2 respectively has been utilized for the separation prior to the determination of these metal ions.

Preconcentration by the binding of dissolved trace metal ions onto a chemically modified solid support is now a well established technique. However, only a few chelating ion exchangers have been synthesized for the separation and preconcentration of beryllium (II)[1,2] and uranium(VI)[3-6].

A chelating ion exchanger containing benzoylacetanilide as the functional group was reported by us[7] for the preconcentration of Ti(IV). The same resin has now been used for the preconcentration and separation of Be(II) and U(VI) from various metal ions.

Experimental

Preparation of the chelating ion-exchanger has been reported earlier[7]. An atomic absorption spectrophotometer (Shimadzu AA-646), a double beam UV-visible spectrophotometer (Beckman-26), a Beckman Acculab-10 IR spectrophotometer, a digital pH meter (Sambros-336), a micro Duma's apparatus and gravity flow columns were used in this investigation.

Solutions of benzoyl-m-nitroacetanilide (0.28 to 0.32 g) were prepared in aqueous ethanol (25 ml) for determination of beryllium. Beryllium solution was prepared from beryllium nitrate (E Merck) and standardised gravimetrically[8,9]. Uranium solution was prepared from uranyl nitrate (E Merck) and the metal content determined by the standard procedure[10]. Aqueous solutions of the desired diverse metal ions were prepared from the corresponding, chloride or sulphate and a little acid was added to avoid hydrolysis.

Sodium chloride-hydrochloric acid buffers were used for the pH range of 0.5 to <4.0, sodium acetate-acetic acid buffers for the pH range of 4.0-6.0 and KH_2PO_4 and Na_2HPO_4 buffers for pH range of 6.0 to 7.5.

Procedure

Ion-exchange capacity of the resin for different metal ions was studied by batch and column operations. As reported earlier[7] 50 ml $4N$ sulphuric acid were sufficient for eluting calcium(II), magnesium(II), copper(II), cobalt(II), nickel(II) and iron(III). For the elution of beryllium(II), titanium(IV) and uranium(VI) 50 ml of $6N$ H_2SO_4 were required. The exchange capacities of the metal ions at different pH are shown in Fig. 1. The column operation was carried out as reported earlier[7].

Concentrations of the metal ions before and after elution from the resin were determined by standard procedures. Beryllium(II)[11], Cu(II)[12], U(VI)[12] and Ti(IV)[12] were determined spectrophotometrically. Na(I), K(I), Co(II), Al(III) and Fe(III) were determined by atomic absorption-flame emission spectrophotometry. Nickel(II) was determined gravimetrically[13] while titration with EDTA using Eriochrome black-T as indicator[13] was applied for Ca(II) and Mg(II).

Separation procedure

For the separation of Be(II) (45mg) from a mixture containing Na(I) (50mg), K(I) (50 mg), Ca(II) (50mg), Mg(II) (50mg) and Al(III) (100 mg) or Fe(III) (50 mg), Ni(II) (100 mg) and Co(II) (100 mg) or Co(II) (100mg), Ni(II) (100 mg) and Cu(II) (100 mg) or Al(III) (100 mg), Fe(III) (50mg) and Ni(II) (100 mg), the resin column was equilibrated with the buffer solution of pH 4.0. The pH of the solution containing the mixture of metal ions was adjusted to pH 4.0 in the presence of EDTA (20ml, $1M$) and percolated through the resin column. The column was washed thoroughly with the same buffer and eluted with $6N$ H_2SO_4 (150 ml). It was observed that $99.35 \pm 0.27\%$ beryllium (av. of three determinations) could be recovered using 150 ml $6N$ H_2SO_4.

For the separation of U(VI) from above mentioned metal ions, the resin column was equilibrated with buffer solution of pH 3.2. The mixture of
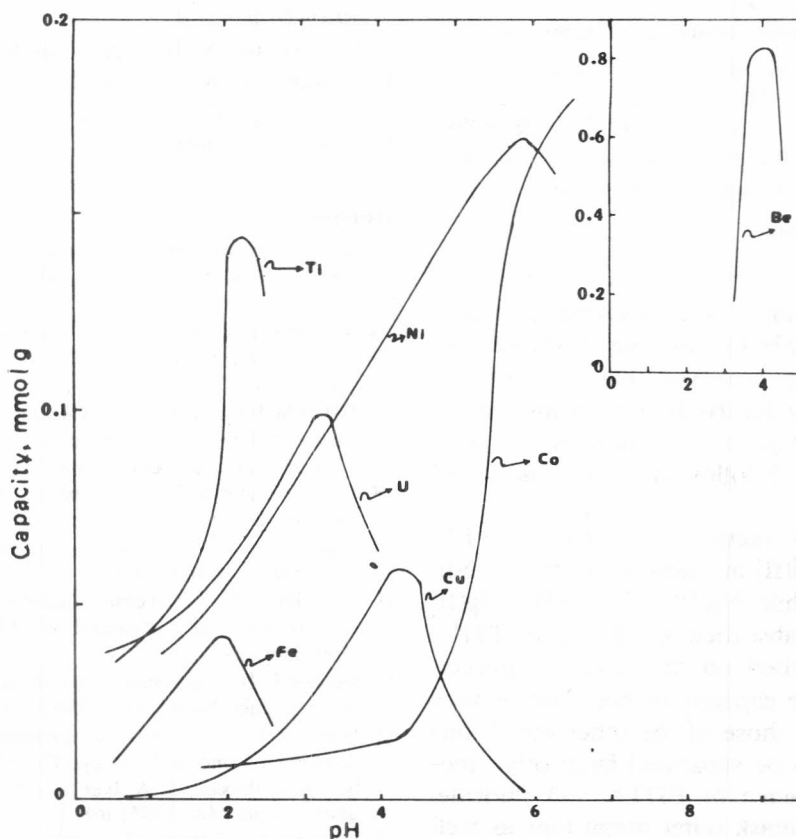
Fig. 1 – Exchange capacity of benzoylacetanilide resin for different metal ions as a function of pH [Inset: Be in a different scale]

metal ions was adjusted to pH 3.2 in the presence of EDTA, and percolated through the resin column, washed with the same buffer and eluted with 150 ml $6N$ H_2SO_4. The experiment with mixtures containing U(VI) (85 mg) and foreign ions like Co(II) (100 mg), Ni(II) (50 mg) and Cu(II) (100 mg) or Al(III) (50 mg), Na(I) (50 mg) and K(I) (50 mg) or Fe(III) (100 mg), Ni(II) (100 mg) and Co(II) (100 mg) in the presence of EDTA (10 ml, 1M)used as masking agent gave $90.15 \pm 0.37\%$ recovery of U(VI) (av. of three determinations).

Separation and determination of beryllium in beryl ore

Finely powdered beryl ore (0.2 g) was decomposed and brought into solution following a standard procedure[14]. The volume was made upto 250 ml. Aliquots of this solution was adjusted to pH 4.0 by acetate buffer and passed through the resin column (initially adjusted to pH 4.0 by the same buffer), when only beryllium was absorbed on the resin column. The column was washed with the same buffer and finally Be(II) was eluted with 50 ml $6N$ H_2SO_4 and determined spectrophotometrically[11]. The results are given in Table 1.

Table 1—Determination of beryllium in beryl ore

Wt of beryl ore (mg)	Beo (%)	
	Found*	Reported
196.4273	12.52 ± 0.03	12.58
227.2385	12.46 ± 0.05	12.58

*Mean of three determinations

Separation and determination of uranium in uraninite ore

Uraninite ore (0.2-0.4 g) was treated with dil HNO_3 followed by conc. H_2SO_4 (5 ml) as reported in literature[15]. The volume was made upto 250 ml and the pH of the solution adjusted to ~ 3.0 after adding 10 ml 1M EDTA as a masking agent for other metal ions present in the solution. The solution was percolated through the resin column; uranium was eluted with $6N$ H_2SO_4 and determined spectrophotometrically using H_2O_2 as reagent[12]. The results are given in Table 2.

Results and discussion

The sorption capacities of beryllium and uranium on resin column were slightly less than those

Table 2—Determination of uranium in uranite ore

Sample	Ore taken (g)	U₃O₈ (%)	
		Found*	Reported
Uraninite I	0.7201	0.172 ± 0.006	0.176
Uraninite II	0.8663	0.185 ± 0.009	0.188

*Mean of three determinations

for the batch operation. The total exchange capacity as a function of pH for the metals studied are shown in Fig. 1. It is observed that the resin exhibits high selectivity for Be(II) and is also selective for U(VI). Sorption of beryllium by the resin starts at about pH 1.5 followed by a peak at pH 4.0.

Among the other metal ions studied, Fe(III), Co(II), Cu(II) and Ni(II) are absorbed by the resin in small amounts while Na(I), K(I), Ca(II), Mg(II) and Al(III) are not absorbed at all. Again Ti(IV) and U(VI) are absorbed on the resin in appreciable amounts. As the capacity of beryllium is very high as compared to those of the other metal ions at pH 4.0, Be(II) can be separated from other metal ions in the presence of EDTA and fluoride. EDTA and fluoride mask other metal ions as well as prevent hydrolysis. However, 10-20 ml of $1M$ EDTA was sufficient to mask the foreign ions.

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