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SHORT COMMUNICATIONS

# ZIRCONIUM ANTIMONATE: ION-EXCHANGE SEPARATION OF SOME METAL IONS

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**ABSTRACT.** Chromatographic separation studies were made on zirconium antimonate with molar ratio 0.5. Zirconium antimonate showed extremely high selectivity for Pb(II), hence the separation of Pb(II) from other metal ions was carried out. Similarly on the basis of the differential selectivity, separation of copper and iron from other metals have been achieved. The recovery of almost all metal ions in the effluent collected is quantitative.

## INTRODUCTION

The synthesis and ion-exchange behaviour of zirconium antimonate with molar ratio 0.5 have been described (1,2). However the analytical applications of this exchanger have not been reported. Hence the analytical utility of zirconium antimonate was explored by achieving separations of some metal ions.

## EXPERIMENTAL

*Synthesis.* The exchanger was obtained by adding 50 ml of 0.5 M antimony pentachloride in 2 M HCl dropwise from a buret into a beaker containing 50 ml of 0.25 M zirconium oxychloride in 2 M HCl at room temperature, then adding ammonia (32%) to decrease acidity (to pH 0-1) and to cause precipitation of zirconium antimonate. The precipitate was filtered and washed with 2 M $HNO_3$, followed by distilled water and dried at 60°C for 4 days. The exchange capacity of the material prepared was found to be identical (0.20 meq/g) to those reported elsewhere (2).

The material was ground and sieved through 90-180 mesh, soaked in 2 M $HNO_3$ overnight, washed with distilled water and air dried before use.

*Separations.* For separation studies 2.0 g of zirconium antimonate in the $H^+$ form was packed in a 0.8 cm inner diameter glass column upto 3.0 cm in height. A 2 µmol amount of each of Ni(II), Co(II), Mn(II), Zn(II), Fe(II) and Pb(II) were loaded on top of the column and the elution was carried out after 30 min with different concentrations (0.05 - 8.0 M) of $HNO_3$. The rate of flow was 0.2 ml/min and 5 ml fractions of effluent were collected for metal ion determination by AAS.

## RESULTS AND DISCUSSION

The solubility of the exchanger in $HNO_3$ has been studied. When 200 mg of exchanger was mixed with 50 ml of 6 M $HNO_3$ and shaken for 12 h at 30°C, < 0.01 mg of zirconium (3) and 16.51 mg of antimony (4) were found in the supernatant liquid. Hence one can assume that the solubilization of Zr and Sb during the elution of the ions with $HNO_3$ at different concentration (0.05 - 8.0 M) would be minimal.

It is evident that separations of metal ions are achieved on the basis of differences in $K_d$ values (5,6). the distribution coefficients for the different metal ions determined by equilibrating with 25 ml of 0.01 M $HNO_3$ or aqueous solution show higher values for Pb(II), Cu(II) and Cd(II) than for other metal ions tested. Hence those metals with higher $K_d$ can be separated from those with lower $K_d$ values.

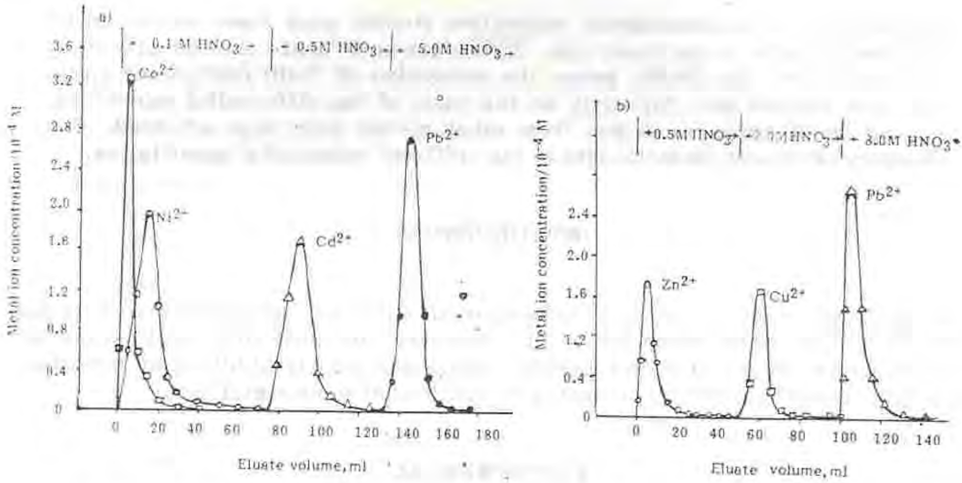


Fig. 1. Separation of a) Ni(II), Co(II) and Cd(II) and b) Zn(II) and Cu(II) from Pb(II) on zirconium antimonate exchanger. Column pre-treated; loading (a) 2 µmol (b) 1 µmol of each metal ion. Flow rate 0.2 mole/min.

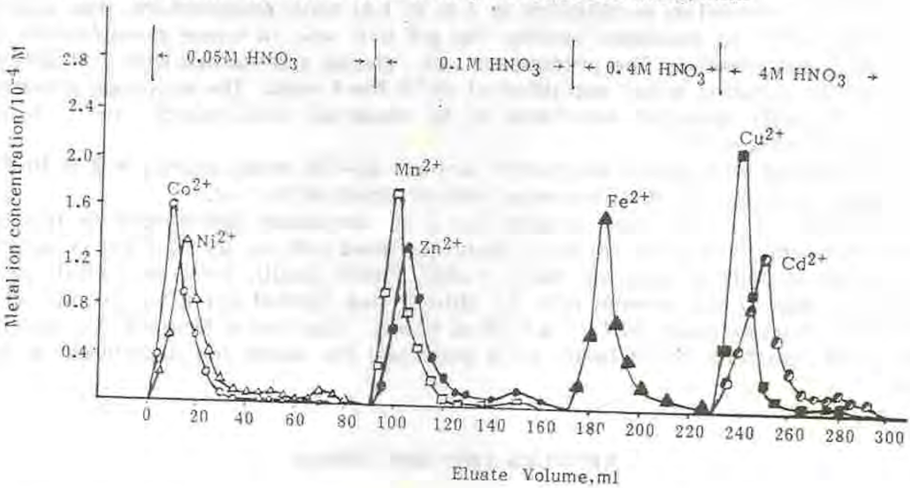


Fig. 2. Separation of mixture of metal ions: Co(II), Ni(II), Mn(II), Zn(II), Fe(II) Cu(II) and Cd(II) on zirconium antimonate exchanger. Loading 2 µmol of each of metal ion, flow-rate 0.2 ml $min^{-1}$; column not treated with nitric acid prior to elution.

Typical plots of the elution curves of the metal ions are shown in Fig. 1 and 2. The elution curves for Pb(II) are well resolved (Fig. 1) and Pb(II) is separated quantitatively from Zn(II), Cu(II), Fe(II), Cd(II), Co(II) and Ni(II) (Table 1). Similarly Fe(II) is separated from other metal ions in good yield (Table 1 and Fig. 2). The tailing observed for some transition metal ions in the separation experiments could be minimized if the zirconium antimonate column is pretreated with dilute nitric acid. The separations achieved on columns pretreated with dilute nitric acid gave a recovery of more than 99% for most of the metal ions studied. Relatively low yields in the recovery for some of the metal ions were considered to be due to strong retention of cations to the exchanger particles during the time interval between feeding and elution.

Table 1. Separation of metal ions from synthetic mixtures on zirconium antimonate columns at room temperature

| Synthetic mixture loaded* | Eluent | Effluent collected (ml) | Recovery (%) |
|---|---|---|---|
| Co(II) + Ni(II) + Mn(II) + Fe(II) + Cu(II) | 0.05 M $HNO_3$ | 90 | 90(Co) + 86.2(Ni) |
| | 0.1 M $HNO_3$ | 80 | 88.6(Mn) + 83.7(Zn) |
| | 0.4 M $HNO_3$ | 60 | 92(Fe) |
| | 4.0 M $HNO_3$ | 70 | 85.8(Cu) + 84.5(Cd) |
| Co(II) + Ni(II) + Cd(II) + Pb(II) | 0.1 M $HNO_3$ | 75 | 99.3(Co) + 98.8(Ni) |
| | 0.5 M $HNO_3$ | 60 | 99.7(Cd) |
| | 5.0 M $HNO_3$ | 45 | 96.6(Pb) |
| Zn(II) + Cu(II) + Pb(II) | 0.5 M $HNO_3$ | 50 | 99.6(Zn) |
| | 2.0 M $HNO_3$ | 50 | 99.0(Cu) |
| | 8.0 M $HNO_3$ | 50 | ∿ 100(Pb) |
| Pb(II) + Zn(II) | 0.08 M $HNO_3$ | 50 | 99.7(Zn) |
| | 3.0 M $HNO_3$ | 50 | 99.4(Pb) |
| Pb(II) + Cu(II) | 1.0 M $HNO_3$ | 50 | ∿ 100(Cu) |
| | 5.0 M $HNO_3$ | 50 | 99.7(Pb) |
| Pb(II) + Fe(II) | 0.05 M $HNO_3$ | 50 | 96.6(Fe) |
| | 1.5 M $HNO_3$ | 50 | 99.2(Pb) |
| Pb(II) + Cd(II) | 0.8 M $HNO_3$ | 50 | 99.5(Cd) |
| | 5.0 M $HNO_3$ | 50 | ∿ 100(Pb) |

* 2 µmole of each ions was loaded.

The exchanger can be utilized for the separation of trace amount of Pb(II) in a wide variety of minerals and materials.
It may be compared with fibrous cerium(IV) phosphate (6), thorium phosphate (6) and niobium selenite (7) which exhibit high selectivity for Pb(II).

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