Journal of Chromatography, 128 (1976) 149–153

CHROM. 9189

INFLUENCE OF DRYING TEMPERATURE ON THE ION-EXCHANGE PROPERTIES OF STANNIC TUNGSTOARSENATE

II. SEPARATION OF Hg^{2+} AND Pb^{2+} AND OF Al^{3+} AND Ca^{2+}

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(First received December 9th, 1975; revised manuscript received March 5th, 1976)

SUMMARY

Stannic tungstoarsenate has been dried at 500°, and K_d values have been determined on this material for 21 cations in distilled water, acetone–0.1 M HNO_3 (1:9 and 2:3) and acetic acid–sodium acetate (2:2, 2:4 and 4:2). Quantitative separations of Ca^{2+} and Al^{3+} and of Hg^{2+} and Pb^{2+} have been achieved. Infrared spectra show that there is no chemical change in the material on heating to 500°.

INTRODUCTION

The synthesis and ion-exchange properties of stannic tungstoarsenate have been described earlier[1]. Stannic tungstoarsenate has promising cation-exchange properties, an outstanding thermal stability, high uptake of certain cations and good resistance to water and dilute acid. It is necessary to study its ion-exchange properties after drying at high temperature so that its usefulness at these temperatures may be elucidated.

In this paper we describe the effect of drying temperature on the ion-exchange properties of stannic tungstoarsenate.

EXPERIMENTAL

Reagents

Sodium arsenate heptahydrate, sodium tungstate and stannic chloride pentahydrate (pure, Poland, Gliwice, Poland) were used.

Apparatus

A Sico temperature-controlled shaker was used. A muffle furnace was used for heating the ion exchanger at different temperatures. In the case of ^{134}Cs, γ counting was carried out on a scintillation counter; a Geiger–Muller counter was used for β counting in the case of ^{86}Rb.

Procedure

Stannic tungstoarsenate was prepared under the same conditions as given in the earlier paper[1]. It was heated further at 500° for 2 h in the muffle furnace.

Ion-exchange studies

The ion-exchange capacity of stannic tungstoarsenate heated to 500° was 0.31 mequiv./g. K_d values for 21 metal ions were determined in different solvent systems on this exchanger. The equation used is

$$K_d = \frac{I - F}{F} \cdot \frac{50}{0.5} \text{ ml/g}$$

where I is the volume of 0.002 M ethylenediaminetetraacetic acid (EDTA) needed to titrate the original cation solution and F is the volume of 0.002 M EDTA used for titration after the equilibration; the total volume of equilibrating solution was 50 ml. The amount of the exchanger used was 0.5 g. The loading of the cations was less than 3% of the ion-exchange capacity of the exchanger.

RESULTS

The colour of stannic tungstoarsenate after heating at 500° is dirty white. A column was filled with the exchanger and then washed successively with dilute nitric acid and water. The following quantitative separations were achieved.

Separation of Hg^{2+} from Pb^{2+}

A mixture of Hg^{2+} and Pb^{2+} was applied to the column. The effluent was recycled three times on the column. Hg^{2+} was eluted with 0.5% NH_4NO_3 in 0.001 M HNO_3 at a flow-rate of 7–8 drops per minute; Pb^{2+} was eluted with 1% NH_4NO_3 in 1 M HNO_3 (Fig. 1).

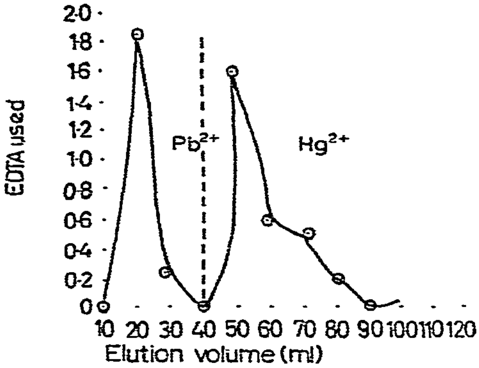

Fig. 1. Separation of Hg^{2+} from Pb^{2+}.

Separation of Ca^{2+} from Al^{3+}

First the column was saturated with 10% acetone. Then a mixture of Ca^{2+} and Al^{3+} was applied to the column. Ca^{2+} was eluted with 1% NH_4NO_3 in 1 M HNO_3 (Fig. 2).

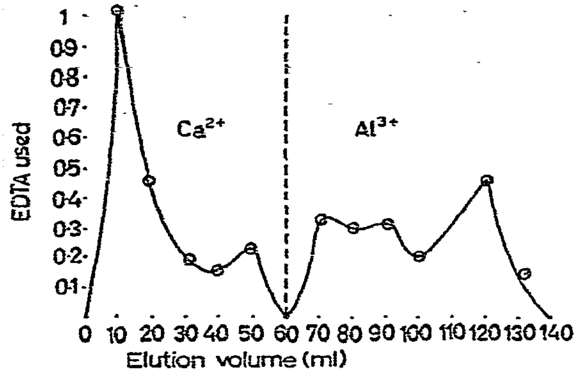

Fig. 2. Separation of Ca^{2+} from Al^{3+}.

DISCUSSION

Table I shows that a number of interesting separations are possible in acetone–nitric acid on the sample heated to 500°. Some of the more important are as follows: Al^{3+}–Fe^{3+}, Mn^{2+}–Al^{3+}, Ca^{2+}–Al^{3+}, Ni^{2+}–Mn^{2+}, Hg^{2+}–Pb^{2+}, Ca^{2+}–Ba^{2+}, Cu^{2+}–Ni^{2+} and La^{3+}–Ga^{3+}. Out of these Ca^{2+}–Al^{3+} and Hg^{2+}–Pb^{2+} have been successfully separated on the column. As the proportion of acetone was increased, the

TABLE I

K_d VALUES (ml/g) OF METAL IONS ON STANNIC TUNGSTOARSENATE PREVIOUSLY HEATED TO 500°

Cation	*K_d (ml/g) (acetone–0.1 M HNO_3)*	
	(1:9)	*(2:3)*
Mg^{2+}	0	1
Ca^{2+}	0	17
Sr^{2+}	66	17
Ba^{2+}	92	40
Zn^{2+}	58	14
Cd^{2+}	17	24
Cu^{2+}	70	112
Ni^{2+}	7189	18900
Mn^{2+}	3	247
Fe^{3+}	0	12700
Al^{3+}	7600	1953
Y^{3+}	53	260
La^{3+}	0	153
Pr^{3+}	193	250
Sm^{3+}	105	175
Gd^{3+}	235	320
Dy^{3+}	195	370
Er^{3+}	107	103
Pb^{2+}	66	1286
Hg^{2+}	7149	500
Th^{4+}	281	133

TABLE II

K_d VALUES OF METAL IONS ON STANNIC TUNGSTOARSENATE PREVIOUSLY HEATED TO 500° IN DEMINERALIZED WATER

Cation	*K_d (ml/g)*
Mg^{2+}	531
Ca^{2+}	350
Sr^{2+}	6900
Ba^{2+}	4340
Zn^{2+}	1532
Cd^{2+}	2040
Cu^{2+}	561
Ni^{2+}	200
Mn^{2+}	1340
Fe^{3+}	265
Al^{3+}	1440
Y^{3+}	4160
La^{3+}	22300
Pr^{3+}	15300
Sm^{3+}	26100
Gd^{3+}	27200
Dy^{3+}	25700
Er^{3+}	25800
Pb^{2+}	1970
Hg^{2+}	26
Th^{4+}	950

TABLE III

K_d VALUES OF METAL IONS ON STANNIC TUNGSTOARSENATE PREVIOUSLY HEATED TO 500°

	K_d (ml/g) *(0.1 M acetic acid–0.1 M sodium acetate)*		
Cation	*(1:1)*	*(1:2)*	*(2:1)*
Mg^{2+}	365	132	762
Ca^{2+}	2150	275	234
Sr^{2+}	8700	346	877
Ba^{2+}	788	1010	303
Zn^{2+}	527	482	444
Cd^{2+}	4180	756	756
Cu^{2+}	1780	1466	221
Ni^{2+}	860	380	162
Mn^{2+}	620	440	276
Fe^{3+}	184	753	122
Al^{3+}	1744	670	20
Y^{3+}	21200	21200	21200
La^{3+}	22300	21406	11100
Pr^{3+}	25300	464	25300
Sm^{3+}	246	1346	10380
Gd^{3+}	542	1720	542
Dy^{3+}	312	665	545
Er^{3+}	396	640	204
Pb^{2+}	360	720	1280
Hg^{2+}	0	20	339
Th^{4+}	162	260	0

K_d value of mercury decreased and an interesting reversal in the selectivity of Hg^{2+} and Pb^{2+} was observed. This occurs because Hg^{2+} is more covalent and hence is more soluble in acetone. For the same reason the uptake of Hg^{2+} from distilled water is very small (Table II). The K_d values of some metal ions were also determined in acetate buffers (Table III). When acetone–sodium acetate (1:2) was used the K_d values of alkaline-earth metals increased with increasing ionic radius. The K_d values of ^{86}Rb and ^{134}Cs were inversely proportional to temperature (Table IV).

Infrared spectra showed that there is no change in the structure of this ion exchanger on heating, and it is therefore very thermally stable (Fig. 3).

TABLE IV

K_d VALUES OF ^{86}Rb AND ^{134}Cs ON STANNIC TUNGSTOARSENATE AT DIFFERENT TEMPERATURES AT pH 2 (0.01 *N* HNO_3)

Cation	K_d			
	25°	*35°*	*45°*	*55°*
^{86}Rb	30.9	29.0	19.8	10.2
^{134}Cs	47.7	25.9	22.0	12.0

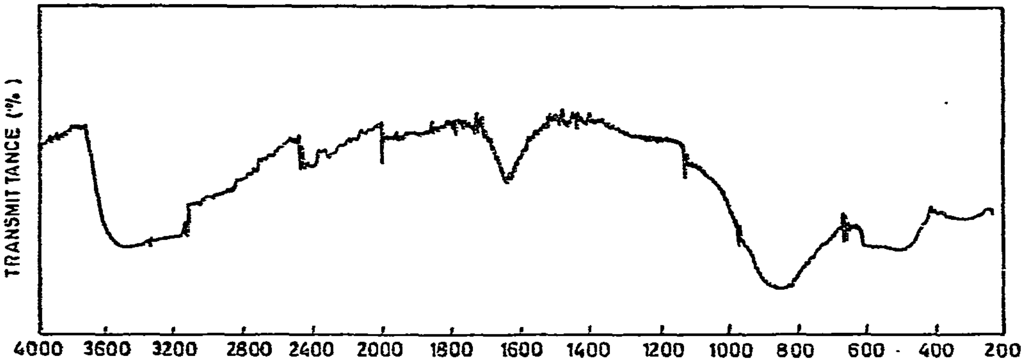

Fig. 3. Infrared spectrum of stannic tungstoarsenate.

ACKNOWLEDGEMENTS

We thank Professor W. Rehman for research facilities, Bhabha Atomic Research Centre (Bombay, India) for financial assistance and Dr. S. N. Tandon for helpful suggestions.

REFERENCE

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