CHROM. 7600

STUDIES ON THORIUM PHOSPHATE ION EXCHANGER

II. DISTRIBUTION COEFFICIENT MEASUREMENTS AND SELECTIVE ION-EXCHANGE SEPARATIONS OF SOME METAL IONS

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SUMMARY

Distribution coefficients of metal ions on thorium phosphate exchanger were determined at pH 2–3 and at pH 5.5–6.5. The distribution coefficients were higher for lead, bismuth and iron(III) than for other metals. On the basis of the distribution coefficients, separations of Pb^{2+} from Cu^{2+}, Cd^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Mn^{2+} and Hg^{2+}, and of Bi^{3+} from Zn^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+} and Hg^{2+}, have been achieved with thorium phosphate.

INTRODUCTION

In Part I of this series[1], the synthesis, physico-chemical properties and ion-exchange behaviour of four different thorium phosphate ion exchangers were described. Thorium phosphate polymers were prepared by the addition of 0.1 M thorium nitrate in 1 M nitric acid and 1 M phosphoric acid under different conditions. The PO_4:Th ratio of the samples varied from 1.69 to 2.1. The products are white, hard and fibrous materials that are suitable for column operation. The exchangers are stable in water, dilute mineral acids and dilute alkalis and can be used in these media without deterioration in ion-exchange properties. In this work thorium phosphate sample No. 2 (PO_4:Th = 2.1) and No. 3 (PO_4:Th = 1.69) have been used in the measurement of the distribution coefficients of various metal ions. On the basis of these measurements, selective ion-exchange separations of lead and bismuth from other metals have been achieved.

EXPERIMENTAL

Apparatus

The apparatus used was as previously described[1]. For separation studies, 10 g of thorium phosphate (sample No. 2) were inserted in a glass column (length 8 cm, I.D. 1.1 cm) with a glass-wool support. The column was washed with demineralized water. The flow-rate was maintained at *ca.* 0.3 ml/min.

TABLE I

DISTRIBUTION COEFFICIENTS OF METAL IONS ON THORIUM PHOSPHATE (BATCHES NOS. 2 AND 3) AT $27 \pm 2°$

Metal ion	Ionic radius (Å)	K_d values at pH 5.5–6.5 (ml/g)		K_d values at pH 2–3 (ml/g)	
		Batch 2	Batch 3	Batch 2	Batch 3
Zn^{2+}	0.74	120	528	29	37
Pb^{2+}	1.21	4160	5225	5225	3450
Cd^{2+}	0.97	83	140	7.5	16.5
Mg^{2+}	0.65	29	32	3.5	3.5
Ca^{2+}	0.99	500	233	200	233
Cu^{2+}	0.92	208	270	85	118
Ni^{2+}	0.69	19	32	0	4
Mn^{2+}	0.80	111	137.5	12	19
Co^{2+}	0.72	43	48	0	5
Hg^{2+}	1.10	9	7	0	3
Sr^{2+}	1.10	125	200	4	12.5
Bi^{3+}	—	—	—	T.A.*	T.A.*
Fe^{3+}	—	—	—	2550	1666
Al^{3+}	0.50	—	—	170	8
La^{3+}	1.15	—	—	2100	878
UO_2^{2+}	—	—	—	557	455
VO^{2+}	—	—	—	1588	1048
Th^{4+}	—	—	—	1870	654

* T.A. = total adsorption.
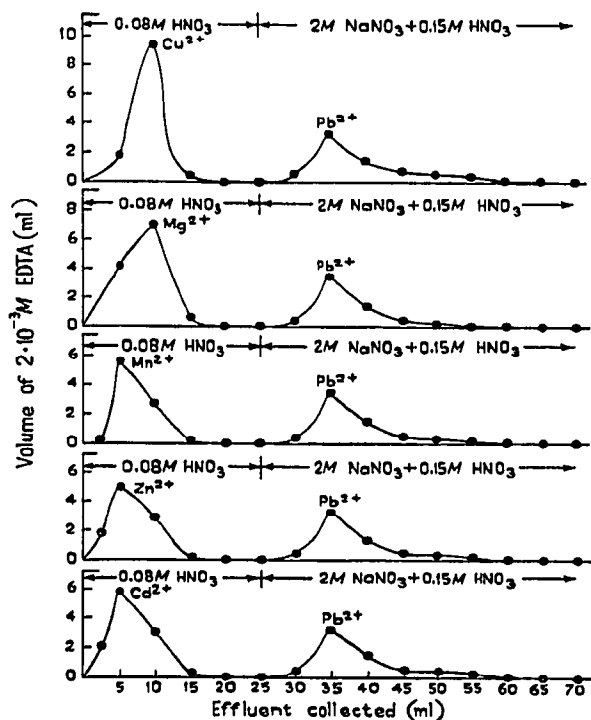
Fig. 1. Separation of Cd^{2+}–Pb^{2+}, Zn^{2+}–Pb^{2+}, Mn^{2+}–Pb^{2+}, Mg^{2+}–Pb^{2+} and Cu^{2+}–Pb^{2+} on a thorium phosphate column (I.D. 1.1 cm). Flow-rate, 0.3 ml/min.

Reagents

Th(NO$_3$)$_4$·4H$_2$O was of reagent-grade quality (E. Merck, Darmstadt, G.F.R.). All other chemicals were of analytical grade.

Synthesis

Thorium phosphate was prepared by mixing 0.1 M thorium nitrate in 1 M nitric acid and 1 M phosphoric acid under different conditions as described in Part I[1].

Distribution coefficients (K$_d$)

The distribution coefficients of metal ions were determined by batch operation as follows. A 500-mg amount of exchanger was shaken with 50 ml of a solution of the metal ion for 2 days at 27 ± 2° with intermittent shaking. The concentration of the metal ion was initially 5·10^{-4} M, and when totally adsorbed by the exchanger, the exchanger was then shaken with a 2·10^{-3} M metal ion solution. Bismuth was totally adsorbed in 2·10^{-3} M solution. K_d values were determined at pH 5.5–6.5 and at pH 2–3 with perchloric acid. The K_d values of the metal ions were calculated after attainment of equilibrium by using the following expression:

$$K_d = \frac{\text{Amount of element in exchanger}}{\text{Amount of element in solution}} \times \frac{\text{ml of solution}}{\text{g of exchanger}}$$

Uranyl ions were determined spectrophotometrically using hydrogen peroxide[2]. All other cations were determined by titration with standard EDTA solution[3,4].

RESULTS AND DISCUSSION

The method of preparation of inorganic ion exchangers has a considerable effect on their degree of hydration and the composition of the sample. These factors are responsible for the shape and size of the cavities inside the exchanger and other properties of the exchanger[5]. Thorium phosphate polymers obtained from 0.1 M thorium nitrate in 1 M nitric acid and 1 M phosphoric acid show various compositions under different conditions. Batches Nos. 2 and 3 have the compositions [Th(HPO$_4$)$_2$·2.1H$_2$O]$_n$ and [Th(HPO$_4$)$_2$·2.5H$_2$O]$_n$, respectively[1]. The distribution coefficients of metal ions on thorium phosphate (sample Nos. 2 and 3) are given in Table I, and the ionic radii[6] are also tabulated. The results show that the thorium phosphate exchanger is specific for the separation of Pb^{2+}, Bi^{3+}, Fe^{3+}, La^{3+}, UO$_2^{2+}$ and VO^{2+} from numerous metal ions. The ion-exchange capacity at different temperatures[1] shows that it is a good exchanger and it can be used successfully at temperatures up to 200°.

From Table I, it can be seen that the distribution coefficients are higher for lead, bismuth, iron(III), lanthanum, thorium, vanadium and uranium than for the other metals, and it is therefore possible to separate these metals from the metals that have much lower distribution coefficients. Bismuth is totally adsorbed by thorium phosphate at pH 2.7. It has also been found that in some instances the K_d values change as the pH of the initial solution is changed. Typical plots of the elution curves of the metal ions separated from lead and bismuth are shown in Figs. 1 and 2. The elution curve for lead (Fig. 1) with 2 M sodium nitrate in 0.15 M nitric acid was sharper than the curve for bismuth with 1 % potassium iodide in 0.03 M sulphuric acid
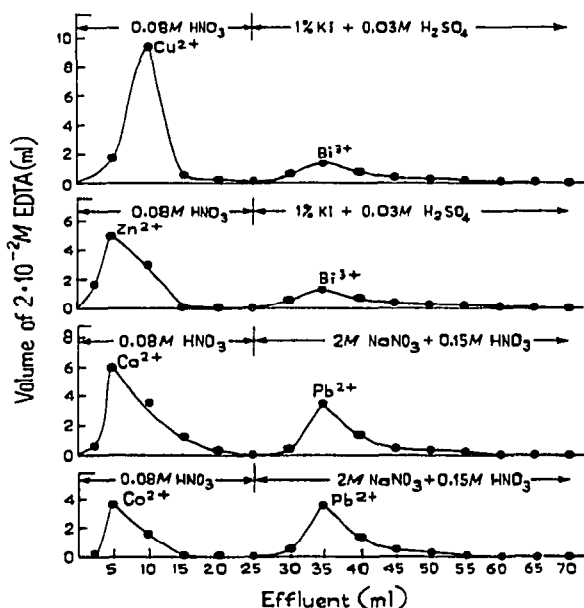
Fig. 2. Separation of $Co^{2+}-Pb^{2+}$, $Ca^{2+}-Pb^{2+}$, $Zn^{2+}-Bi^{3+}$ and $Cu^{2+}-Bi^{3+}$ on a thorium phosphate column (I.D. 1.1 cm). Flow-rate, 0.3 ml/min.

TABLE II

SEPARATION OF LEAD FROM OTHER METALS ON THORIUM PHOSPHATE (BATCH NO. 2) COLUMNS AT $27 \pm 2°$

Mixture separated	Eluent	Volume of effluent (ml)	Taken (mg)	Found (mg)	Error (%)
Cd^{2+}	0.08 M HNO_3	20	2.50	2.51	+0.4
Pb^{2+}	2 M $NaNO_3$ + 0.15 M HNO_3	40	2.60	2.57	−1.15
Zn^{2+}	0.08 M HNO_3	25	1.49	1.50	+0.67
Pb^{2+}	2 M $NaNO_3$ + 0.15 M HNO_3	40	2.60	2.59	−0.38
Cu^{2+}	0.08 M HNO_3	25	1.50	1.50	0.00
Pb^{2+}	2 M $NaNO_3$ + 0.15 M HNO_3	40	2.60	2.59	−0.38
Mg^{2+}	0.08 M HNO_3	25	0.56	0.56	0.00
Pb^{2+}	2 M $NaNO_3$ + 0.15 M HNO_3	40	2.60	2.56	−1.53
Mn^{2+}	0.08 M HNO_3	25	0.95	0.94	−1.05
Pb^{2+}	2 M $NaNO_3$ + 0.15 M HNO_3	40	2.60	2.58	−0.76
Co^{2+}	0.08 M HNO_3	20	0.60	0.58	−3.33
Pb^{2+}	2 M $NaNO_3$ + 0.15 M HNO_3	40	2.60	2.63	+1.15
Hg^{2+}	0.01 M HNO_3	25	0.79	0.77	−2.53
Pb^{2+}	2 M $NaNO_3$ + 0.15 M HNO_3	40	2.60	2.61	+0.38
Ca^{2+}	0.08 M HNO_3	25	1.05	1.01	−3.8
Pb^{2+}	2 M $NaNO_3$ + 0.15 M HNO_3	40	2.60	2.66	+2.3

(Fig. 2); good elution occurred for copper, while bismuth showed poor elution. Satisfactory elutions were also observed in other instances[7].

On the basis of the K_d values in Table I, some quantitative separations of lead and bismuth from other metals are shown in Tables II and III.

TABLE III

SEPARATION OF BISMUTH FROM OTHER METALS ON THORIUM PHOSPHATE (BATCH NO. 2) COLUMNS AT $27 \pm 2°$

Mixture separated	Eluent	Effluent (ml)	Taken (mg)	Found (mg)	Error (%)
Zn^{2+}	0.08 M HNO_3	25	1.49	1.52	+2.01
Bi^{3+}	1% KI + 0.03 M H_2SO_4	35	1.48	1.50	+1.35
Cu^{2+}	0.08 M HNO_3	25	1.50	1.52	+1.33
Bi^{3+}	1% KI + 0.03 M H_2SO_4	35	1.48	1.46	−1.35
Co^{2+}	0.01 M HNO_3	20	0.60	0.61	+1.66
Bi^{3+}	1% KI + 0.03 M H_2SO_4	35	1.48	1.50	+1.35
Cd^{2+}	0.08 M HNO_3	20	0.40	0.40	0.00
Bi^{3+}	1% KI + 0.03 M H_2SO_4	35	1.48	1.48	0.00
Hg^{2+}	0.01 M HNO_3	25	0.79	0.80	+1.26
Bi^{3+}	1% KI + 0.03 M H_2SO_4	35	1.48	1.46	−1.35
Ni^{2+}	0.01 M HNO_3	30	0.16	0.16	0.00
Bi^{3+}	1% KI + 0.03 M H_2SO_4	35	1.48	1.47	−0.67

Table II shows that lead is separated quantitatively from cadmium, zinc, copper, magnesium, manganese, cobalt, mercury(II) and calcium. Similarly, Table III shows that bismuth is separated from zinc, copper, cobalt, cadmium, mercury(II) and nickel.

The exchanger has also a good regeneration capacity and is very useful for some analytical separations. It may be compared with fibrous cerium(IV) phosphate reported by Alberti et al.[8]. Fibrous cerium(IV) phosphate exhibits high selectivity for Pb^{2+}, Bi^{3+} and Fe^{2+}. This was taken advantage of in the chromatographic separation of inorganic ions on cerium (IV) phosphate sheets.

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