Use of Chelating Ion Exchanger Containing Acetoacetanilide Group in Selective Separation of Beryllium

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A macroreticular styrene-divinylbenzene based chelating resin having acetoacetanilide as the functional group has been synthesized and characterised. The resin is stable in fairly strong acid or alkaline solution. The sorption patterns of Na(I), K(I), Ca(II), Mg(II), Co(II), Cu(II), Ni(II), Fe(III), Al(III), Ti(IV) and U(VI) have been studied at varying pH. The selective nature of the absorption of Be(II) at pH 4.0 has been utilized for the separation and concentration of the metal ion in synthetic mixtures and in beryl. Strong H$_2$SO$_4$ (6 N) has been used for the elution of Be(II) from the resin.

In trace analysis preconcentration of metal ion is often a vital step and various chelating resins having chelating groups like hydroxylamine and its derivatives, iminodiacetate, thioglycolates, dithiozone, hydroxyquinoline, $\alpha$-hydroxylaldoxime, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol have been used for the separation of different metal ions.

Acetoacetanilide is a very selective reagent for gravimetric determination of beryllium. So far only one chelating resin containing 1,3-diketo compound has been synthesized. In this work acetoacetanilide has been incorporated in styrene divinylbenzene (DVB) polymer and the resulting ion-exchanger has been characterised. The absorption behaviour of several metal ions on this resin has been studied and a method for the separation and preconcentration of Be(II) has been developed.

Materials and Methods
An atomic absorption spectrophotometer (Shimadzu AA-646) and a double beam UV-visible spectrophotometer (Beckmann 26) were used for measurement of concentrations of the metal ions. Infrared spectra were recorded in KBr matrix on a Beckmann Acculab-10 IR spectrophotometer. Gravity flow columns were made of glass with appropriate reservoirs.

Fresh solution of benzoyl-$m$-nitroacetanilide was prepared by dissolving 0.28 to 0.32 g of the reagent in aqueous ethanol (25 ml). Beryllium solution was prepared from beryllium nitrate (E. Merck) in dilute nitric acid. The metal content was determined gravimetrically. Aqueous solutions of the desired diverse metal ions were prepared from their nitrates, chlorides or sulphates and a little acid was added to avoid hydrolysis.

For adjusting the pH sodium chloride-hydrochloric acid buffers were used for the pH range of 0.5 to pH less than 4.0 and sodium acetate-acetic acid buffers were used for the range of pH between 4.0 and 6.0. For studying the exchange behaviour of metal ions above pH 6.0 to 7.5 buffers were prepared from KH$_2$PO$_4$ and Na$_2$HPO$_4$.

Synthesis and ion exchange capacity of resin
Styrene-DVB polymer beads (80-100 mesh) containing 8% DVB (Thermax Private Ltd.; Ponna, India) was nitrated using a mixture of concentrated sulphuric acid and nitric acid. The wet nitrated product was mixed with tin (20 g), industrial ethanol (50 ml) and sufficient amount of conc. hydrochloric acid and refluxed for 12 hr to obtain aminopolystyrene. Finally, the aminated product was condensed with ethyl acetoacetate (4 g for every 3 g of aminopolystyrene) by refluxing the mixture at 110-15°C for 24 hr in toluene to get the desired acetoacetanilide resin.

Ion exchange capacity of the resin for metal ions was studied by batch and column operation methods. In batch operation, air-dried resin (0.5 g) was stirred for 24 hr with an excess of the desired metal ion solution of known strength (~ 0.1 M) and pH controlled by adding suitable buffer; the mixture was filtered and the resin was thoroughly washed with the same buffer until free from the metal ions. The sorbed metal ions were then completely eluted by H$_2$SO$_4$ of appropriate strength. The whole process was repeated with buffers of different pH. The eluted metal ions were determined by standard methods.
It was found that 50 ml 4 N sulphuric acid were sufficient for eluting cobalt(II), copper(II), iron(III), calcium(II), magnesium(II) and nickel(II) while 50 ml 6 N sulphuric acid were required for titanium(IV), uranium(VI) and beryllium(II).

In column operation, a glass column (30 cm length and 1 cm i.d.) was packed with ~ 25 g of air-dried resin (initially swollen with 2 N hydrochloric acid for 24 hr). The bed was thoroughly washed with deionised water at a flow rate of 0.5-1.0 ml/min till free from acid. This rate of flow was maintained in all subsequent steps. Known volumes of the desired metal ion (50 ml, ~ 2 M), adjusted to the desired pH by adding appropriate buffer, was passed through the column, washed with sufficient amount of deionised water and finally the sorbed metal ions were eluted with sulphuric acid of appropriate strength and determined by appropriate method.

Concentrations of the metal ions before and after elution from the resins were determined by standard procedures. Titanium(IV), uranium(VI), beryllium(II) and copper(II) were determined spectrophotometrically, titanium(IV) was determined with hydrogen peroxide in acid medium\(^\text{12}\), beryllium(II) with benzoyl-\(m\)-nitroacetanilide\(^\text{13}\) and copper(II) with sodium diethyl dithiocarbamate\(^\text{12}\), aluminium(III), iron(III), cobalt(II), sodium(II) and potassium(I) were determined by atomic absorption spectrophotometry. Nickel(II) was determined gravimetrically with dimethylglyoxime\(^\text{14}\). Calcium(II) and magnesium(II) were determined by titration with EDTA using Eriochrome black-T as indicator\(^\text{14}\).

**Separation procedure**

For the separation of Be(II) from its binary mixture with Cu(II), Co(II), Ca(II), Mg(II), Ni(II), Al(III), Fe(III), Ti(IV) or U(VI), 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 4.0 in the presence of EDTA. The solution was then percolated through the resin column, washed thoroughly with the same buffer and eluted with 150 ml 6 N H\(_2\)SO\(_4\).

It was observed that over 99% beryllium could be recovered using 150 ml of 6 N H\(_2\)SO\(_4\) as eluant.

**Results and Discussion**

**Characterisation of the resin**

The resin was characterised by its water regain value, infrared spectrum, its stability towards acid and alkali, elemental analysis and metal ion exchange capacity.

A sample of dry resin was immersed in deionised water for 48 hr, centrifuged, air-dried and weighed. It was then dried at 100°C for 48 hr and weighed again. Water regain, calculated from the difference in weight, was found to be 0.21 g/g resin.

Infrared spectrum exhibited two bands at 1500 and 1330 cm\(^{-1}\) assignable to \(-\text{CONH}–\) and CH\(_3\)CO– groups respectively. The resin was found to be stable in 6 N H\(_2\)SO\(_4\) and 4 N NaOH since no appreciable change in its nitrogen content and sorption capacity for titanium was found.

**Estimation of nitrogen and amino group**

Small amounts of the air-dried resin of the nitrated polystyrene, aminopolystyrene and the chelating resin containing diketo group (all belonging to the same batch) were thoroughly dried by heating at 80°C for 48 hr and then keeping in a desiccator over phosphorus pentoxide. Nitrogen in each case was determined by micro Duma's method. The amino group content of the aminopolystyrene was determined by titration in nonaqueous medium\(^\text{15}\).

The nitrogen content and the capacity for Ti(IV) remained unchanged after treatment with 6 N H\(_2\)SO\(_4\) or less or with 2 N NaOH or less. The small value of water regain of the resin indicated that its sorption capacity may not be very high, but experiments showed that the resin had a moderate capacity for beryllium.

The nitrogen content of the nitrated polymer was found to be 5.53%. After reduction, the percentage of nitrogen of the amino resin was found to be 7.1% as total nitrogen and 5.23% as amino nitrogen (from the estimation of amino group) with 1.87% nitrogen as unconverted nitro group. The nitrogen content of the final resin was found to be 5.47%.

In order to study the cation retention capacity of the residual nitro and amino groups of the resin, the capacities of both polynitrostyrene-divinylbenzene and polyaminostyrene-divinylbenzene have been studied and found to be negligible.

**Metal absorption capacity and separation**

The absorption capacity of beryllium on resin column was slightly lower than that in batch operation (Fig. 1). The total capacity versus pH curves for the metals studied, shown in Fig. 1, indicate that the resin exhibits high selectivity for Be(II), which starts getting absorbed by the resin around
pH 1.5, followed by a maximum with a peak at pH 4.0.

Among the other metal ions studied, Fe(III), Co(II), Cu(II) and Ni(II) are only negligibly absorbed by the resin, while Na(I), K(I), Ca(II), Mg(II) and Al(III) are not absorbed at all. So a clear separation of Be(II) from Al(III), Na(I), K(I) Ca(II) and Mg(II) is possible. Separation of Be(II) from Fe(III), Ni(II) and Co(II), separation of Be(II) from Co(II), Ni(II) and separation of Be(II) from Al(III), Fe(III) and Ni(II) are also possible. Addition of 10-20 ml of Na₂EDTA (0.1%) and boiling the mixture for 2 min prevent precipitation of base metals due to hydrolysis at pH 4.0. Some examples of separation of Be(II) in synthetic mixture are shown in Table 1.

Separation and determination of beryllium in beryl

Finely powdered beryl (~0.2 g) was decomposed by fusion with NaF, cooled and taken up in conc. H₂SO₄. The mixture was heated to fumes to drive out all the fluoride and transferred into a beaker containing water (~100 ml). A clear solution was obtained by boiling and the volume was made up to 250 ml.

Aliquots of this solution was adjusted to pH 4.0 by acetate buffer and passed through resin column (initially adjusted to pH 4.0 by the same buffer), when only beryllium was absorbed on the column. The resin column was washed with the same buffer and finally Be(II) was eluted with 50 ml 6 N H₂SO₄ and collected in a 100 ml volumetric flask. Beryllium was determined spectrophotometrically using benzoyl-m-nitroacetanilide. The results are given in Table 2.

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