

# Cation Exchange Separation of Transition Metals and Calcium with Zirconium Phosphate

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**Summary:** The cation exchange behaviour of the divalent transition elements, manganese to copper and calcium was studied over zirconium phosphate dried at 35 °C using hydrochloric acid as eluent. The adsorption of elements differ sufficiently as a function of hydrochloric acid concentration. The adsorption and the stability of the positively charged complexes is found to be in the order of Fe(II) > Ni(II) > Cu(II) > Ca(II) > Co(II) > Mn(II).

## Introduction

Considerable interest has been focussed upon the possible use of inorganic ion-exchange materials under conditions unfavourable towards the more conventional organic resin exchangers. Some of the inorganic ion-exchange materials which have been studied in the past include zirconium phosphate, zirconium tungstate, zirconium molybdate, hydrous zirconium oxide and hydrous chromium oxide [1-6]. Our earlier report [6] indicates that zirconium phosphate exhibits remarkable selectivity for alkaline earth metals and their adsorption increases sharply as atomic number increases. The present study describes the use of zirconium phosphate resin for separation of transition elements manganese to copper and calcium. The primary aim was to find conditions that would improve the convenience and broaden the scope of the type of analytical separation.

## Results and Discussion

Since in alkaline media some metals are precipitated out as their hydroxides, the  $k_d$  studies were restricted in the acidic media. The  $k_d$  values increased as the concentration of acid decreased and attained maximum adsorption at  $10^{-5}$  M HCl. The log  $k_d$  and the separation factor ( $\alpha$ ) of transition metals are summarized in Table-1. The selectivity decreased in the order of Fe(II) > Ni(II) > Cu(II) > Ca(II) > Co(II) > Mn(II). It is of interest that at high concentration of HCl (0.1 M), the selectivity is very

Table 1:  $k_d$  and separation factor ( $\alpha$ ) for Manganese, Cobalt, Calcium, Copper, Nickel and Iron on Zirconium Phosphate

Concentration of HCl (M)	Parameters	Ions					
		Mn <sup>2+</sup>	Co <sup>2+</sup>	Ca <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Fe <sup>2+</sup>
$5 \times 10^{-1}$	log $k_d$	1.06	1.20	1.42	1.60	1.86	3.20
	$\alpha$	1.13	1.18	1.13	1.16	1.72	
$5 \times 10^{-2}$	log $k_d$	1.23	1.32	1.77	2.10	2.31	3.40
	$\alpha$	1.07	1.34	1.19	1.10	1.47	
$5 \times 10^{-3}$	log $k_d$	1.36	1.57	2.05	2.40	2.63	3.59
	$\alpha$	1.15	1.31	1.17	1.10	1.37	
$5 \times 10^{-4}$	log $k_d$	1.47	1.68	2.30	2.70	3.10	3.80
	$\alpha$	1.14	1.37	1.17	1.15	1.23	

close to each other (Fig. 1). Mn(II) and Co(II) show slight adsorption below  $10^{-4}$  M HCl, whereas Ca(II) shows some adsorption at this concentration. Fe(II) shows the strongest adsorption amongst all the metals studied and the total adsorption takes place at  $10^{-5}$  M HCl. From these studies, it can be concluded that the separation of these elements can readily be achieved by ZrP.

The large difference in the cation-exchange behaviour of these elements suggest large difference in their complexing properties and considerable irregularities in the extent of complexation as a function of atomic number. A different adsorption order has been reported by Kraus and Moore [9] for

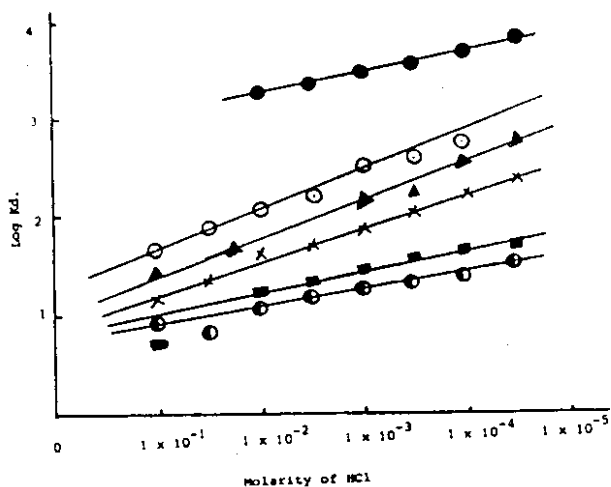


Fig. 1: Long Kd. of transition metal ions against molarity of HCl, Mn<sup>2+</sup> (○), Co<sup>2+</sup> (■), Ca<sup>2+</sup> (x), Cu<sup>2+</sup> (▲), Ni<sup>2+</sup> (⊙), Fe<sup>2+</sup> (●).

cation exchange behaviour on quaternary amine polystyrene-divinylbenzene resin Dowas-1 in concentrated HCl (1M to 4M), viz., Zn(II) > Cu(II) > Co(II) > Fe(II) > Mn(II) > Ni(II) which is parallel to the normal sequence observed in their  $MCl_3^{-1}$  complex formation. However, the present study reveal that a lower concentration of HCl ( $10^{-5}$  to 0.1 M), the formation of negatively charged chloride complex is negligible, rather  $MCl^+$  or  $MCl_2$  complexes are formed. The existence of such complexes have also been recognized by Bjerrum [10] where selectivity order is Zn(II) > Fe(II) > Cu(II) > Co(II). However, Bjerrum did not include Ni(II) and Mn(II) and therefore, a detailed comparison is not feasible. It is believed that Fe(II) is more strongly complexed than Cu(II) on the basis of the stability constant  $FeCl^+$ .

#### *Separation of transition elements manganese to copper and calcium*

A considerable difference in the separation factor 'α' (Table 1) implies that their separation on cation-exchange column of moderate length should be possible. The separation of the transition elements Mn (II) to Cu(II) and Ca(II) was carried out and the results are shown in Fig. 2. A solution of each element (0.1 mg/2ml) was placed in the column containing 100 mesh ZrP resin. Mn(II) is less adsorbed and immediately appears with  $10^{-5}$  M HCl. Co(II) was removed with  $10^{-4}$  M HCl, Ca(II),

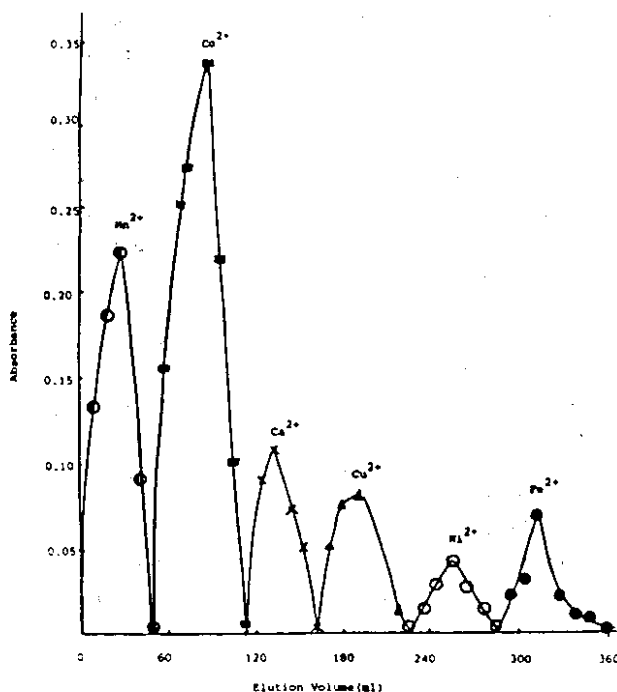


Fig. 2: Elution of transition metal ions on zirconium phosphate dried at 35 °C. Flow rate 1 ml/min., concentration of metal ions, 0.1 mg each.

Cu(II), Ni(II) and Fe(II) were eluted respectively with  $10^{-3}$  M,  $5 \times 10^{-3}$  M,  $10^{-2}$  M and  $10^{-1}$  M HCl solutions. The separation of these elements is quite satisfactory at the flow rate 0.1ml/min and probably would also be satisfactory at considerably higher flow rates. The quantitative determination showed recoveries of 85%, 88%, 95%, 95.8%, 94% and 95% for Fe(II), Ni(II), Cu(II), Ca(II), Co(II) and Mn(II) respectively. Special care was taken to observe the adsorption behaviour of Mn(II). Since  $KMnO_4$  dissolves in water to give  $MnO_4^-$  ion which is adsorbed on the solid resin and gave reverse adsorption as compared with the cations. Therefore,  $MnCl_2$  was used and the solution was pretreated with small amount of sodium adipate for reduction of the oxidized manganese.

#### **Experimental**

Analytical grade reagents were used throughout the experiment work. Zirconium tetrachloride was obtained from E. Merck. All other chemicals were from Fluka. The cation-exchanger zirconium phosphate (ZrP) was prepared as described earlier [6]. The standard stock solutions (100 ppm) of manganese, iron cobalt, nickel, copper and calcium

were prepared by dissolving an appropriate amount of chloride/sulphate of each metal in distilled water. Further metal ion concentrations were prepared by appropriate dilution of respective stock solutions. Hydrochloric acid dilutions ranging from  $10^{-5}$  M to 0.1 M were used as eluent. The glassware and the column was washed thoroughly with hot HCl (1:1) and the resin column was cleaned by passing through 50 ml of 1 M HCl followed by pouring large amount of distilled water. The concentration of metal ions, manganese, iron, cobalt, nickel, copper and calcium were determined spectrophotometrically [7,8]. The cation exchange column was prepared and used in an identical manner as described in the previous communication [6]. The distribution coefficient ( $k_d$ ) of the metal ions was determined by batch equilibrium technique [4] at  $25 \pm 2$  °C. The amount adsorbed was determined from the difference between the initial and the final concentration in clear supernatant solution.

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