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A Systematic Cation Exchange Separation with Oxalate

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A few years ago, one of the authors had an interest in oxalatocomplexes and reported spectrophotometric1–3) and polarographic4) investigations of several oxalato complexes. Recently, knowledge on stability constants of oxalato metal complexes has accumulated,5) while only relatively few cation exchange separations with oxalate as an eluting agent have been reported.6) The present paper contains a systematic, preliminary study of cation exchange separations of nineteen metallic elements with oxalate as an eluting agent. This investigation covered the range of pH 2 to 5 and concentration 0.01 to 0.5 M for the eluant.

It was found that these elements can be roughly classified into three groups according to their ion-exchange behavior. As examples, mutual separations of several metals were carried out.

Experimental

Standard Solutions of Metals. Perchlorates of Be, Al, Ga(III), In(III), Zr, Hf, Th, Fe(III), Co(II), U(VI), Cu(II), Zn, Cd, Mn(II) and Ni, chlorides of Sn(IV), Ti(IV) and Cr(III) and the nitrate of Pb(II) were dissolved in water containing minimum amounts of perchloric, hydrochloric and nitric acid, respectively, sufficient to suppress their hydrolysis and diluted to the concentration of 1×10^{-2} M with distilled water.

Eluting Agents. Oxalate solutions of 0.01, 0.02, 0.05, 0.1, 0.2, 0.4 and 0.5 M adjusted to pH 2.0, 3.0, 4.0 and 5.0, respectively, using a pH meter, were used. All reagents used were of guaranteed grade.

Resin and Column. The resin used was 60—100 mesh "Amberlite IR-120" in ammonium form. The resin bed of the column was 10 cm in height and 0.9 cm in diameter. Each column was preconditioned with 2 N hydrochloric acid, and 0.2 M ammonium chloride solution was passed through the resin bed for conversion to the ammonium form.

Decomposition of Oxalic Acid. For the chelatometric or colorimetric determination of the metals, except for Zn, Mn(II) and Cd, interfering oxalate in solution was eliminated. Various investigations indicated that the method of decomposition of oxalic acid by oxidation with ammonium peroxodisulfate was most suitable. Into a 100-m*l* flask, 10 m*l* of 0.1 M oxalate solution and 2.5 m*l* of 10% ammonium peroxodisulfate was taken, and about 40 m*l* of distilled water added. Being boiled for 5 to 10 min, the oxalate decomposed. Further, heating was continued for about an hour to decompose excess ammonium peroxodisulfate.

Methods for the Determination of the Metals. The concentrations of Be, Ti(IV) and Cr(III) were determined colorimetrically by the quinalizarine, hydrogen peroxide and chromate methods, respectively. For the other elements, chelatometric titration was used.

Distribution Coefficients. In order to find favorable conditions and a criterion for the separation of the metals adsorbed in the resin bed by elution with oxalate solution, the magnitude of the distribution coefficients

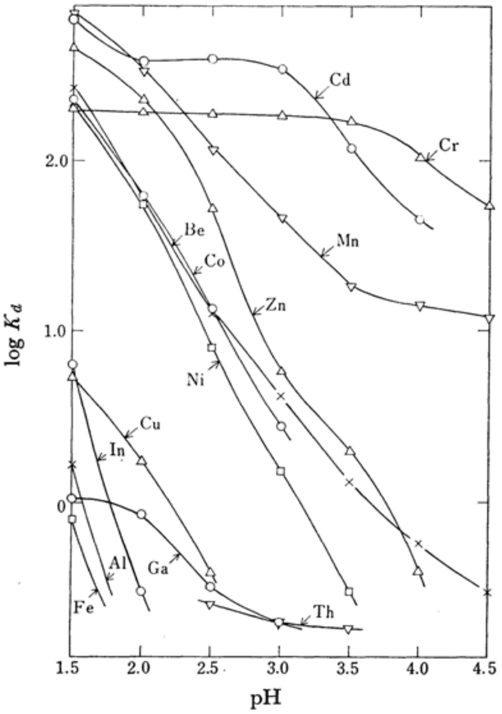

Fig. 1. Distribution coefficients in 0.1 M oxalate.

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6) H. Kakihana and K. Narita, "Saishin Ion Kokan (The Newest Ion Exchange)," Hirokawa Shoten, Tokyo (1961).

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TABLE 1. CLASSIFICATION OF METALLIC ELEMENTS

	pH of eluant	Elution range (m*l*)	log K_d	Elements
Group I	2.0	0—120	<1	Cu(II), Al, Ga, In, Fe(III), Sn(IV) Ti(IV), Zr, Hf, U(VI), (Th)
Group II	3.0	10—180	<1	Be, Zn, Ni, Co(II)
Group III	3.0	220—	>1	Cd, Mn(II), Pb(II)

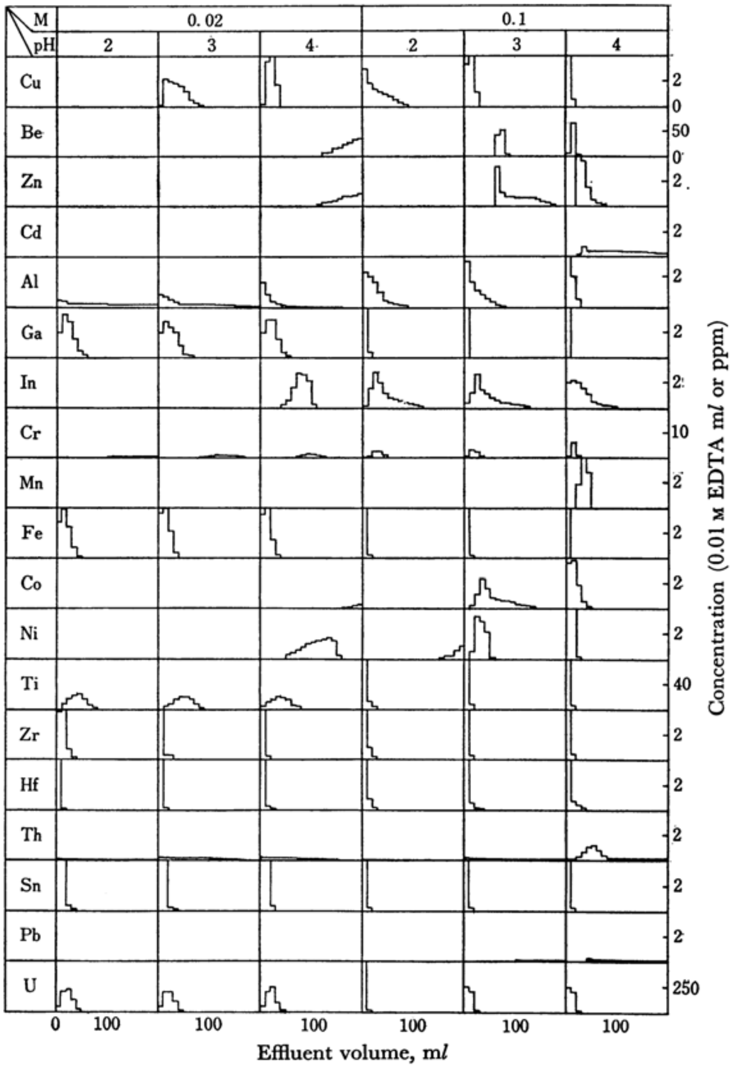

Fig. 2. Elution curves.

was measured by a batch method at varying concentrations and values of pH of oxalate solution. Into a 50-m*l* volumetric flask, 30 m*l* of the oxalate solution of varying concentration from 0.01 to 0.4 M and 10 m*l* of standard metal solution were taken, followed by adjustment of pH to a value between 2.0 and 4.0 with ammonia-water or perchloric acid, and 500 mg of air-dried resin was added and the solution diluted to the mark with distilled water. After standing for 24 hr at 25°C, the concentration of the metal in the aqueous phase was determined.

Elution Curves. Each solution containing about 10^{-4} mol of a metallic element was added to the top of the column. After washing the column with 2 m*l* of water twice, the eluant was passed through the column at a flow rate of 0.5 m*l*/min, and 10 m*l* of the effluent collected with a fraction collector. Each fraction being transferred to a 100-m*l* flask, the concentration of the metal in the fraction was determined after decomposition of the oxalato complex and excess oxalate with ammonium peroxodisulfate.

Results and Discussion

Some of the results on the distribution coefficients and elution curves are shown in Figs. 1 and 2, respectively. The elements investigated can be roughly classified into three groups in Table 1 according to their ion-exchange behavior which is reflected in the pH-distribution coefficient curves.

As shown in Fig. 2, there are many cases where mutual separation seems possible. As examples, the results of mutual separations of several metals are shown in Fig. 3.

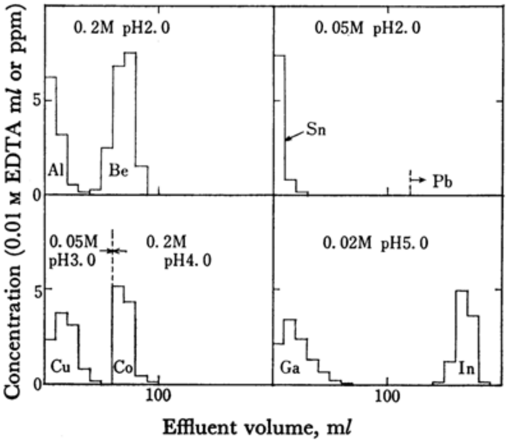

Fig. 3. Mutual separations.

Effect of pH. With 0.1 м eluant at pH 2.0, Be, Zn, Co(II), Mn(II) and Cd were not eluted until 200 m*l*, and Ni was not removed until 150 m*l* of effluent was reached. The rise in pH from 2.0 to 3.0 caused the beginning of elution of Be and Zn from 60 m*l*, and the elution of Ni and Co(II) from 20 m*l*, but Mn(II) and Cd did not elute until 200 m*l*.

Increasing the pH value to 4.0, Mn(II) and Cd began to elute from 30 m*l*.

Thus, the elutions of Be, Zn, Ni, Co(II) and Mn(II) were most sensitive to the pH value of the eluant, and next, those of Cu(II), Cd and Al were most sensitive. In addition, a shortening of the elution range with increase in pH of eluant to 3.0 or 4.0 was found especially with Cu, Zn, Al and Co(II).

Effect of Concentration. As shown in Fig. 2, the effect of concentration of eluant was not found to be great over the concentration range 0.2 to 0.05 м, but considerable delay in elution with 0.02 м eluant was found for In, Be, Zn, Co and Ni. In the case of Al, tailing was small with 0.2 м eluant at pH 2.0, whereas a decrease in concentration at the same pH caused greater tailing.

TABLE 2. STABILITY CONSTANTS OF METAL-OXALATO COMPLEXES

Metal	log K_1	log K_2	log K_3	Literature
Cd	2.78	1.60	0.98	4
Zn	5.15	2.21	1.15	5
Co(II)	4.7	2.0	3.0	5
Mn(II)	2.60	2.04	—	4
Ni	4.1	3.1	1.3	7
Al	7.25	5.75	3.3	5
Fe(III)	10.2	7.2	3.6	1
U(VI)	7.3	6.0	5.1	3

The elements in group 1, which are sharply eluted in 0—30 m*l* with 0.1 м eluant at pH 2.0, have large successive stability constants, whereas some elements in group 3 which show large tailing have smaller stability constants, as given in Table 2. Because of this for the latter elements, precipitates seem to form in the column and take much time to dissolve in the eluant at pH 3.0. Detailed mutual separations of the elements will be reported later.

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