

Extraction Chromatographic Separation of Cobalt (II) Thiocyanate Complex with Dibenzo-18-Crown-6

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Cobalt is separated from 0.25-2 *M* thiocyanate as a complexing agent with Dibenzo-18-Crown-6 in 1,2-dichloroethane by extraction chromatography. It is stripped with various mineral acids in concentration ranges of 0.5-2 *M* of hydrochloric or sulphuric acid as well as with 0.01-0.5 *M* ammonium chloride. The metal from aqueous phase after stripping has been determined spectrophotometrically with Nitroso-R-salt at 530 nm. Separation of cobalt from its binary mixtures with metal ions such as chromium, molybdenum, nickel, copper, lead, bismuth, vanadium, iron, zinc, cadmium, manganese and aluminium is described.

Several macrocyclic polyethers have been recently used for solvent extraction of *S*-block elements¹. However similar work on *d*-block elements is rather scanty. Yoshio and Noguchi² have described the extractive spectrophotometric determination of cobalt at *pH* 5.0-7.5 with 18-Crown-6 in the presence of protonated *n*-hexylamine and with 4-(2-pyridylazo) resorcinol (PAR) as a counter ion. Yoshio *et al.*³ attempted to extract cobalt thiocyanate complex with 18-Crown-6 in 1,2-dichloroethane between *pH* 1.0 and 7.0 and its subsequent spectrophotometric determination. However, systematic investigations on the extraction chromatographic separation of cobalt with crown ether as the stationary phase are lacking. The results of such a study are reported in this note.

Standard cobalt solution was prepared by dissolving cobalt chloride (BDH, AR) in deionised water and standardized complexometrically⁴. Dibenzo-18-Crown-6 (Aldrich Chemicals) was used as such. Purified silica gel (100-200 mesh) was rendered hydrophobic by the procedure described earlier⁵ and coated with Dibenzo-18-Crown-6 taken in 1,2-dichloroethane. This gel was used both for column extraction and separation work.

To an aliquot of solution containing 15 μg /ml of cobalt, ammonium thiocyanate was added so as to have its concentration as 1 *M*. The solution was passed through the column at a flow rate of 0.5 ml/min. The extracted cobalt was stripped with various mineral acids. Ten fractions of 5 ml each were collected and cobalt from each fraction was determined spectrophotometrically as its complex with Nitroso-R-salt at 530 nm⁶.

The results of varying ammonium thiocyanate concentration (from 0.25 to 2.0 *M*) indicate that the extraction of cobalt was quantitative (100%) at 0.5 and 1.0 *M* ammonium thiocyanate. Above or below these concentrations, extraction was less than 99.0% only.

Stripping of cobalt was quantitative with 0.5-2.0 *M* hydrochloric or sulphuric acids or 0.2-1.0 *M* nitric acid. It was also quantitative with 0.01-5.0 *M* ammonium chloride. The stripping was incomplete in concentration less than 0.1 *M* acid.

Certain elements like alkali and alkaline earths as well as chromium, nickel, silver, tin, lead and bismuth do not form extractable complexes in the presence of 1 *M* ammonium thiocyanate. Hence, when the binary mixtures containing cobalt and any of these ions were passed through the column, only cobalt was retained by the column, which could be eluted with 1 *M* ammonium chloride.

Similarly elements like vanadium (V), iron (III), aluminium and antimony form extractable complexes which cannot be stripped with 0.5 *M* ammonium chloride. Hence when binary mixtures containing any of these ions were passed through the column both species were extracted. However, cobalt was first stripped with 0.1 *M* ammonium chloride while other ions were stripped with 4 *M* hydrochloric acid.

Beryllium, cadmium, zinc and manganese also formed thiocyanate complexes along with cobalt and

Table 1—Separation of Cobalt from Binary Mixtures with Other Metal Ion (Co = 15 μg)

Metal ion	Amount taken mg	% Recovery of Co(II)
Na	2.5	100.0
K	2.5	99.3
Cs	2.5	98.7
Be	0.2	100.0
Ca	2.5	101.0
Sr	2.5	99.3
Ba	2.5	100.0
V(V)	0.1	102.0
Cr(VI)	2.0	98.0
Fe(III)	0.1	99.3
Mn(II)	0.1	102.0
Ni	2.5	99.3
Ag	5.0	98.0
Zn	0.1	100.0
Cd	0.1	101.0
Bi	2.0	99.3
Sb	2.5	99.3
Pb	5.0	101.0
Sn	5.0	95.0
Al	2.5	99.0

were co-extracted. They were then separated by stripping cadmium with 0.2 *M* ammonium acetate followed by cobalt with 2 *M* ammonium chloride. Similarly in mixtures of cobalt and beryllium or cobalt and manganese, first cobalt was eluted with 0.01 *M* ammonium chloride while beryllium or manganese was eluted with 0.5 *M* hydrochloric acid. It was thus possible to separate the elements which are generally associated with each other in binary mixtures in ratios varying from 1:1 to 1:10. In all the cases cobalt after stripping was determined spectrophotometrically at 530 nm (Table 1).

The method is simple, rapid and reproducible and permits separation of cobalt at microgram concentration.

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