Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Korkisch, Johann and Gross, Harald(1967) 'Selective Cation-Exchange Separation of Cobalt in Hydrochloric Acid-Acetone Solutions', Separation Science and Technology, 2: 2, 169 — 176
To link to this Article: DOI: 10.1080/01496396708049924
URL: http://dx.doi.org/10.1080/01496396708049924

SEPARATION SCIENCE, 2(2), 169–176 (1967)

Selective Cation-Exchange Separation of Cobalt in Hydrochloric Acid–Acetone Solutions

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Summary

In the present paper a method is described for the selective separation of cobalt from 29 metal ions. This technique is based on the uptake of cobalt together with several other metal ions on Dowex 50, X8, a strong acid cation-exchange resin, from a solution consisting of 80% acetone and 20% 3 *N* hydrochloric acid. After this adsorption, which is accompanied by the simultaneous removal of many elements, the cobalt is eluted with 90% acetone–10% 6 *N* hydrochloric acid. The only element which passes into the eluate together with cobalt is manganese (II). This method can be successfully employed to separate milligram and microgram amounts of cobalt from large quantities of other metal ions, e.g., iron, nickel, aluminum, uranium, etc.

Relatively great attention has been paid to cation-exchange studies and separations of various elements employing acetone–hydrochloric acid mixtures as eluents. They were used to fractionate the alkali metals lithium, sodium, and potassium (*2,5*) and to separate calcium from copper, zinc, mercury(II), cadmium, and iron(III) (*11*); copper from nickel (*7*); iron, copper, zinc, and lead from cobalt; and manganese and those from the alkali metals, alkaline earths, magnesium, molybdate, sulfate, and phosphate (*15*); and to separate bismuth, cadmium, indium, zinc, iron(III), copper(II), uranium(VI), cobalt, gallium, and manganese(II) (*3,4*). Acetone–hydrochloric acid solutions as eluting agents have also been employed to separate copper and zinc (*1,6*) and in acetone media the adsorption of cerium(III) and praseodymium(III) was studied (*12*). An effective separation of large amounts of iron(III) from cobalt, nickel, and aluminum is possible using tetrahydrofuran-hydrochloric acid mixtures as eluents (*9*).

This rather extensive application of acetone–hydrochloric acid systems for the solution of specific analytical problems is based on the fact that in such media many metal ions, e.g., iron(III), gallium (III), molybdenum(VI), etc., form strong anionic chloride complexes which prevent their adsorption on cation exchangers. Thus they can be separated from those metal ions (e.g., aluminium, magnesium, calcium, and thorium) which do not form such complexes and hence are strongly retained by the resins. Because such separations cannot be achieved with the same selectivity in either pure aqueous or other organic solvents, such as the aliphatic alcohols containing hydrochloric acid, the good separability of cobalt from other metal ions in the acetone systems described in the present paper is caused by the effect of combined ion exchange–solvent extraction (CIESE) earlier described (*8*).

EXPERIMENTAL

Reagents and Solutions

Ion-Exchange Resin. The strongly acid cation exchanger Dowex 50, X8 (100–200 mesh, hydrogen form) was used for the column and batch experiments. For the former purpose it was slurried in solution A (see below) and then transferred to the ion-exchange columns. In the case of the batch experiments, air-dried resin was employed (see Determination of Distribution Coefficients).

Eluent Solutions. Solution A: 80% acetone + 20% 3 *N* hydrochloric acid (v/v); solution B: 90% acetone + 10% 6 *N* hydrochloric acid (v/v). Both solutions have the over-all acid concentration of 0.6 *N* hydrochloric acid.

Solvent. Reagent-grade acetone.

Standard Solutions. Stock solutions of 30 metal ions were prepared by dissolving their reagent-grade chlorides or other suitable compounds in 3 or 6 *N* hydrochloric acid. These solutions usually contained from 5 to 50 mg/ml of the following metal ions: Co(II), Fe(III), Ni(II), Al(III), Ga(III), In(III), Mg(II), Ca(II), Sr(II), Ce (III), Cr(III), Ti(IV), Zr(IV), Th(IV), Cu(II), Au(III), Zn(II), Cd(II), Hg(II), UO_2(II), Pb(II), Bi(III), Sn(II and IV), V(V), Mo(VI), Ge (IV), Os(IV), Pt(IV), Pd(II), and Mn(II).

Apparatus

The ion-exchange columns used for the separation experiments had a diameter of 1.0 cm and contained in each case 10 g of the resin.

Determination of Distribution Coefficients

The determination of the distribution coefficients of the elements in the various acetone–hydrochloric acid mixtures was made by the use of the batch equilibrium method (batch method) (*10*). Each equilibrium experiment was performed in 20 ml of mixture, consisting of 0 or 80 or 90% acetone and 10% of 6 *N* hydrochloric acid and water up to 100%, containing 5 mg of the element in question (the over-all acidity of all mixtures was 0.6 *N* hydrochloric acid). To this mixture 1 g of the air-dried resin was added and the solution agitated on a shaking machine for 12 hr. Then the resin was filtered off and the element determined in the filtrate. By means of this method the results presented in Table 1 were obtained. The experimental error of the measurements of the distribution coefficients was usually ±5 to 10% for low distribution values (below 100), but for high values an error of about 10 to 20% was frequently observed.

Quantitative Determination of the Elements

Cobalt. The eluate obtained by eluting the cobalt with solution B (see Separation Procedure) is evaporated to dryness and organic matter is destroyed by ignition. The cobalt oxide residue is dissolved in a few milliliters of hydrochloric acid, the solution is diluted with water to about 50 ml, and then cobalt is determined by titration with 0.01 *M* EDTA (disodium salt) using Murexide as metal indicator. In case manganese is present (the only element which is coeluted with cobalt; see Separation Procedure), or if cobalt is present only in microgram amounts, this method cannot be used, so cobalt must be determined by other means [e.g., by using a photometric procedure in which manganese does not interfere (*13*)].

Other Elements. Most of the other investigated elements (in amounts exceeding about 100 μg) were also determined volumettrically, using suitable chelatometric methods with EDTA as the titrant. Uranium was determined fluorometrically (*14*), whereas microgram quantities of the other elements were determined spectrophotometrically (*13*).

Separation Procedure

The Separation of Cobalt from Accompanying Metal Ions. The resin soaked in solution A was transferred to the ion-exchange column and the resin bed was washed with 50 ml of solution A. Twenty ml of 3 *N* hydrochloric acid containing cobalt and the foreign ions to be separated from it are diluted with acetone to 100 ml, and this mixture (which is now 80% in acetone and 20% in 3 *N* hydrochloric acid) is passed through the pretreated resin bed using a flow rate of about 0.5 ml/min. During this operation cobalt is retained by the resin, together with the following metal ions: Ni(II), Al(III), Mg(II), Ca(II), Sr(II), Ce(III), Cr(III), Ti(IV), Zr(IV), Th(IV), V(IV), and Mn(II). The effluent contains the elements Fe(III), Ga(III), In(III), Cu(II), Au(III), Zn(II), Cd(II), Hg(II), Pb(II), UO_2(II), Bi(III), Sn (II and IV), V(V), Mo(VI), Ge(IV), and the platinum metals. To be certain that these elements are quantitatively removed from the column, the resin bed is then washed at the same flow rate with 100 to 150 ml of solution A. Finally cobalt is eluted with 50 ml of solution B and is either determined volumetrically (see above) or spectrophotometrically. Coeluted with cobalt is only manganese (II), while all other elements which were coadsorbed from solution A are further strongly retained by the resin. The cobalt eluate shows a bright blue color which suggests an easy photometric determination of cobalt directly in the eluate. This can be done (maximum of absorption = 650 mμ) but the sensitivity is too low to allow small amounts of cobalt to be determined. Furthermore, yellow condensation products of acetone, e.g., mesityl oxide, may cause interference, especially if the eluate is left to stand for awhile before the photometric measurements are made.

RESULTS

In Table 1 the results of measurements of the distribution coefficients of various metal ions in solutions A and B are recorded. For the purpose of comparison, distribution values obtained at the same acidity but in the absence of acetone have been included in this table. From these results it is seen that the selectivity of separations

TABLE 1

Distribution Coefficients of Cobalt and Various Other Elements in Acetone–Hydrochloric Acid Media at the Constant Over-All Acidity of 0.6 *N* Hydrochloric Acid (1 g Dowex 50; 5-mg load)

	Acetone, %		
Metal ion	0	80 (solution A)	90 (solution B)
Co(II)	44	77	<1
Ni(II)	46	250	227
Cu(II)	32	<1	<1
Zn(II)	38	<1	<1
Cd(II)	6	~2	~2
Hg(II)	~1	<1	<1
Pb(II)	~1	<1	<1
UO_2(II)	40	4	<1
Mg(II)	33	264	332
Ca(II)	74	>1000	>1000
Sr(II)	90	>1000	>1000
Mn(II)	80	216	4
Fe(III)	84	<1	<1
Al(III)	186	>1000	>1000
Ga(III)	242	<1	<1
In(III)	~1	<1	<1
Bi(III)	<1	<1	<1
Ce(III)	>1000	>1000	>1000
Cr(III)	20	>1000	>1000
Ti(IV)	15	>1000	>1000
Zr(IV)	>1000	>1000	>1000
Th(IV)	>1000	>1000	>1000
Au(III)	<1	<1	<1
Sn(II,IV)	~1	<1	<1
V(V)	~3	~1	<1
Mo(VI)	~1	<1	<1
Ge(IV)	~1	<1	<1
Os(IV)	~1	<1	<1
Pt(IV)	~1	<1	<1
Pd(II)	~1	<1	<1

of cobalt from other elements in acetone–hydrochloric acid media is far greater than in pure aqueous–hydrochloric acid systems, in which, for example, a separation of cobalt from divalent metal ions such as nickel, copper, uranyl ion, magnesium, etc., is impossible, because of the similarity of the distribution coefficients. Also separation of cobalt from trivalent metal ions, e.g., from iron(III), is in some cases only possible by means of elution chromatography on relatively long columns of the resin, and, because the trivalent metal ions are more strongly adsorbed, rather large amounts of the resin must be employed if iron, for example, is present in large quantities. All these disadvantages can be overcome in the acetone systems, especially by using solutions A and B in succession. Under

TABLE 2

Separation of 5 mg Each of Cobalt from 29 Metal Ions on Dowex 50

Foreign ion simultaneously present, mg		Recovered amount of Co, mg
Fe(III)	1000	5.01
Ni(II)	100	5.02
Fe(III) Ni(II)	1000 100	5.00
Al(III)	100	4.98
Ga(III)	10	4.97
In(III)	10	5.00
Mg(II)	100	4.99
Ca(II)	100	5.02
Sr(II)	10	5.01
Ce(III)	40	4.97
Cr(III)	10	4.97
Ti(IV)	10	4.97
Zr(IV)	25	5.00
Th(IV)	10	5.01
Cu(II)	100	5.01
Au(III)	10	5.02
Zn(II)	100	4.97
Cd(II)	100	4.99
Hg(II)	10	4.99
UO_2(II)	100	5.00
Pb(II)	100	5.00
Bi(III)	50	4.97
Sn(II)	10	4.98
Sn(IV)	15	4.98
V(V)	10	4.99
Mo(VI)	5	4.97
Mn(II)	100	>12
Ge(IV)	10	4.98
Os(IV)	10	5.03
Pt(IV)	10	5.02
Pd(II)	10	4.99

these conditions, cobalt can be separated from all elements listed in Table 1 except manganese.

From the results shown in Table 2 it is seen that by application of this separation principle (see Separation Procedure) a quantitative separation of cobalt can be achieved.

This method was also tested using microgram amounts and quantities of cobalt up to 100 mg. Also in these cases a complete separation of cobalt from the other elements, as well as a quantitative recovery of this element, is possible.

The amount of washing solution (solution A) required to remove the last traces of foreign ions from the column can be varied within rather great limits because cobalt (5 mg) does not start to break through until 500 ml of solution A have passed.

In the presence of vanadium, a partial reduction of this element to tetravalent vanadium is caused by the acetone present in solution A. The vanadium(IV) is coadsorbed with the cobalt and can only be removed with difficulty by washing with solution A. Furthermore, by elution of cobalt with solution B, some vanadium passes into the eluate together with cobalt. To avoid this, the vanadium is best removed from the column, before the elution of cobalt, by means of a solution consisting of 80% acetone, 10% 6 *N* hydrochloric acid, 5% water, and 5% hydrogen peroxide (30%). This mixture oxidizes the vanadium to the pentavalent state, which is not adsorbed on Dowex 50.

It is to be expected that this method can be successfully applied to the analysis of various materials for cobalt, especially those containing large amounts of iron (e.g., ferrous alloys and iron meteorites).

Acknowledgment

Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, for support of this research (PRF Grant 1587-A3).

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Received by editor November 28, 1966
Submitted for publication December 27, 1966