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 Sitaram, R. and Khopkar, S. M.(1973) 'Separation of Copper by Anion Exchange in Malonate Media', Separation Science and Technology, 8: 6, 701 — 707
To link to this Article: DOI: 10.1080/00372367308056064
URL: http://dx.doi.org/10.1080/00372367308056064

SEPARATION SCIENCE, 8(6), pp. 701–707, 1973

NOTE

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Abstract

The anion exchange behavior of the negatively charged complex of copper(II) in malonate solution was studied on Dowex 21K. Hydrochloric, sulfuric, and nitric acids as well as chlorides, sulfates, and nitrates of ammonium, and sodium chloride and nitrate were used as the eluants. The efficiency of the various eluants was evaluated in terms of elution constants and bed-distribution coefficients. The separation of these elements from a large number of diverse elements was effected either by selective sorption or selective elution with water or specific eluants. The method was found to be applicable to the separation of copper from gunmetal and brass.

Malonic acid forms negatively charged complexes with number of elements (*1*). Copper also forms such anionic complex at pH 4.0 to 4.5 which can be explored for its separation from others by anion exchange chromatography.

Copper was separated from antimony (*2*) by anion exchange in thiocyanate media while tartaric acid was used as the complexing acid for its separation (*3*) from cobalt and manganese. Several mineral acids were also used (*4*) as the complexing acids but systematic studies in the organic acid media are lacking.

The method proposed in this paper is simple, rapid, and reproducible. It was extended to separation of copper from gunmetal and brass.

EXPERIMENTAL

Apparatus and Reagents

The ion exchange column (1.4 × 18 cm) was similar to one described earlier (*5*). Automatic fraction collector (Tower's type) fitted with a 10-ml siphon and a Cambridge pH meter with glass electrode was used.

Stock solution of copper(II) was prepared by dissolving about 4.752 g of cupric nitrate trihydrate (B.D.H. AnalaR) in 250 ml distilled water. The solution was standardized volumetrically (*6*) and was found to contain 5.10 mg/ml of copper.

Dowex 21K (Dow Chemical Co., Midland, Michigan) (50 to 100 mesh, Cl^- form) was used throughout the experiment. The resin was converted into the malonate form by passing a 5% solution of malonic acid buffered at pH 4.5. The column was subsequently washed free of malonic acid with water.

RESULTS AND DISCUSSION

An aliquot of solution containing 12.75 mg of copper(II) was taken. Then about 2 g of malonic acid was added and the pH of the solution was adjusted to 4.0 to 4.5 with 0.01 *M* ammonium hydroxide or 0.01 *M* malonic acid solutions. The solution was then sorbed on the column at the flow rate of 1 ml/min. After washing the column with 25 ml of water at the same flow rate, copper was eluted with an appropriate eluant (Table 1). The effluent lot was collected in 20 fraction, each of 10 ml. After destroying the organic matter with a mixture of nitric and perchloric acids, copper from each fraction was determined complexometrically (*7*) with PAN as an indicater. Various mineral acids and their salts in the concentration range of 0.25 to 1 *M* were tested as the eluants. The elution curve is shown in Fig. 1. The elution constants (E) and the volume distribution coefficients (D_v) were computed from peak elution volume (V_{max}) as usual.

The eluants can be arranged as per their efficiency as $H_2SO_4 > HNO_3 > HCl > NaNO_3 > (NH_4)_2SO_4 > NH_4Cl > CH_3COONH_4$. Other acids like perchloric, phosphoric, tartaric, citric, and acetic acids proved to be inefficient eluants for copper.

Ion Exchange Separations

Since the *s*-block elements do not form complexes with malonic acid, they can be separated by selective sorption from copper. Second, some

TABLE 1

Anion Exchange Studies of Copper(II)[a]

Eluant No.	*M*	Peak elution volume V_{max} (ml)	Total volume of the eluant V_t (ml)	Total recovery (%)	Elution constant *E*	Volume distribution coefficient D_v
1. HCl	0.25	70	120	96.30	0.52	1.90
	0.50	60	80	100.08	0.65	1.54
	1.0	40	60	100.17	1.22	0.82
2. H_2SO_4	0.25	60	90	99.48	0.65	1.54
	0.50	80	80	99.65	0.65	1.54
	1.0	50	60	99.99	0.85	1.18
3. HNO_3	0.25	80	130	99.97	0.44	2.26
	0.50	50	70	100.18	0.84	1.18
	1.0	40	50	100.35	1.22	0.82
4. NH_4Cl	0.25	130	180	78.96	—	—
	0.50	70	130	99.56	0.52	1.90
	1.0	50	90	100.85	0.85	1.18
5. $(NH_4)_2SO_4$	0.25	110	170	99.5	0.31	3.20
	0.50	70	110	100.25	0.52	1.90
	1.0	60	120	100.50	0.65	1.34
6. NaCl	0.25	100	200	99.67	0.33	2.98
	0.50	80	160	100.24	0.44	2.26
	1.0	40	90	100.66	0.84	1.18
7. $NaNO_3$	0.25	90	150	99.50	0.38	2.62
	0.50	70	100	99.97	0.52	1.90
	1.0	40	90	100.99	1.22	0.81
8. CH_3COONH_4	1.0	110	150	100.89	0.31	3.2

[a] Copper = 12.75 mg.

elements form very weak complexes with malonic acid as compared to copper, hence they can be eluted first with water followed by elution of copper with a suitable eluant. If both the elements form complexes with malonic acid, they can be separated by selective elution (Table 2).

Separation of Copper from Alkali and Alkaline Earths, Thallium(I), Mercury(II), Iron(II), and Bismuth(III)

The solution containing either copper(II) and the other foreign ions was taken. Then 2 g of malonic acid was added. The pH of the solution was adjusted to 4.5 using 0.01 *M* ammonium hydroxide and 0.01 *M* malonic acid. As before, the mixture was sorbed on the column at a flow rate of 1 ml/min. The ions which are incapable of forming negatively charged

TABLE 2

Ion Exchange Separations[a]

Foreign ion	Amount added (mg)	Copper	
		Found	Recovery (%)
Li	65.2	12.75	100.00
Mg	65.2	12.75	100.00
Ba	71.12	12.74	99.94
Sr	50.02	12.74	99.94
Ca	50.11	12.75	100.00
Be	60.00	12.75	100.00
Tl(I)	75.61	12.75	100.00
Hg(II)	52.3	12.73	99.84
Bi(III)	42.5	12.74	99.94
Fe(II)	50.51	12.75	100.00
Cd	62.8	12.74	99.94
Zn	62.8	12.74	99.94
Ni	40.05	12.75	100.00
Co	45.11	12.73	99.84
Pd	52.2	12.72	99.77
Sb(III)	50.15	12.75	100.00
Pb(II)	45.9	12.72	99.77
Al(III)	51.0	12.75	100.00
Fe(III)	47.7	12.75	100.00
V(IV)	39.9	12.72	99.77
Zr(IV)	43.21	12.72	99.77
Th(IV)	35.5	12.75	100.00
U(VI)	40.1	12.72	99.77
CrO_4^{2-}	16.21	12.75	100.00
ReO_4^-	22.62	12.73	99.84
VO_3^-	30.15	12.72	99.77

[a] Copper added = 12.75 mg

malonate complexes, such as lithium, magnesium, barium, strontium, calcium, beryllium, thallium(I), mercury(II), bismuth(III), and iron(II), passed through the column, whereas the malonate complex of copper(II) was quantitatively retained by the resin which was subsequently desorbed with 200 ml of 0.25 *M* sulfuric acid.

Separation from Cadmium, Zinc, Cobalt, Nickel, Palladium, and Antimony(III)

It was observed that cadmium, zinc, cobalt, nickel, palladium, and

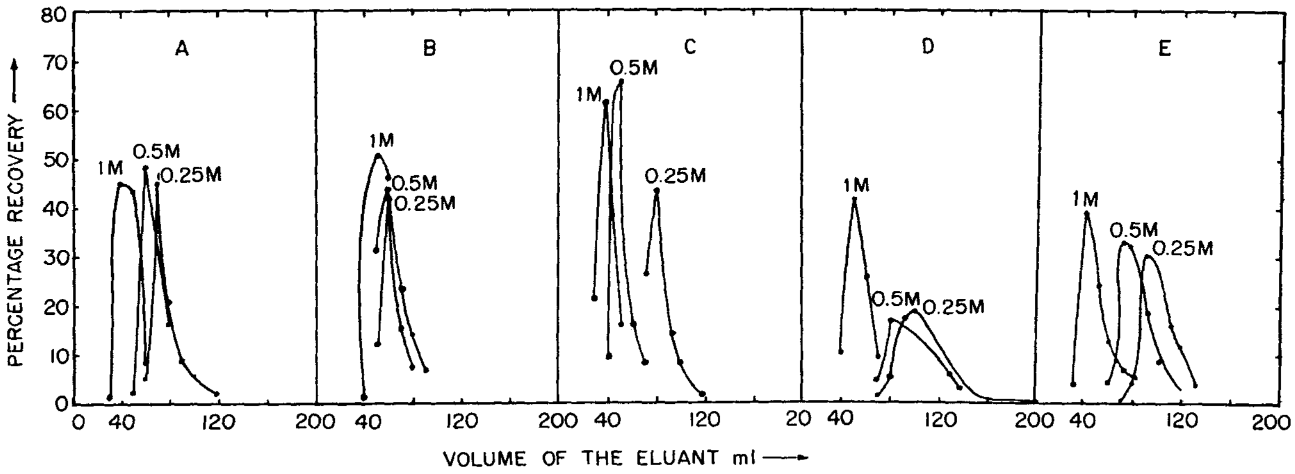

FIG. 1. Elution curves for copper(II) with (a) hydrochloric acid, (b) sulfuric acid, (c) Nitric acid, (d) sodium chloride, (e) sodium nitrate.

antimony(III) (*8*) formed weak complexes with malonic acid as compared to that of copper. After sorbing the mixture of these complexes along with copper, the weakly bound complexes were desorbed with 300 ml of water followed by elution of copper which formed a reasonably stable complex with 0.25 *M* sulfuric acid.

Separation from Lead(II), Zirconium(IV), Thorium(IV), and Uranium(VI)

The separation of lead(II) from copper(II) was accomplished by passing the mixture of their malonato complexes on the column. Copper(II) was first eluted with 0.25 *M* nitric acid followed by elution of lead(II) (*9*) with 6 *M* nitric acid.

The separation of zirconium(IV) from copper(II) was achieved by first eluting copper with 0.5 *M* hydrochloric acid followed by elution of zirconium with 2 *M* hydrochloric acid (*10*). Similarly uranium(VI) or thorium were separated from copper(II) by first eluting copper with 0.25 *M* nitric acid followed by the elution of uranium or thorium with 1 *M* hydrochloric or 2 *M* nitric acid, respectively.

Separation of Copper(II), Aluminum, Iron(III), and Vanadium(IV) from Each Other

The mixture of the malonato complexes of these elements were sorbed on the column. It was seen (Table 1) that 0.25 *M* ammonium sulfate is an efficient eluant for copper(II) but not for aluminum, iron(III), or vanadium(IV) (*11*). Therefore copper(II) was first eluted with 170 ml of 0.25 *M* ammonium sulfate, then aluminum was eluted with 250 ml of 1 *M* ammonium sulfate, vanadium(IV) was eluted with 70 ml of 0.5 *M* hydrochloric acid, and finally iron(III) was eluted quantitatively from the column with 120 ml of 1 *M* hydrochloric acid.

Separation from Chromate, Rhenate, and Vanadate

The mixture of anionic malonato complex of copper with oxyanions such as chromate, rhenate, or vanadate was sorbed on the column. Copper complex was first eluted with 0.25 *M* nitric acid followed by the elution of chromate with 2 *M* ammonium chloride, rhenate with 2 *M* potassium chloride, and vanadate with 2 *M* ammonium hydroxide.

The method was extended to the separation of copper from gunmetal and brass.

Separation of Copper from Gunmetal and Brass

About 1 g of the gunmetal was dissolved in 8 to 10 ml of concentrated nitric acid. The tin was separated as metastannic acid and weighed as an oxide. The filtrate was made to 250 ml. An aliquot of the sample solution containing 10 ml was taken. Then 2 g of malonic acid was added and the pH of the solution was adjusted to 4.5. It was sorbed on the column. Then zinc was eluted with 300 ml of water followed by the elution of copper with 200 ml of 0.25 *M* nitric acid and finally lead was eluted with 200 ml of 6 *M* nitric acid. The results from duplicate analysis showed 5.45% tin, 4.45% zinc, 83.5% copper, and 5.9% lead as against 5.40% tin, 4.40% zinc, 83.5% copper, and 5.9% lead given.

The sample of brass was dissolved in 10 ml of concentrated nitric acid and tin was determined as tin oxide as before. The filtrate was evaporated with concentrated sulfuric acid to white fumes. The lead was removed as insoluble lead sulfate. The resulting filtrate was made to 250 ml. Then 10 ml of solution was taken. As before, the malonate complex of copper was formed and was sorbed on the column. First zinc was eluted with 300 ml of water followed by the elution of copper with 0.25 *M* ammonium sulfate. Iron was eluted with 1.0 *M* hydrochloric acid. The results with duplicate analysis showed copper 67.3%, zinc 28.5%, tin 1.1%, lead 2.2%, and iron 0.3% as against copper 67.4%, zinc 28.4%, tin 1.1%, lead 2.2%, and iron 0.35% given.

The overall operation takes about 2 hr. The results are reproducible to ±2%.

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Received by editor June 4, 1973