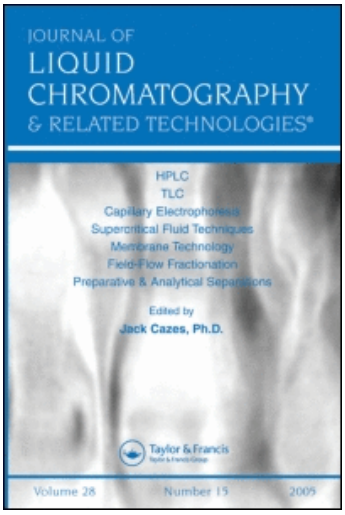

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Cation Exchange Chromatographic Separation Of Lead From Mixed Solvents

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CATION EXCHANGE CHROMATOGRAPHIC SEPARATION OF LEAD FROM MIXED SOLVENTS

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ABSTRACT

The cation exchange separation of lead from associated elements on Dowex 50W-X8 was carried out in mixed solvent systems. Elution behaviour was studied with 0.75 M HCl in the presence of various concentrations of solvents such as methanol, ethanol, 2-propanol, acetone, 1, 4 dioxane and tetrahydrofuran. Tetrahydrofuran, 1, 4 dioxane and acetone were effective in the presence of hydrochloric acid. At low concentrations of methanol, ethanol and 2-propanol in hydrochloric acid were useful for the separation of ions from lead. Lead was separated from binary and as well as multicomponent mixtures. The method was extended to the separation of lead from lead base alloys.

INTRODUCTION

The cation-exchange chromatographic separations of lead from the mixed solvents are very limited. The distribution coefficient of lead (1) in dimethyl sulphoxide - hydrochloric acid solution was measured by ion-exchange. The separation of lead was carried in ethanolamine solutions (2). Isopropanol along with hydrochloric acid (3) was used for the separation of heavy metals. Lead was separated from zinc (4) in media comprising acetonitrile and hydrochloric acid. Lead was

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separated from indium with hydrochloric acid containing acetone (5). Acetone-hydrochloric acid mixtures were used as the eluants for the separation of lead from other bivalent metal ions (6). Although investigations on the cation-exchange separation of lead (7) were carried out, no systematic studies have been made on cation-exchange separation of lead in mixed solvents. Such studies are reported in this paper. The method is extended to the analysis of lead in solder.

EXPERIMENTAL

Apparatus and Reagents

The ion-exchange column 20 x 1.4 cm was similar to the one described earlier (8). Digital pH meter type PH-822 (ECIL, India) with glass and calomel as the reference electrodes.

A stock solution of lead was prepared by dissolving 2.00 g of lead nitrate in 250 ml distilled water containing 1% nitric acid. It was standardized complexometrically (9). It was found to contain 5 mg ml^{-1} lead. Dowex 50W-X8 (Dow Chemical Co. Midland, Mich. U.S.A.) 20-50 mesh (H^+ form) was used.

GENERAL PROCEDURE

An aliquot of solution containing 15 mg lead was passed on the column at flow rate of 1 ml/min. Then lead was eluted with various eluants consisting of mineral acids or mixture of 0.75 M hydrochloric acid with either of non-aqueous solvents such as methanol, ethanol, 2-propanol, acetone, tetrahydrofuran and 1, 4 dioxane (Tables 1, 2). Ten to twelve fractions of eluants containing 25 ml of eluant were collected. Each fraction was evaporated almost to dryness prior to the determination of lead.

TABLE - 1

Elution Behaviour of Lead

Pb(II) = 15.0 mg Weight of resin = 12.55 gms Flow rate 2 ml/min.

Eluant (M)	Peak elution volume V_{max}, ml	Total elution volume V_t, ml	Lead recovery %	Elution constant (E)	Volume distribution coefficient (D_v)	Weight distribution coefficient (D_w)
HCl						
0.75	150	300	99.8			
1.00	75	175	100.0	0.58	1.74	1.21
1.50	50	175	100.1	1.08	0.93	0.65
2.00	50	175	99.9	1.08	0.93	0.65
HNO_3						
1.0	-	300	94.3	-	-	-
2.0	75	175	100.0	0.58	1.74	1.21
3.0	50	150	100.0	1.08	0.93	0.65
$HClO_4$						
2	-	300	6.0	-	-	-
3	-	300	77.54	-	-	-
4	100	300	98.0	-	-	-
$NaNO_3$						
1	-	300	29.0	-	-	-
2	100	250	100.0	0.39	2.55	1.77
3	75	250	99.8	0.58	1.74	1.21
NH_4NO_3						
1	-	300	24.2	-	-	-
2	100	250	100.0	0.39	2.55	1.77
3	75	225	100.0	0.58	1.74	1.21
CH_3COONH_4						
1	100	250	98.8	0.39	2.55	1.77
2	75	225	100.0	0.58	1.74	1.21
3	50	200	100.1	1.08	0.93	0.65
4	50	175	101.0	1.08	0.93	0.65

TABLE - 2

Elution Behaviour of Lead in Mixed Solvent System

Pb(II) = 15.0 mg Column = 1.4 x 20 cm

Organic solvents in(%) with 0.75 MHCl	Peak elution volume $V_{max,ml}$	Total elution volume $V_{t,ml}$	Lead recovery (%)	Elution constant (E)	Volume distribution coefficient (D_v)	Weight distribution coefficient (D)
0.75 MHCl	150	300	99.8	-	-	-
Methanol						
20	125	275	99.6	-	-	-
40	100	275	99.9	0.39	2.55	1.77
60	100	275	99.1	0.39	2.55	1.77
80	75	275	86.6	0.58	1.74	1.21
Ethanol						
20	125	275	99.1	-	-	-
40	100	275	99.1	0.39	2.55	1.77
60	75	275	89.8	0.58	1.74	1.21
80	50	275	86.9	1.08	0.93	0.65
2-Propanol						
20	125	275	97.5	-	-	-
40	100	275	95.0	0.39	2.55	1.77
60	75	275	87.8	0.58	1.74	1.21
Acetone						
20	100	250	100.0	0.39	2.55	1.77
40	75	225	100.0	0.58	1.74	1.21
60	50	175	100.0	1.08	0.93	0.65
80	50	150	85.0	1.08	0.93	0.65
1,4 Dioxane						
20	75	225	99.9	0.58	1.74	1.21
40	50	175	100.0	1.08	0.93	0.65
60	50	150	100.0	1.08	0.93	0.65
THF						
20	100	250	100.0	0.39	2.55	1.77
40	75	225	99.9	0.58	1.74	1.21
60	50	175	100.0	1.08	0.93	0.65
80	50	150	90.0	1.08	0.93	0.65

RESULTS AND DISCUSSION

The elution constant (E) and volume and weight distribution coefficients (D_v, D_w) were evaluated as usual (7). On the basis of elution constants, the eluants can be arranged in order of their selectivity as

$$HCl > CH_3COONH_4 > HNO_3 > NH_4NO_3 > NaNO_3 > HClO_4$$

In the presence of 0.75 M hydrochloric acid containing organic solvents the selectivity scale for mixed solvents is

Dioxane > Tetrahydrofuran > Acetone > Ethanol > 2-Propanol > Methanol

Greater than 0.75 M of mineral acids were efficient eluants (7). Hydrochloric acid was the best eluant due to large value of elution constant, sulphuric acid proved to be poor eluant due to precipitation of lead as lead sulphate. Although nitrates of sodium and ammonia were efficient eluants, they were not used in combination of non-aqueous solvents. For 0.75 M hydrochloric acid the peak elution volume was small, it was preferred along with varying concentration of non-aqueous solvents, such as methanol, ethanol, 2-propanol, acetone, 1,4 dioxane and tetrahydrofuran. Tetrahydrofuran, 1, 4 dioxane and acetone were effective in the presence of 0.75 M hydrochloric acid. While methanol, ethanol and 2-propanol were inefficient eluants as there was incomplete elution. However, for the separation of lead from the mixtures at the lower concentrations, they were very much useful.

SEPARATION OF LEAD FROM BINARY MIXTURES

0.25 M hydrochloric acid in 80% acetone was efficient for lead, but not for alkali metals. Hence after sorption of the

binary mixtures containing lead and any of these ions, lead was first eluted with 0.25 M hydrochloric acid in 80% acetone. While all these ions were eluted latter with 2 M hydrochloric acid. Since the elements like thallium (III), germanium (IV), arsenic (III), selenium (IV) and palladium (II) were weakly bound to the resin in comparison with lead, they were eluted first with 0.1 M hydrochloric acid in 60% acetone, followed by elution of lead with 0.25 M hydrochloric acid in 80% acetone.

Manganese (II), iron (III), cobalt (II), copper (II) and nickel (II) were strongly retained by the resin in comparison with lead. Therefore after sorption of binary mixtures containing any of these ions with lead, lead was first eluted with 0.5 M hydrochloric acid containing 40% 1, 4 dioxane, followed by elution of other ions (except nickel 2 M hydrochloric acid) with 1 M hydrochloric acid containing 90% acetone.

As 0.1 M hydrochloric acid in 75% tetrahydrofuran was efficient eluant for zinc (II), cadmium (II), mercury (II), indium (III), tin (IV) and bismuth (III) when sorbed with lead, these ions were eluted first with 0.1 M hydrochloric acid in 75% tetrahydrofuran and lead was eluted latter with 0.25 M hydrochloric acid in 80% tetrahydrofuran.

As 0.75 M hydrochloric acid in 60% 2-propanol was good eluant for lead, lead was separated from alkaline earth and aluminium by eluting it first with 0.75 M hydrochloric acid in 60% 2-propanol, followed by elution of these ions with 4 M hydrochloric acid. Similarly, 0.75 M hydrochloric acid in 60% ethanol was efficient eluant for lead, but not for scandium(III), titanium(IV), uranium(VI) and gallium(III). Hence after sorption of the mixture, lead was first eluted with 0.75 M

TABLE - 3

Ion Exchange Separation of Lead from Binary Mixtures in Mixed Solvent Systems

Foreign ions	Amount added mg	Lead found mg	Recovery of lead %	Eluant for other elements	Eluant for lead
1.					
Li	40.0	10.50	100.0	2M HCl(II)	0.25M HCl in 80% acetone(I)
Na	50.0	10.50	100.0	"	"
K	60.0	10.50	100.0	"	"
Rb	55.0	10.50	100.0	"	"
Cs	50.0	10.50	100.0	"	"
2.					
Tl	40.0	10.50	100.0	0.1M HCl in 60% acetone(I)	0.25M HCl in 80% acetone(II)
Ge	45.0	10.49	99.9	"	"
As	40.0	10.50	100.0	"	"
Se	35.0	10.48	99.8	"	"
Pd	40.0	10.50	100.0	"	"
3.					
Mn	45.0	10.48	99.8	1M HCl in 90% acetone(II)	0.5M HCl in 40% 1,4 dioxane(I)
Fe	30.0	10.49	99.9	"	"
Co	50.0	10.50	100.0	"	"
Cu	40.0	10.48	99.8	"	"
Ni	50.0	10.50	100.0	"	"
4.					
Zn	30.0	10.51	100.1	0.1M HCl in THF 75%(I)	0.25M HCl in 80% THF(II)
Cd	40.0	10.50	100.0	"	"
Hg	50.0	10.49	99.9	"	"
In	45.0	10.50	100.0	"	"
Sn	48.0	10.50	100.0	"	"
Bi	50.0	10.50	100.0	"	"

Contd.

TABLE - 3 (CONTD.)

Foreign ions	Amount added mg	Lead found mg	Recovery of lead %	Eluant for other elements	Eluant for lead
5.					
Mg	40.50	10.49	99.9	4M HCl(II)	0.75M HCl in 60% 2-propanol(I)
Ca	45.0	10.50	100.0	"	"
Sr	50.0	10.50	100.0	"	"
Ba	52.0	10.50	100.0	"	"
Al	48.0	10.50	100.0	"	"
6.					
Sc	40.0	10.50	100.0	4M HCl(II)	0.75M HCl in 60% ethanol(I)
Ti	35.0	10.50	100.0	"	"
U	30.0	10.48	99.8	2M HCl	"
Ga	38.0	10.49	99.9	1M HCl in 90% ethanol (II)	"
Sb	25.0	10.50	100.0	0.25M HCl in 85% ethanol(I)	" (II)
7.					
Y	50.0	10.50	100.0	3M H_2SO_4(II)	0.75M HCl in 20% methanol(I)
La	52.0	10.50	100.0	"	"
Ce	45.0	10.48	99.8	"	"
Th	60.0	10.50	100.0		
Zr	55.0	10.50	100.0		

Eluant (I) : Indicates initial elution of ion.
Eluant(II) : Indicates subsequent elution of ion.

hydrochloric acid in 60% ethanol, scandium (III) and titanium(IV) were latter eluted with 4 M hydrochloric acid, uranium (VI) was eluted with 2 M hydrochloric acid, gallium (III) was eluted with 1 M hydrochloric acid in 90% ethanol. While antimony(III) was eluted first with 0.25 M hydrochloric acid in 85% ethanol when lead was latter eluted.

The separation of lead from yttrium (III), lanthanum (III), cerium (III), thorium (IV) and zirconium (VI) was possible by the exploring the difference in elution behaviour of these ions with 0.75 M hydrochloric acid in 20% methanol. These ions were not eluted before lead, hence after desorption of lead, these ions were eluted with 3 M sulphuric acid.

SEPARATION OF LEAD FROM MULTICOMPONENT MIXTURES

Lead was separated from multicomponent mixtures by exploiting the difference in elution with of hydrochloric acid in the presence of different concentration of non-aqueous solvents.

The mixture of bismuth (III), cadmium (II), lead (II), copper (II) and nickel (II) was separated after sorption, by elution of bismuth (III) with 0.1 M hydrochloric acid in 75% methanol, cadmium (II) with 0.4 M hydrochloric acid in 20% 2-propanol, lead (II) with 0.25 M hydrochloric acid in 80% acetone, copper (II) with 0.75 M hydrochloric acid in 80% tetrahydrofuran, finally nickel (II) was eluted with 2 M hydrochloric acid.

The mixture of iron (III), manganese (II), titanium (IV), barium (II) and lead was separated by eluting lead (II) first with 0.5 M hydrochloric acid in 40% acetone, elution of iron(III) with 0.5 M hydrochloric acid in 80% tetrahydrofuran, elution of

manganese (II) with 0.75 M hydrochloric acid in 90% acetone, elution of titanium (IV) with 2 M hydrochloric acid in 40% 2-propanol, finally elution of barium (II) with 3 M nitric acid.

The mixture of mercury (II), indium (III), lead (II), cobalt (II), and magnesium was resolved by eluting mercury(II) with 0.1 M hydrochloric acid in 20% methanol, indium (III) with 0.5 M hydrochloric acid in 20% tetrahydrofuran, lead (II) with 0.25 M hydrochloric acid in 60% 1, 4 dioxane, cobalt (II) with 1 M hydrochloric acid in 90% acetone and finally magnesium with 2 M hydrochloric acid.

The mixture of eight elements containing bismuth (III), tin (IV), cadmium (II), zinc (II), lead (II), copper (II), manganese (II) and thorium (IV) was passed on column, then bismuth (III) was eluted with 0.25 M hydrochloric acid in 20% methanol, tin (IV) with 0.1 M hydrochloric acid in 60% acetone, cadmium (II) with 0.25 M hydrochloric acid in 75% 2-propanol, zinc (II) with 0.25 M hydrochloric acid in 85% ethanol, lead(II) with 0.25 M hydrochloric acid in 75% acetone, copper (II) with 0.5 M hydrochloric acid in 80% tetrahydrofuran, manganese(II) with 1 M hydrochloric acid in 90% acetone and thorium (IV) with 1 M sulphuric acid.

It was necessary to use successively higher concentration of hydrochloric acid to effect the separation of elements (Table 4). The predominant trend with of non-aqueous solvent was indicated during the sequential separation, as eluant was that it was essential to use increase in concentration of non-aqueous solvents. Those of metal ions which were loosely bound could be eluted with hydrochloric acid in methanol, ethanol or

TABLE - 4

Cation Exchange Separation of Lead from Multicomponent Mixtures

S.No.	Element	Amount added mg	Amount found mg	Recovery (%)	Eluant
1	Bi	10.00	10.0	100.0	0.1M HCl in 75% methanol
	Cd	12.50	12.55	100.4	0.4M HCl in 20% 2-propanol
	Pb	10.50	10.48	99.8	0.25M HCl in 80% acetone
	Cu(II)	12.00	12.00	100.0	0.75M HCl in 80% THF
	Ni	10.00	10.00	100.0	2M HCl
2	Pb	10.50	10.49	99.9	0.5M HCl in 40% acetone
	Fe(III)	9.50	9.50	100.0	0.5M HCl in 80% THF
	Mn	12.50	12.49	99.9	0.75M HCl in 90% acetone
	Ti(IV)	10.0	10.0	100.0	2M HCl in 40% 2-propanol
	Ba	12.0	12.0	100.0	3M HNO_3
3	Hg(II)	10.0	9.95	99.5	0.1M HCl in 20% methanol
	In	12.50	12.48	99.8	0.5M HCl in 20% THF
	Pb	10.50	10.50	100.0	0.25M HCl in 80% dioxane
	Co(II)	15.00	15.00	100.00	1M HCl in 90% acetone
	Mg	10.50	10.45	99.5	2M HCl
4	Zn	10.00	10.00	100.0	0.1M HCl in 80% acetone
	Pb	10.50	10.50	100.0	0.5M HCl in 60% acetone
	Ga	7.50	7.45	99.3	0.5M HCl in 90% ethanol
	U(VI)	10.0	9.98	99.8	1.0M HCl in 90% THF
	Al	10.0	10.0	100.0	2M HCl

Contd.

TABLE - 4 (CONTD.)

S.No	Element	Amount added mg	Amount found mg	Recovery (%)	Eluant
5	Bi	10.0	10.0	100.0	0.25M HCl in 20% methanol
	Sn(IV)	10.0	10.0	100.0	0.1M HCl in 60% acetone
	Cd	8.50	8.50	100.0	0.25M HCl in 75% 2-propanol
	Zn	7.50	7.45	99.3	0.25M HCl in 85% ethanol
	Pb	10.50	10.48	99.8	0.25M HCl in 75% acetone
	Cu(II)	7.50	7.40	98.7	0.5M HCl in 80% THF
	Mn	10.0	9.98	99.8	1M HCl in 90% acetone
	Th	12.50	12.50	100.0	1M H_2SO_4

2-propanol, while those elements which were strongly bound were eluted with hydrochloric acid in acetone, tetrahydrofuran or 1, 4 dioxane. The very strongly bound metal ions were invariably separated with mineral acids without non-aqueous solvents.

ANALYSIS OF LEAD FROM VARIOUS ALLOYS

The sample of alloy was dissolved in aqua-regia, tin was removed as metastannic acid and was determined gravimetrically. After evaporation of excesses acid, the solution was extracted in distilled water and made to appropriate volume. An aliquot of solution was sorbed on the column and different samples of alloys such as brass, gun-metal, lead-bismuth alloy, wood's metal, sealing alloy and bismuth solder were analysed by

TABLE - 5

Chemical Analysis of Lead from Alloy

Alloy	Element	Percentage of element found	Percentage of element present	Eluant
1. Brass	Sn	1.5	1.5	Gravimetry
	Zn	31.0	31.0	0.25M HCl in 85% ethanol
	Pb	1.7	1.7	0.5M HCl in 40% dioxane
	Fe	0.3	0.3	0.25M HCl in 80% acetone
	Cu	64.50	64.60	1.0M HCl in 80% THF
2. Gun-metal	Sn	5.2	5.3	Gravimetry
	Zn	4.3	4.3	0.1M HCl in 80% THF
	Pb	5.8	5.9	0.25M HCl in 80% acetone
	Cu	84.0	84.1	1M HCl in 80% THF
3. Lead-bismuth alloy	Bi	5.30	5.30	0.1M HCl in 75% ethanol
	Pb	93.60	93.70	0.25M HCl in 80% THF
4. Wood's metal	Sn	11.5	11.5	Gravimetry
	Bi	50.0	50.0	0.25M HCl in 20% methanol
	Cd	11.6	11.8	0.5M HCl in 40% ethanol
	Pb	26.0	26.0	0.5 M HCl in 60% acetone
5. Sealing alloy	Sb	7.0	7.0	Gravimetry
	Bi	58.9	59.0	0.1M HCl in 75% methanol
	Pb	34.0	34.0	0.5M HCl in 60% acetone
6. Bismuth solder	Sn	46.0	46.0	Gravimetry
	Bi	26.0	26.0	0.1M HCl in 75% acetone
	Pb	27.0	27.2	0.25M HCl in 80% dioxane

procedure described in Table 5. It is quite clear from table that separations are clear cut. It was possible the quantitative recovery of elements in samples.

With the increasing applications of nuclear energy from the fission products for peaceful purpose, the separation of lead from associated elements such as bismuth, tin, cadmium, zinc and copper is important. The separation of lead from zirconium, titanium, thorium and barium is important as they are found in fission products.

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