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Note

Synthetic ion-exchange materials

XVII. Chromatographic separation of trace amounts of transition metals from large amounts of calcium with hydrous zirconium dioxide as ion exchanger*

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The analytical applications of inorganic ion exchangers have received considerable attention owing to their high selectivities with respect to certain elements[1–3]. The hydrous oxides of various metals have an accepted position among the inorganic ion exchangers[4]. Our earlier work indicated that the hydroxides and hydrous oxides of polyvalent metals might be classified as anion, amphoteric and cation exchangers on the basis of the ionic potentials of the central metal ion[5,6]. Among these oxides, hydrous zirconium dioxide (HZO) is a sorbent with well characterized ion-exchange properties, which contains a random polymer in which hydroxyl bridges link tetramers[7]. Useful separations on HZO have been reported, for example Na–Cs, Cs–Rb, Cs–Ba, Cs–Eu and ^{90}Sr–^{90}Y separations by column chromatography[8,9] and ^{90}Sr–^{90}Y, ^{140}Ba–^{140}La and ^{233}Ra–^{233}Fr separations by thin-layer chromatography[10]. Further useful separations of certain pairs of elements may be possible with this exchanger.

It has been reported that strong matrix effects in atomic-absorption measurements cause some difficulties in determining trace amounts of transition metals in lime for water treatment, although these problems can be overcome in flame systems by using ion-exchange separations or solvent extraction[11]. By using a strongly basic anion-exchange resin, calcium ions can be separated from transition metals which form negatively charged complexes in an ammoniacal medium containing citrate or 2-hydroxy-isobutyronitrile[12,13]. More selective separations may be needed for this purpose.

This paper describes the adsorption behaviour of transition metals and calcium ions at different pH values, and the applicability of the group separation of transition metals from large amounts of calcium.

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[*] Throughout this article, the term "hydrous oxides" has been used in its widest sense to refer to insoluble oxides containing water as indefinite composition (either as precipitates, or, more usually, as dried products).

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TABLE I

K_d VALUES (ml/g) FOR TRANSITION METAL AND CALCIUM IONS ON HZO

Ion exchanger	*Solution*	*Parameter*[*]	*Ions*												
			Ca		*Mn(II)*		*Ni*		*Co*		*Cd*		*Zn*		*Cu(II)*
HZO dried at 40°	0.1 *M* NH_4Cl (final pH = 7.0)	K_d	$2.4 \cdot 10$		$2.7 \cdot 10^2$		$8.6 \cdot 10^2$		$1.4 \cdot 10^3$		$1.6 \cdot 10^3$		$1.6 \cdot 10^4$		$4.6 \cdot 10^5$[**]
		α		11		3.2		1.6		1.1		10		29	
HZO dried at 140°	0.1 *M* NH_4Cl (final pH = 7.0)	K_d	5.8		$1.6 \cdot 10^2$		$6.3 \cdot 10^2$		$8.5 \cdot 10^2$		$1.2 \cdot 10^3$		$3.9 \cdot 10^3$		$1.0 \cdot 10^6$[**]
		α		28		3.9		1.4		1.4		3.3		256	
			Zn		*Cu(II)*		*Ni*		*Cd*		*Co*		*Ca*		
Dowex 50W-X8	0.2 *M* HNO_3	K_d	$3.5 \cdot 10^2$		$5.0 \cdot 10^2$		$5.5 \cdot 10^2$		$5.8 \cdot 10^2$		$6.1 \cdot 10^2$		$1.2 \cdot 10^3$		
		α		1.4		1.08		1.06		1.05		1.98			

[*] Separation factor for neighbouring ions.

[**] Extrapolating values from Fig. 1.

EXPERIMENTAL

Material

HZO was prepared by adding 1.0 l of 6% ammonia solution to 1.5 l of 0.2 *M* zirconium oxychloride solution with constant stirring until precipitation was complete (the final pH was adjusted to 6.0). The precipitate was allowed to stand overnight at 40° and was then washed with demineralized water by decantation until the supernatant solution was free from ammonium and chloride ions. The precipitate was filtered and dried at 40°. After immersion in water, the granular material was re-dried at 40 or 140° (see below). The dried samples were sieved to give a 100–200-mesh fraction.

The thermogram of HZO dried at 40° agreed well with the result reported by Onorin *et al.*[14]. The water content was 24.5% in the material dried at 40° and 20.0% in that dried at 140°, which was determined on the basis of the formation of ZrO_2 at 600°, and the molar ratio of ZrO_2 to H_2O was 1:2.22 in the material dried at 40° and 1:1.71 in that dried at 140°.

Distribution coefficients and separation factors for transition metals

The determination of the distribution coefficients (K_d) of the metal ions was carried out by batch equilibriation. HZO (0.250 g) was treated with 25.0 ml of a $1.0 \cdot 10^{-4}$ *M* solution of transition metals containing ammonium chloride and either hydrochloric acid or ammonia, with a constant ionic strength of 0.1 at different pH values. The mixture was shaken occasionally for 48 h at 30° until equilibrium was attained. The amount of metal ions adsorbed was determined from the difference between the initial and final concentrations in the clear supernatant solution by using a Varian-Techtron 1100 atomic-absorption spectrophotometer. A Model HM-5A pH meter (Toa Electric, Tokyo, Japan) was employed to determine the hydrogen ion concentration. The reproducibility of the reading was ± 0.05.

RESULTS AND DISCUSSION

The K_d values were calculated in the usual manner. The values obtained and the separation factors, $\alpha(A/B) = K_{d_A}/K_{d_B}$, where A and B are transition metals, are summarized in Table I, values obtained on Dowex 50W-X8 being included for comparison.

The selectivities for transition metals on both types of HZO decrease in the order Cu(II) > Zn > Cd > Co > Ni > Mn(II) > Ca. Amphlett and Kennedy[15] studied selectivities on HZO and reported that the sequence of affinities for bivalent ions, Cu(II) > Ni > Sr, parallels the normal sequence observed in their complex formation. A slightly different affinity series has been reported[16] on HZO dried at 200°, *viz.*, Cu(II) > Zn > Ni > Co > Mn, but only initial pH values were listed. Much higher separation factors were observed for Cu(II)–Zn and Ca–transition metals and slightly higher factors for transition metals other than those on Dowex 50W-X8.

The plot of log K_d against the final pH values (Fig. 1) was linear with a slope of 1.1–1.4, which did not correspond to the valency of the ions exchanged. This may be due to the uptake of chloride ions for amphoteric behaviour of HZO, although

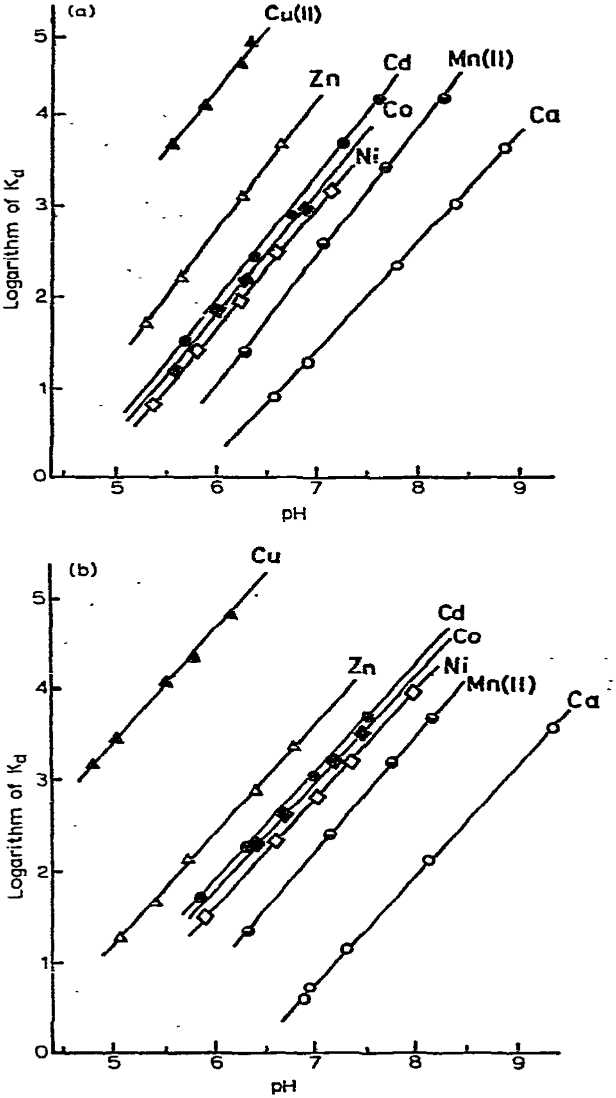

Fig. 1. Logarithm of K_d values of transition metals and calcium ions against final pH. (a) Exchanger: HZO dried at 40°. Initial metal concentration: $1.00 \cdot 10^{-4}$ mole/l. (b) Exchanger: HZO dried at 140°. Initial metal ion concentration: $1.00 \cdot 10^{-4}$ mole/l.

an ion-exchange reaction of the transition metal ion takes place. The relationship between log K_d and pH is independent of the ammonium ion concentration and the K_d values depend only on the final pH value of the equilibrating solution, even if the ion-exchange reaction takes place according to scheme

$$2RNH_4 + M^{2-} \rightleftharpoons R_2M + 2NH_4^+$$

The K_d values on HZO dried at 140° change slightly for cadmium, nickel, cobalt and zinc, while at the same pH the sample gives a higher K_d value for copper(II) and a lower value for calcium than those on HZO dried at 40°. Increased selectivities are also observed for the transition metals on hydrous thorium oxide, in which the changes in the K_d values on heating are smaller for the transition metals than alkali or alkaline earth metals[17]. The increased K_d values for copper(II) on HZO dried at 140° may be due to a larger Jahn–Taller deformation from an octahedral configuration of $Cu(H_2O)_6^{2+}$ than on HZO at 40°, as pointed out by Sakellaridis and Nobelis[16].

Elution curves for the transition metals and calcium

The column technique was used for various ions in order to obtain a more precise selectivity sequence of competing ions and to establish the applicability of an effective separation. An HZO column (9.5 × 0.8 cm I.D.) was pre-treated with 0.1 *M* ammonium acetate solution adjusted to pH 8. The mixed solution was passed through the column and the adsorbed metal ions were eluted with 0.1 *M* ammonium acetate solution at different pH values. The mixed solution was pre-treated with small amounts of sodium hexanedioate (sodium adipate) for reduction of the oxdized manganese. Small amounts of hydroxylamine were added to the eluent in order to prevent the oxidation of manganese(II) during the elution. The order of elution of the metal ions agrees well with the affinity sequence of the batch equilibration, although the peaks are not separated in Fig. 2. The affinity sequence is Cu(II) > Zn > Cd > Co > Ni > Mn(II) > Ca. A similar affinity sequence is observed on hydrous tin(IV) oxide: Cu(II) > Zn > Co > Fe(II) > Ni > Mn(II), which parallels the order of the equilibrium constants of the hydrolytic reaction[18,19]:

$$M^{2+} + H_2O \rightleftarrows MOH^+ + H^+$$

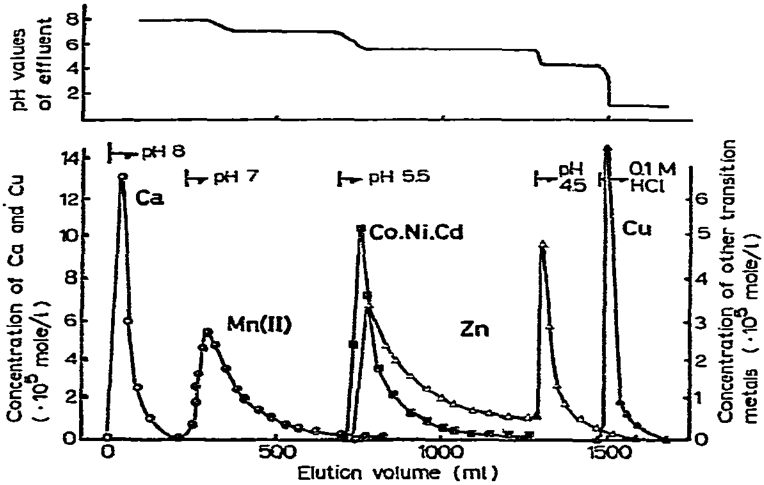

Fig. 2. Elution of transition metals and calcium with eluent at different pH values on HZO dried at 40°. Column, 9.5 × 0.8 cm I.D.; flow-rate, 1.0 ml/min; eluent, 0.1 *M* ammonium acetate solution at different pH values and 0.1 *M* HCl; metal ions, 0.014 mmole each.

Effective separations were observed in the elution of Ca–Mn(II)–Ni, Co, Zn–Cu(II). As can be seen in Fig. 2, the individual curves show a long tailing effect, indicating the presence of a number of different sites available for exchange as a

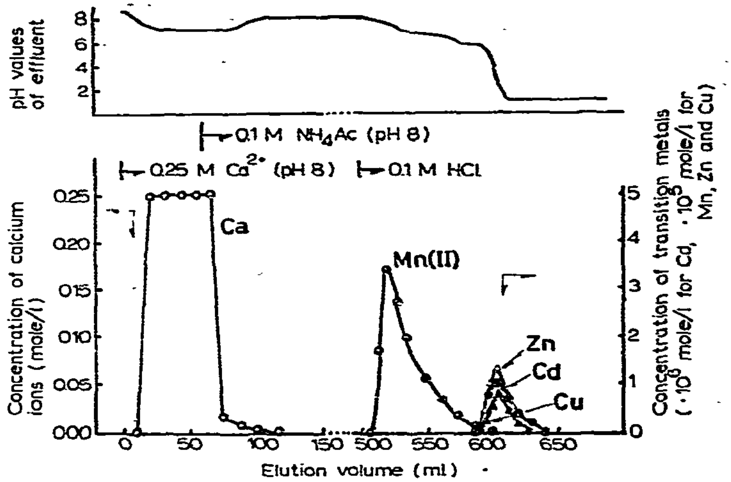

Fig. 3. Separation of small amounts of transition metals from large amounts of calcium. Exchanger, HZO dried at 140°; column, 9.5 × 0.8 cm I.D.; flow-rate, 1.0 ml/min; conditioning, 0.1 *M* ammonium acetate solution (pH 9.0).

function of the concentration of the solute[20]. Further, the pH values of the effluent did not change quickly at favourable values for the separation of transition metals.

Separation of transition metals from large amounts of calcium

The excellent separation behaviour can be applied to the group separation of small amounts of transition metals from large amounts of calcium. A 50-ml volume of 0.25 *M* calcium chloride (commercial grade) solution was adjusted to pH 8.0 and then applied continuously to the top of a column of HZO dried at 140°. The calcium ions were adsorbed slightly from the influent and were then eluted completely by further passage of 0.1 *M* ammonium acetate solution adjusted to the same pH. The transition metal ions were eluted as a group with 0.1 *M* hydrochloric acid containing the reducing agent, except for manganese(II), which was separated only partially. The quantitative determination showed recoveries of 102, 115, 110 and 98% for manganese(II), cadmium, zinc and copper(II), respectively. The recoveries were calculated on the basis of the results of the standard addition method with these metals in 0.25 *M* calcium chloride solution. More careful experiments would be needed for the accurate determination of transition metals by this elution method, because the commercial reagents used here contain trace amounts of these metals, even when of analytical-reagent grade.

This procedure can be applied to the enrichment and determination of trace amounts of transition metals in commercial calcium compounds, *e.g.*, calcium oxide, hydroxide and chloride.

HZO has good regeneration properties for transition metals, and can be used repeatedly under the usual column operating conditions.

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