

## Solvent Extraction and Adsorption Chromatographic Separation of Lead and Environmental Samples using Crown Ethers

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**Abstract** - A Simple method has been developed for the extractive separation analysis of lead from picric acid solution with dibenzo- 18- crown -6. Insolvent extraction separation studies lead was extracted with 0.01 M dibenzo -18-crown-6 in nitrobenzene from 0.2 M picric acid. It was stripped from the organic phase with 2 M nitric acid and determined spectrophotometrically with 4 (2-pyridylazo) resorcinol disodium salt at 530 nm. In extraction chromatographic separation studies, dibenzo -18-crown-6 was coated on hydrophobic silica gel and extraction separation studies were carried out from 0.045M picric acid solution. Various mineral acids were used as eluents, By proposed methods lead was separated from large number of elements by selective extraction and then stripping/elution. In binary as well as from multicomponent mixtures. The method was applied for the determination of lead in real samples.

### INTRODUCTION

Lead and lead compounds are toxic. The important sources of lead pollution are auto exhaust emission, paint and glass industries, lead storage batteries and low fusible alloy industries. Because of its adverse toxic effects, the need for its reliable determination is well recognized.

Crown ethers are finding increasing applications in extractive separation analysis. Extractive photometric determination of lead was carried out with various crown ethers in presence of chromogenic reagents (1). Eosin was used for the fluorometric determination of lead with 18-crown - 6 (2) and cryptand-222 (3). Kinetics of lead complexation was studied with dibenzo-18-Crown-6 and various cryptands (4). Synergistic extraction studies of lead were carried out using bis (2-ethylhexyl) phosphoric acid . Extraction studies of lead were carried out from mineral acid media in which effect of salting out agent was also studied using nitrate salts. Solvent extraction separation of lead was carried out using cryptand -222B in toluene and eosin(5). Using picrate as a counteraction extraction studies of lead are reported with various Crown ethers (6). Dibenzo-18-Crown-6 was immobilized on polyurethane foam which was then used for the removal of lead from solution containing HBr and picric acid . The sorbents of benzo-15-crown-5 and dibenzo-18 -Crown-6 with molybdophosphoric acid were used to detect lead from water samples (7). Several phenol-formaldehyde crown ether polymers were used for the sorption studies of lead (8).

No systematic efforts have been made for the separation of lead from the associated elements and also from the multicomponent mixture with dibenzo-18-Crown-6 from picrate medium using solvent extraction and extraction chromatographic techniques. This paper describes the systematic investigation of the separation of lead from associated elements using solvent extraction and extraction chromatographic techniques. The method has been extended to the separation of lead from a large number of other elements in binary mixture as well as multicomponent mixtures and also to the analysis of lead from alloy and environmental samples.

### General Procedure

In solvent extraction separation studies, an aliquot of solution containing lead (50 µg) was mixed with picric acid (0.05M) so that its concentration was  $2 \times 10^{-2}$  M in 10ml final total volume. The solution was then transferred to a separating funnel and was equilibrated with 10ml  $\times 10^{-2}$ M crown ether in nitrobenzene for 10 min on a wrist action flask shaker. The two phases were allowed to settle and separate. From the organic phase lead was stripped with 10ml of 2M nitric acid. It was then determined spectrophotometrically with 4-(2-pyridylazo) resorcinol disodium salt (33) at 530nm. The concentration of lead was calculated from the calibration curve.

In extraction chromatographic separation studies, an aliquot of solution containing 50 µg of lead was mixed with  $5 \times 10^{-2}$  M picric acid so as to have its concentration of  $4.5 \times 10^{-2}$  M in final total volume of 10ml. The solution was then passed through the column (preconditioned with  $4.5 \times 10^{-2}$  M picric acid) at a flow rate of 0.5 ml min<sup>-1</sup>. The column was then washed with  $4.5 \times 10^{-2}$ M picric acid and then with water. The lead was then stripped from the column using various mineral acids (described latter). 5ml fractions were collected and after evaporation of acid lead was determined spectrophotometrically at 530nm with PAR. The concentration of lead was computed from the calibration curve.

### RESULTS AND DISCUSSION

Extraction of lead as a Function of Picric Acid Concentration, in Solvent Extraction and Extraction Chromatographic Studies.

### Solvent Extraction Studies :

Lead was extracted with  $1 \times 10^{-2} M$  of various crown ether in nitrobenzene as the diluents. Picric acid concentration was varied from  $5 \times 10^{-3} - 5 \times 10^{-2} M$ . The results show that there was quantitative extraction of lead with dibenzo-18-Crown-6 and 15-Crown-5 from  $1 \times 10^{-2} - 5 \times 10^{-2}$  picric acid. With dibenzo-18-Crown-6 there was quantitative extraction of lead from  $2 \times 10^{-2} - 5 \times 10^{-2}$  Picric acid while with 18 - Crown-6 lead was extracted quantitatively from  $4 \times 10^{-2} - 5 \times 10^{-2}$  M picric acid. There was only 76% extraction at  $1 \times 10^{-2}$  M picric acid with dicyclohexano-24-crown-8, whereas dicyclohexano-18-crown-6 was found to be inefficient extractant for lead with nitrobenzene as the diluents. Further studies were carried out with dibenzo-18-Crown-6 in nitrobenzene.

### Extraction Chromatographic Studies

In order to study the extraction of lead on silica gel coated with dibenzo-18-Crown-6, various experiments were carried out by varying the concentration of picric acid from  $1 \times 10^{-2} - 5 \times 10^{-2}$  M. The studies revealed that there was 20% extraction of lead with  $1 \times 10^{-2}$  M Picric acid, 52% with  $2 \times 10^{-2}$  M 86% with  $3 \times 10^{-2} M$ , 96% with  $4 \times 10^{-2} M$  and there was quantitative extraction of lead with  $4.5 \times 10^{-2}$  M picric acid concentration. Further extraction studies were carried out with  $4.5 \times 10^{-2}$  M picric acid.

### Solvent Extraction Separation of Lead from Multicomponent Mixtures

Molybdenum (VI) can be extracted with dibenzo-18-Crown-6 from 8 M hydrochloric acid, when lead is not extracted, which remains in the aqueous phase. Barium and lead can be extracted with dibenzo-18-crown-6 in nitrobenzene from  $2 \times 10^{-2} M$  picric acid. From the organic phase barium was first stripped with 7M perchloric acid, when lead remained in organic phase, which was then stripped with 2 M nitric acid. Similarly uranium (VI) can be extracted with dibenzo-24-crown-8 from 7 M hydrochloric acid, when lead is not getting extracted. This condition was exploited for the separation of lead from multicomponent mixtures.

A mixture of molybdenum (VI), barium (II), lead (II) and thorium (IV) was separated by extracting molybdenum (VI) from 8 M hydrochloric acid with  $1 \times 10^{-2} M$  dibenzo-18-crown-6 in nitrobenzene, when barium, lead, thorium remained in the aqueous phase. From the organic phase molybdenum was stripped with 2 M nitric acid. The aqueous phase containing lead, barium and thorium was evaporated to dryness and was treated with  $1 \times 10^{-2} M$  dibenzo-18-Crown-6 from  $2 \times 10^{-2} M$  picric acid, when thorium remained in the aqueous phase. From the organic phase barium was stripped with 7M perchloric acid, when lead remained in the organic phase from which lead was stripped with 2M nitric acid.

When a mixture containing uranium (VI), barium (II), lead (II) and aluminium (III) was extracted with  $1 \times 10^{-2}$

M dibenzo-24-crown-8 from 7M hydrochloric acid, barium, lead and aluminium remained in the aqueous phase. From the organic phase uranium was stripped with 2M nitric acid. The aqueous phase containing barium, lead and aluminium was evaporated to dryness and was treated with water from which barium and lead were extracted with  $1 \times 10^{-2} M$  dibenzo-18-crown-6 in nitrobenzene from  $2 \times 10^{-2}$  picric acid, when aluminium remained in the organic phase from which lead was stripped with 2M nitric acid.

The separation of lead from other multicomponent mixture was accomplished in a similar manner.

### Extraction Chromatographic Separation of Lead from Multicomponent Mixture

A mixture containing uranium (VI), lead (II) and barium (II) was mixed with picric acid so that its concentration was  $4.5 \times 10^{-2} M$  in a total volume of 10ml. The solution was then passed through DB-18-Crown-6 column preconditioned at  $4.5 \times 10^{-2} M$  picric acid, at a flow rate of  $0.5 \text{ ml} \cdot \text{min}^{-1}$ . The column was then successively washed with  $4.5 \times 10^{-2}$  M picric acid to remove unextracted element. At this condition uranium (VI) was not extracted hence passed through the column whereas lead and barium were extracted on the column. The extracted lead was eluted with  $1 \times 10^{-2} M$  nitric acid, when barium remained on the column. Barium was then eluted with 2M nitric acid.

The separation of uranium (VI), potassium (I), lead (II); germanium (VI), rubidium (I), lead (II) and cerium (III), rubidium (I), lead (II) were accomplished similarly (Table 3). In all the separations volume of the eluent employed was 30 ml. After stripping uranium, lead, barium, germanium, (IV), cerium (II) the effluent was evaporated to dryness and was extracted with water and these elements were determined spectrophotometrically. Whereas potassium and rubidium were determined by flame emission spectroscopy.

### APPLICATIONS

I. **Tin Base White Metal** : 0.1 gm of tin base white metal (BCS-CRM No.178/2) was dissolved in aqua-regia. Tin was precipitated as metastannic acid and was removed by filtration. The filtrate was evaporated and treated with distilled water and was finally diluted to 50ml. An aliquot of solution was mixed with picric acid and the lead content was determined by both methods of solvent extraction and extractions chromatography as per the general procedure described. The amount of lead found in alloy by both methods, is shown in Table -4.

**II. Environmental Samples**

8) B.S. Mohite, C.D. Jadge and S.R. Pratap, Analyst 115, 1367,(1990)

**Table - 4**
**Determination of Lead in Alloy and Environmental Samples**

No.	Sample	Amount of lead %		
		Present	Found	
			A	B
1	Tin base white metal (BCS-CRM No.178/2)	3.18	3.175	3.15
	Environmental samples	Amount of lead $\mu\text{g/gm}$		
		Present	Found	
			A	B
2	Grass	1700	1690	1696
3	Grass	1650	1658	1652
4	Grass	1570	1578	1580
5	Tree Bark	1230	1220	1230
6	Tree Bark	2490	2500	2486
7	Soil	670	676	680
8	Soil	290	300	292
9	Soil	945	940	950
10	Soil	1430	1434	1426

A = By Solvent Extraction, B = extraction chromatography

2 - (Grass - 4); 3 - (Grass - 8); 4 - (Grass - 19); 5 - (A in tree bark)

6 - (Tree bark from Kherdi village); 7 - (Soil - 11); 8- (Soil - 4)

9 - (Nulla Soil); 10- (Galina Slurry)

( ) samples from various spots from the factory side (34)

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