

Selective Separation of Copper(II) on a Cobalt Hexacyanoferrate(III) Ion-exchange Column

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Cobalt hexacyanoferrate(III), prepared by adding cobalt chloride to potassium hexacyanoferrate(III) solution and heating at 80 °C, is stable in water, acids and salt solutions. The compound was characterised and its solubility determined in different media. The exchange capacity of the exchanger in the H⁺ form was found to be 0.45 mequiv g⁻¹. Distribution coefficients determined for various metal ions show that the exchanger is highly selective towards Cu(II) ions, unlike other hexacyanoferrate(II) and -(III) compounds, and can, therefore, be used for its separation from other ions.

Keywords: Cobalt hexacyanoferrate(III); ion-exchange separation; static and dynamic sorption of copper(II)

Insoluble metal hexacyanoferrate(II) compounds exhibit ion-exchange properties and show selectivity in their exchange behaviour.¹ The most investigated hexacyanoferrate(II) compounds are those of cobalt²⁻⁴ and zinc,^{5,6} which have been used for various useful separations. Although a large number of metal hexacyanoferrate(III) compounds have been found to be insoluble⁷ and can be expected to act as sorbents like hexacyanoferrate(II) compounds, it is surprising that they have not been studied from this point of view in any detail. Ganzerli-Valentini and co-workers described the exchange properties of zinc hexacyanoferrate(III)^{8,9} and recently we have reported the use of chromium hexacyanoferrate(III) gel as a caesium-selective ion exchanger.¹⁰

Generally metal hexacyanoferrate(II) and -(III) compounds are studied with special reference to their affinity for alkali metals^{1,10}; they have not been used for the selective separation of other metal ions, especially transition metals. High K_d values for bivalent transition metal ions are observed with cobalt,⁴ zinc,⁹ chromium¹¹ and tin¹² hexacyanoferrate(II) compounds but they are not found to be specifically selective for a particular transition metal and are therefore of little use for isolation and separation purposes.

In this paper we report the synthesis of insoluble cobalt hexacyanoferrate(III), which has been found to possess a high affinity for copper(II) and can be used for its selective separation from various other ions that generally interfere in its determination.

Experimental

Reagents and Materials

Cobalt(II) chloride (BDH Chemicals) and potassium hexacyanoferrate(III) (Merck), both of analytical-reagent grade, were used without further purification for the preparation of the exchanger. All other salts and acids were also of analytical-reagent grade.

Solutions of metal ions were prepared in doubly distilled water to contain 0.01 mol dm⁻³ of the corresponding acid. ¹¹⁰Ag^m, ¹³⁴Cs, ⁸⁶Rb, ⁸⁵Sr + ⁸⁹Sr, ¹³³Ba, ⁵⁴Mn, ⁵⁸Co, ⁶⁵Zn, ²⁰³Hg and ⁵⁵Fe + ⁵⁹Fe radioisotopes were obtained from the Bhabha Atomic Research Centre, Bombay, India.

Preparation of Cobalt Hexacyanoferrate(III)

The solutions of cobalt(II) chloride (0.006–0.18 mol dm⁻³) and potassium hexacyanoferrate(III) (0.03–0.30 mol dm⁻³) were thermostatically controlled at 80 °C and mixed in wide-mouthed Pyrex glass tubes, the total volume being 40 cm³ in each instance. The precipitates thus obtained were digested for about 35 h. All samples were prepared in duplicate, the order of mixing being different in the two instances. The precipitates were finally washed with distilled water and dried in an oven at 80 °C. These samples were then converted into the H⁺ form by immersing them in 1 mol dm⁻³ nitric acid, and their hydrogen liberation exchange capacities were determined. The product, obtained with maximum exchange

capacity, was prepared in bulk and sieved to the desired mesh size (-50 to $+100$ mesh) and converted into the H^+ form. All subsequent studies were carried out with this product only.

Analysis of the Ion Exchanger

A known amount (0.2 g) of the exchanger (H^+ form) was dissolved in hot concentrated sulphuric acid (about 10 cm^3). The solution was cooled and transferred into a 100-cm^3 calibrated flask and diluted to the mark with distilled water. Cobalt and iron were determined in this solution by atomic-absorption spectrophotometry and potassium by flame photometry.

Apparatus

Bausch and Lomb Spectronic-20 and Unicam SP-500 spectrophotometers and an IL 751 atomic-absorption/atomic-emission spectrophotometer using an air-acetylene flame (except for tin, for which a dinitrogen oxide flame was used) (2300°C) were used. Radiometric determinations were carried out with a scintillation counter (ECIL, Hyderabad, India) employing a well-type sodium iodide (thallium) crystal. A Carl Zeiss Jena, Model 111, flame photometer was used for the flame photometric determination of ions.

Thermogravimetric analysis of the product was performed with a Stanton Redcroft TG-750 thermobalance fitted with a temperature programmer and recorder, taking 5-mg samples in a nitrogen atmosphere (flow-rate of nitrogen, $10\text{ cm}^3\text{ min}^{-1}$), maintaining the heating rate at $10^\circ\text{C min}^{-1}$ and the chart speed at 120 mm h^{-1} . The infrared spectra of dried samples of the compound were recorded at room temperature (30°C) in potassium bromide pellets on a Beckman IR-20 spectrophotometer. A Philips X-ray diffractometer employing $\text{Mo K}\alpha$ ($\lambda = 0.0711\text{ nm}$) radiation was used for X-ray diffraction studies. Magnetic susceptibility measurements were carried out on a Model 155 vibrating sample magnetometer.

Determination of Metal Ions

Magnesium, calcium, nickel, copper(II), lead, cadmium, aluminium and bismuth were determined by EDTA titrations. Lithium, iron, cobalt, tin and antimony were determined by atomic-absorption/atomic-emission spectrophotometry and the radiometric method was used for the determination of silver, rubidium, caesium, strontium, barium, manganese, cobalt, zinc, mercury(II) and iron(III). Sodium and potassium were determined by flame photometry and ZrO_2^{2+} and UO_2^{2+} were determined by spectrophotometry.

Determination of Distribution Coefficients

The distribution coefficients (K_d) were determined by the batch equilibrium method by shaking the exchanger (0.1 g) with 10 cm^3 of 0.002 mol dm^{-3} metal ion solution in 0.01 mol dm^{-3} of the corresponding acid for 48 h .

Sorption and Desorption Studies on Copper(II)

Sorption of copper(II) under static conditions was carried out by shaking 50 mg of the ion exchanger with a 10 cm^3 solution of copper(II) (10^{-5} – $10^{-1}\text{ mol cm}^{-3}$). For sorption and elution of copper(II) under dynamic conditions, a column of i.d. 0.5 cm containing 0.5 g of ion exchanger was used. The column capacity was determined from breakthrough experiments using copper(II) solution (0.01 mol dm^{-3}) at the rate of 4 drops per minute. For separation, the ion-exchange column was loaded with a mixture of any pair of ions to be separated. Elution was started after 15 min at a flow-rate of 4 drops per minute.

Results and Discussion

Preparation of Ion Exchanger

The insolubility and exchange capacity of the product formed vary with the concentration of the reactants, their mixing ratio and the mode of mixing. A product with a maximum hydrogen liberation capacity of $0.45\text{ mequiv g}^{-1}$ of the exchanger was obtained with $\text{Co}^{2+} = 0.12\text{ mol dm}^{-3}$, $\text{Fe}(\text{CN})_6^{3-} = 0.06\text{ mol dm}^{-3}$ and mixing ratio $\text{Co}^{2+}/\text{Fe}(\text{CN})_6^{3-} = 2.00$, the cobalt(II) chloride being gradually added to potassium hexacyanoferrate(III). The cobalt hexacyanoferrate(III) thus obtained is dark brown and can be converted into any desired mesh size.

Chemical Stability

The exchanger is fairly stable in water, dilute acids and salt solutions, and shows no dispersion. The solubilities of this compound in various solvents are given in Table I.

TABLE I
SOLUBILITY OF COBALT HEXACYANOFERRATE(III)

Temperature, 22 °C; time, 3 d.

Solvent	Fe dissolved/g dm ⁻³	Solvent	Fe dissolved/g dm ⁻³
H ₂ O	Negligible	NH ₄ NO ₃ (10 mol dm ⁻³) ..	0.020
HNO ₃ (1 mol dm ⁻³) ..	0.015	H ₂ SO ₄ (conc.) ..	Dispersed
HCl (1 mol dm ⁻³) ..	0.015	HNO ₃ (conc.) ..	Negligible
HNO ₃ (5 mol dm ⁻³) ..	Negligible	NaCl (2 mol dm ⁻³) ..	0.030
HCl (5 mol dm ⁻³) ..	Negligible	KCl (2 mol dm ⁻³) ..	0.035
HNO ₃ (10 mol dm ⁻³) ..	Negligible	NH ₄ Cl (5 mol dm ⁻³) ..	0.030

Characterisation

On the basis of chemical analysis, the exchanger has been assigned a tentative molecular formula K[CoFe(CN)₆].5H₂O, which requires K 9.77, Co 14.73, Fe 13.96 and H₂O 22.5% (found: K 9.6, Co 15.2, Fe 14.50 and H₂O 23%). The number of water molecules per unit formula were calculated by the method of Alberti *et al.*¹³ from the pyrolysis curve of the product, which showed a first mass loss from 50 to 170 °C apparently due to the loss of water. At 170 °C, a 23% loss in mass was observed. The presence of water molecules was further confirmed by the bands at 3400 and 1610 cm⁻¹ in the infrared spectrum, which disappeared when the compound was heated to 170 °C.

X-ray studies showed that the compound is crystalline and primitive cubic with a cell edge of 0.51 nm. As the unit cell is small, it is expected to have only one molecule. A tentative structure for cobalt hexacyanoferrate(III) may be proposed, similar to the K[Fe^{II}Fe^{III}(CN)₆] structure,¹⁴ where each Fe(III) and Co(II) is surrounded octahedrally by cyanide ions, which act as bridge leading to the formation of a super complex in the solid state. This super complex structure is supported by the magnetic measurements. The compound has a magnetic moment of 6.1 BM, which corresponds to the presence of two unpaired electrons per molecule, compared with a magnetic moment of 3.67 BM for K[Fe^{II}Fe^{III}(CN)₆], which has one unpaired electron.¹⁵ Hence the magnetic data show that Co(II) has one unpaired electron, which is possible only when it exists in the lattice in the form of a cyanide inner complex.

On equilibrating the compound with nitric acid (1 mol dm⁻³), a small amount of water is expected to be converted into H₃O⁺, which undergoes exchange¹⁶ with metal ions. The presence of H₃O⁺ in the exchanger is supported by a band at 1390 cm⁻¹ in the infrared spectrum due to NO₃⁻ ions, which are adsorbed as co-ions. It may be added that the amount of H₃O⁺ and NO₃⁻ is small (as is evident from the small exchange capacity, Table II) in the H⁺ form of the ion exchanger and does not significantly alter the percentage calculated from the formula proposed.

TABLE II
EXCHANGE CAPACITY OF COBALT HEXACYANOFERRATE(III) IN TERMS OF
mequiv g⁻¹ OF H⁺ IONS LIBERATED AS A FUNCTION OF TEMPERATURE
AND EXCHANGING CATION

Exchanging cation	Capacity/ mequiv g ⁻¹	Temperature/ °C	Capacity/mequiv (exchanging cation K ⁺)
Li(I)	0.07	80	0.45
Na(I)	0.17	100	0.45
K(I)	0.45	150	0.35
		200	0.12
		400	0.02

Ion-exchange Capacity

All sorption studies were carried out with the ion exchanger in the H^+ form. The ion-exchange capacity as the hydrogen-ion liberation capacity was determined by a batch method. The effect of equilibration time and concentration of potassium chloride solution on the exchange capacity was determined and it was found that a constant capacity is achieved after 40 h of equilibration in 1 mol dm^{-3} potassium chloride solution and at concentrations greater than 0.8 mol dm^{-3} . Thus the exchange capacity value reported was determined in 1 mol dm^{-3} potassium chloride solution after equilibration for 48 h to ensure complete exchange.

The ion-exchange capacities of the exchanger for different alkali metal ions are reported in Table II. It can be seen that the exchange capacity increases with a decrease in hydrated ionic radii, *i.e.*, $Li(I) < Na(I) < K(I)$. The exchange capacity remains unaffected up to $100^\circ C$ and decreases thereafter with further increase in temperature (Table II), apparently owing to loss of water.

Distribution Studies

The distribution coefficients (K_d) for various metal cations are given in Table III. It can be seen that the exchanger shows a very high affinity for $Cu(II)$ ions and adsorbs these ions completely at this concentration. Among the other metal ions, the order of sorption is $Ag(I) > Rb(I) > K(I) > Ca(II) > Fe(III) > Fe(II) < U(VI) > Bi(III) > Co(II) > Zr(IV) > Zn(II) > Sr(II)$. The exchanger shows no or little affinity for other ions, *viz.*, $Li(I)$, $Na(I)$, $Mg(II)$, $Ba(II)$, $Mn(II)$, $Ni(II)$, $Hg(II)$, $Cd(II)$, $Sn(II)$, $Al(III)$, $Sb(III)$, $La(III)$, $Th(IV)$ and $Sn(IV)$. It is therefore clear that $Cu(II)$ can be separated from a large number of other ions.

TABLE III

DISTRIBUTION COEFFICIENTS FOR METAL CATIONS ($0.002 \text{ mol dm}^{-3}$) IN 0.01 mol dm^{-3} OF THE CORRESPONDING ACID, UNLESS STATED OTHERWISE

Cation	$K_d/\text{cm}^3 \text{ g}^{-1}$	Cation	$K_d/\text{cm}^3 \text{ g}^{-1}$
Li(I)	0	Zn(II)	16
Na(I)	0	Hg(II)	1
K(I)	292	Cd(II)	0
Rb(I)	2401	Pb(II)	5
Cs(I)	200	Sn(II) [†]	0
Ag(I)	8523	Al(III)	11
Mg(II)	0	Fe(III)	134
Ca(II)	0	Sb(III) [‡]	0
Sr(II)	12	Bi(III)	43
Ba(II)	1	La(III)	0
Mn(II)	4	Th(IV)	0
Fe(II)	83	Sn(IV) [‡]	0
Co(II)	37	ZrO(IV)	25
Ni(II)	0	UO ₂ (VI)	66
Cu(II)	C.A.*		

* C.A. = Complete adsorption.

[†] 0.3 mol dm^{-3} acid.

[‡] 0.1 mol dm^{-3} acid.

Sorption of Copper(II) Under Static Conditions

The sorption of copper(II) (static) from highly dilute solutions was studied and the results are given in Table IV. Copper can be completely adsorbed from dilute solutions (up to a concentration of $0.002 \text{ mol dm}^{-3}$), so the exchanger can be used to concentrate copper(II) ions present at very low levels, and the process will be economical for its recovery as a maximum of $7.0 \text{ mequiv g}^{-1}$ of copper(II) can be adsorbed under static conditions as observed at a concentration of 0.1 mol dm^{-3} .

Sorption and Desorption of Copper(II) Under Dynamic Conditions

The breakthrough curve for copper(II) ions is shown in Fig. 1; the capacity is $0.16 \text{ mequiv g}^{-1}$. The experiment indicates that only one tenth of the copper(II) ions are adsorbed under

TABLE IV
ADSORPTION OF Cu(II) IONS ON COBALT HEXACYANOFERRATE(III) AS A
FUNCTION OF THE CONCENTRATION OF COPPER SALT

Copper added/ mol dm ⁻³	Copper added, p.p.m.	Copper adsorbed, p.p.m.	Adsorption, %
1×10^{-1}	6354.00	1111.95	17.5
1×10^{-2}	635.40	301.82	47.5
5×10^{-3}	317.70	223.10	70.2
2×10^{-3}	127.08	127.08	100.0
1×10^{-3}	63.54	63.54	100.0
1×10^{-4}	6.35	6.35	100.0
1×10^{-5}	0.64	0.64	100.0

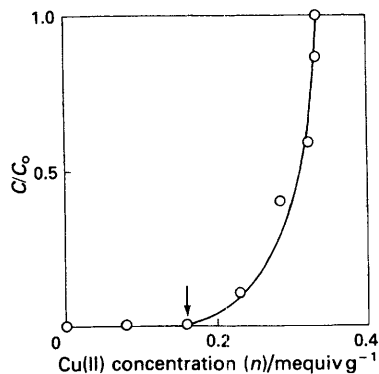


Fig. 1. Breakthrough curve for Cu(II) ions on a cobalt hexacyanoferrate(III) column (drop time 4 drops min⁻¹). C/C_0 , ratio of Cu(II) concentration in effluent to original Cu(II) concentration.

dynamic conditions in comparison with those obtained in a static experiment (Table IV, concentration 0.01 mol dm⁻³). This may be due to equilibrium not being attained under dynamic conditions (flow-rate 4 drops per minute). For separation, the column was loaded with a mixture of 2 cm³ each of 0.002 mol dm⁻³ of copper(II) and other metal ions. The amount of metal ions loaded on to the column was kept much below the breakthrough capacity in order to ensure complete adsorption.

Binary separations of copper(II) from magnesium(II), cadmium(II), calcium(II), lead(II) and nickel(II) (Fig. 2) and aluminium(III), lanthanum(III), bismuth(III) and thorium(IV)

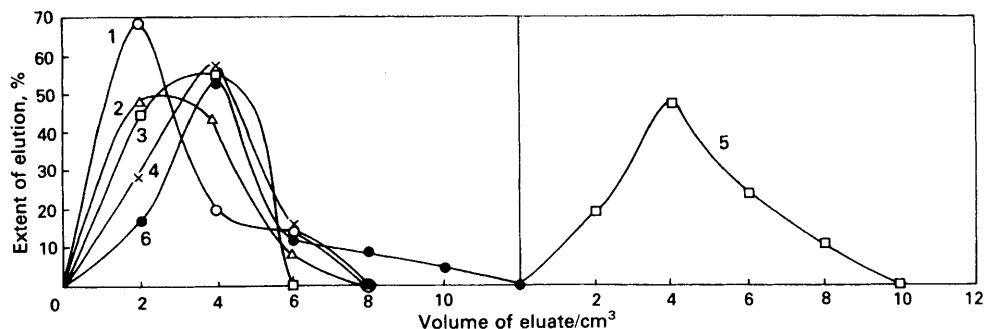


Fig. 2. Binary separations of: 1, Mg(II); 2, Cd(II); 3, Ca(II); 4, Pb(II); and 6, Ni(II) from Cu(II) (5) on a cobalt hexacyanoferrate(III) column. Eluent for Cu(II) was 1 mol dm⁻³ nitric acid, eluent for other ions was water.

(Fig. 3) were successfully achieved on these columns. Elution of all the ions except copper(II) is possible with water (pH 2–3) whereas copper(II) ions can readily be desorbed from the column with 1 mol dm⁻³ nitric acid. The elution curves show sharp peaks and recoveries are quantitative. Thus the high affinity of this exchanger for copper, leading to its separation and isolation from other ions, can be useful in many applications. For example, the exchanger can be used (i) for separations of Cu²⁺ from Ni²⁺ and Pb²⁺ from Cu²⁺, which are required in the analysis of natural raw materials,¹⁷ (ii) for concentrating trace amounts of copper in wine, cognac, milk, mineral oil, natural water¹⁸ and sea water¹⁹ before determination and (iii) for the recovery of copper from waste solutions obtained on processing of ores and other commercial processes.²⁰

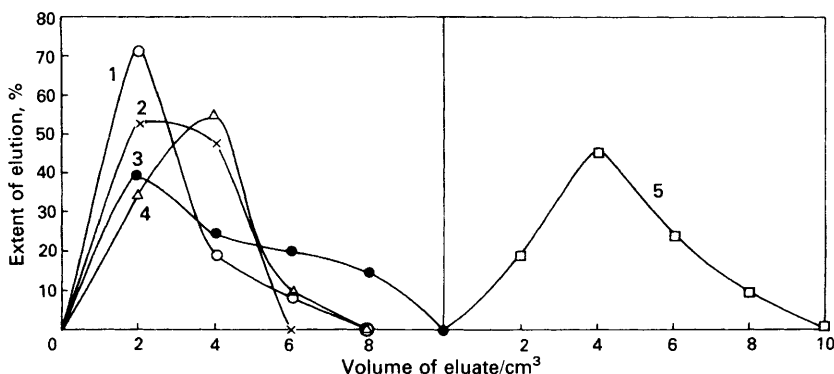


Fig. 3. Binary separations of: 1, Al(III); 2, La(III); 3, Bi(III); and 4, Th(IV) from Cu(II) (5) on a cobalt hexacyanoferrate(III) column. Eluent for Cu(II) was 1 mol dm⁻³ nitric acid, eluent for other ions was water.

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