Reversed phase extraction chromatrographic study of copper(II) with a high molecular weight carboxylic acid and its analytical applications

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A selective method for the extraction of copper(II) by reverse phase extraction chromatographic technique on silica gel impregnated with a high molecular weight carboxylic acid (SRS-100) has been developed. Quantitative extraction has been achieved in the pH range 4.6-6.8. Effects of variables like pH, eluting agents and flow rate on extraction and elution have been studied. Several metal ions like Mn(II), Co(II), Ni(II), Mg(II), Sr(II), Ba(II), Pd(II), La(III) and U(VI) do not interfere in the extraction. Some metal ions like Pb(II), Hg(II), Al(III), Ce(IV) and Th(IV) interfere in the extraction, but these can be separated by selective elution. In order to assess the possible analytical applications, copper(II) has been separated from multicomponent mixtures containing metal ions generally associated with it as well as from standard ore and alloy samples.

There are several reports in the literature on the extraction of metal ions with carboxylic acids[1]. High molecular weight carboxylic acids (Versatic 10, SRS-100) have been used in our laboratory for the extraction of di-, tri- and tetra-valent metal ions[2,3]. Copper(II) is one of the toxic metals present in industrial effluents, so it was thought worthwhile to work out an exchange chromatographic method for its removal. In this note a simple rapid and selective method for the extraction and separation of copper from its binary and ternary mixtures as well as from industrial effluents has been proposed.

Experimental

A digital pH-meter (Elico model LI-120), a spectrophotometer (ECIL model GS 5700 A) and a chromatographic column (i.d., 1 cm and bed height 7.5 cm) of borosil glass with a glass wool plug at the bottom were used in the present studies.

SRS-100 (Shell Chemical Co., London), a high molecular weight synthetic mono-carboxylic acid (C_{15}-C_{16}), was used as the liquid cation exchanger[4].

A stock solution of copper(II) (1.01 mg/ml) was prepared by dissolving $CuSO_4.5H_2O$ (AR) in deionised water and it was standardised complexometri-

cally using murexide (murexide: potassium chloride 1:100) indicator[5]. The solution containing 202 µg/ml of copper(II) was prepared by appropriate dilution. The buffer solutions of different pH were prepared from sodium acetate (0.2 M) and acetic acid (0.2 M) solutions. All the chemicals used were of analytical reagent grade.

Silica gel (60-120 mesh, BDH) was rendered hydrophobic by exposing it to the vapours of dimethyldichlorosilane in a nitrogen atmosphere; then it was washed with anhydrous methanol and dried at 100°C. Hydrophobic silica gel was coated by treatment with a benzene solution of SRS-100 and evaporation was done using a rotary vacuum evaporator. Excess organic reagent present in the exchanger was washed with 4 M HCl[6].

General extraction procedure

An aqueous solution containing 202 µg of copper(II) was mixed with 10 ml acetic acid-sodium acetate buffer solution and its pH was adjusted to 4.8. The solution was then passed through a silica gel column coated with SRS-100 at a flow rate of 0.5 ml/min. The column was washed with 10 ml buffer solution (pH 4.8). Copper(II) was eluted with a variety of mineral acids and salt solutions, and its amount in each fraction (5 ml) was determined spectrophotometrically[7].

Results and discussion

Effect of pH

The extraction behaviour of copper(II) with SRS-100 was studied at different pH values keeping copper(II) concentration constant. The extraction of Cu(II) increased with increasing pH and became quantitative in the pH range 4.6-6.8.

Eluting agents

It was found that mineral acids were efficient eluting agents at lower concentrations. Acids like nitric, hydrochloric, sulphuric, perchloric and nitrates of sodium and potassium were tested as the eluants. The results show that stripping of copper(II) is complete with 0.02 M HNO_3, 0.1 M HCl and 0.1 M H_2SO_4 while KNO_3, $NaNO_3$, $NaCl$ and H_2O are poor eluants.

Exchange capacity

The exchange capacity of the exchanger was determined by measuring the number of milligram equivalents of sodium ion absorbed per gram of the dry exchanger in the hydrogen form at different temperatures. 1.0 g of exchanger was taken in a standard-joint

bottle containing 20 ml of 2.5 M sodium chloride, 15 ml of 0.21 M sodium hydroxide and 15 ml of deionised water. The exchanger was shaken for 10 hr in a hot-cum-cold bath at different temperatures. The hydrogen ion liberated from the exchanger reacted with sodium hydroxide and excess sodium hydroxide was determined by titration with standard hydrochloric acid. The exchange capacity (Table 1) was determined according to the following relation,

Exchange capacity = av/w;

where v = volume of NaOH consumed by exchanger, a = strength of NaOH and w = weight of exchanger.

Separation of copper(II) from binary mixtures

Copper(II) was separated from several metal ions in its binary mixtures by exploiting the differences in pH at which quantitative extraction takes place for different metal ions. At pH 4.8, manganese(II), cobalt(II), nickel(II), magnesium(II), strontium(II), barium(II), cadmium(II), palladium(II), chromium(III), lanthanum(III), neodymium(III), praseodymium(III), samarium(III), dysprosium(III) and uranium(IV) did not interfere in the extraction. These metal ions passed through the column. Later, Cu(II) was eluted with 0.1 M HNO$_3$. Elements like aluminium(III), cerium(IV), lead(II), mercury(II) and thorium(IV) interfered under the recommended extraction conditions. However, their interferences were removed by using selective eluants. Mixtures containing Cu(II) and the above mentioned metal ions were passed through the column at pH 5.5. After sorption, Cu(II) was eluted first with 0.02 M HNO$_3$, then rest of the metal ions were eluted with 1 M HNO$_3$. After separation, copper(II) was estimated spectrophotometrically.

Separation of Cu(II) from synthetic mixtures

To assess the possible analytical applications the proposed method was applied for the separation of copper from some synthetic mixtures. A mixture containing iron(III), copper(II), and cobalt(II) or nickel(II), or chromium(III), or aluminium(III) was passed through the column at pH 2.8, when iron(III) separated from rest of the metal ions. Iron(III) was eluted with 0.5 M HCl. The effluent was passed through the column at pH 4.8 to extract copper(II); copper(II) was eluted with 0.02 M HNO$_3$. In the case of mixture containing aluminium, the effluent after removal of iron was passed through the bed at pH 5.5. Both copper and aluminium were extracted; copper was eluted with 0.02 M HNO$_3$ followed by the elution of aluminium with 1 M HNO$_3$. A mixture containing zinc(II), mercury(II) and copper(II) was passed through the column at pH 4.8. Mercury(II) and copper(II) were sorbed; copper(II) was eluted with 0.02 M HNO$_3$ followed by elution of mercury(II) with 1 M HNO$_3$. In the case of a mixture of cerium(IV), lanthanum(III), neodymium(III) and copper(II), on passing it through the column at pH 4.8, lanthanum(III) and neodymium(III) passed through the column. Copper(II) was eluted with 0.02 M HNO$_3$ and finally cerium(IV) with 1 M HNO$_3$. In almost all the cases quantiative separation of Cu(II) was achieved.

Separation of copper(II) from alloy samples

The proposed method was applied to the extraction of copper(II) from some of the standard alloy samples. In all the cases quantitative extraction and separation of copper(II) were achieved. Results were compared with standard data (Table 2).

Removal of copper from effluent water

The effluent water sample was collected from M/s Hindustan Copper Ltd at Ghatsila, Bihar. 500 ml of the solution was treated with NH$_4$HF$_2$ and passed through the column at pH 4.8. After sorption, copper was eluted with 0.02 M HNO$_3$ (80 ml) and estimated spectrophotometrically. Copper content in the effluent water was found to be 0.23 mg/litre.

Table 1—Exchange capacity at different temperatures

Temp. (°C)	Amount of exchanger (g)	Volume of NaCl(2.5 M) (ml)	Volume of NaOH(0.21 M) (ml)	Exchange capacity (meq of H$^+$/g)
10	1.005	20	15	1.82
15	1.002	20	15	1.72
25	1.006	20	15	1.68
30	1.002	20	15	1.68
40	1.004	20	15	1.56
50	1.003	20	15	1.49

Shaking time = 10 hr; volume of water taken = 15 ml.

Table 2—Determination of copper in alloy samples

Sample	Copper extracted (%)	Certified value
* Brass-5G	66.54	67.4
* H.T. Brass-10 G	61.25	60.8
* Cupro-Nickel-180/2	69.12	68.12
Lead Copper matte-46 G	38.21	39.6

pH = 4.8; eluant 0.02 M HNO$_3$, *NH$_4$HF$_2$

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