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Extractive Separation and Determination of Lead in Alloys and Environmental Samples

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A method is proposed for the solvent extraction of lead salicylate using triphenylphosphine oxide as an extractant. The optimum extraction conditions were evaluated from a critical study of effects of pH, sodium salicylate concentration and triphenylphosphine oxide concentration. The probable composition of the species has been deduced from log–log plots and the extraction mechanism is suggested. The method has been used to separate lead from commonly associated elements such as copper, nickel, antimony; and also from chromium, iron, and mercury. The method has been further extended to separate and estimate lead in standard alloys, gasoline, and air-borne particulate samples.

The environmental chemistry of lead owes its importance to the pollution caused by autoexhaust emission. The chief source of atmospheric lead is comprised by the variety of antiknock additives in the gasoline which serves the internal combustion engine. Organic lead poisoning is primarily due to the inhalation of the antiknock additive compound viz. tetraethyllead. Lead and its compounds constitute one of the most important industrial health hazards. It is a cumulative poison; hence the toxicity of lead is not immediately felt. It could remain in the bone immobilized for several years. Chronic exposure to lead causes nephritis, scaring, and shrinking of kidney tissues; while, short but intense exposure causes only functional injury. Premature loss of teeth in lead poisoning, is attributed to a demineralization caused by the chemical displacement of the jaw bone calcium by the lead present in the circulatory blood.

In view of the toxic effects of environmental lead, and its compounds, the separation and estimation of lead from the air-borne particulates is desired.

In the various extraction methods available, use has been made of neutral extractants,1—13) acidic extractants,14—18) and basic extractants.19—26) These methods however, have a shortcoming in that, they require a prolonged shaking period,4,9,13,19) suffer from interference and co-extraction of common cations9,15) and require high acid concentration for extraction.19) It is also conspicuous that none of these methods have been applied for the determination of lead in atmospheric air particulate samples.

The proposed method is simple and rapid. It finds a wide range of applications in the separation and determination of lead from a variety of samples.

Experimental

Apparatus and Reagents. A Pye Unicam SP-200 Spectrophotometer and Varian Techron-Model 70 Atomic Absorption Spectrophotometer were used for absorbance measurements. Measurement of pH values was done on a Control Dynamics pH meter.

The stock solution of lead was prepared by dissolving 2.00 g of lead nitrate in 250 ml of distilled water containing 0.5 ml of concentrated nitric acid. The solution was standardized complexometrically27) using EDTA and test solutions of lower concentration were prepared by suitable dilutions.

A 5% solution of triphenylphosphine oxide (Fluka Grade, mp 156—158 °C) in toluene was used for all extractions.

A 0.1% aqueous solution of 4-(2-pyridylazo)resorcinol was used for spectrophotometric determination of lead.

All other chemincals used were of guaranteed grade and pure, distilled solvents were used throughout the work.

General Extraction Procedure. To an aliquot of solution containing 1 mg of lead, was added 40 mg of sodium salicylate in order to make its concentration of 0.01 M (1 M=1 mol dm^{-3}) in a total volume of 25 ml. The pH of the solution was adjusted to 6.5 with dilute nitric acid and sodium hydroxide solutions. The solution was then transferred to 125 ml separatory funnel and shaken for 90 s with 10 ml of 5% triphenylphoshine oxide in toluene. After separating the two phases, lead was stripped from the organic phase by shaking for 1 min with distilled water (2×10 ml containing 0.5 ml of 0.05 M nitric acid) and estimated complexometrically.27)

For microgram amounts of lead, the extraction was done using 5 ml of 5% triphenylphosphine oxide solution. The lead was backstripped with distilled water (3×4 ml containing a drop of 0.05 M nitric acid) and estimated spectrophotometrically as follows:

The pH of the aqueous solution was adjusted to 6.5; 1 ml of 0.1% aqueous soltion of PAR was added and diluted to 25 ml. The absorbance of the orange-colored complex was measured at 520 nm28) against a reagent blank prepared analogously.

Results and Discussion

Extraction Conditions. The extraction of lead was investigated at varying pH (4.0 — 9.0), salicylate concentration (1.0×10^{-3} — 2.0×10^{-2} M) and triphenylphosphine oxide concentration (1 — 5%). It was observed, that quantitative extraction of lead (in mg amounts) takes place with 10 ml of 5% triphenylphosphine oxide solution from 9.0×10^{-3}—1.0×10^{-2} M sodium salicylate concentration at pH 6.0—6.7. For microgram amounts of lead (25 — 100 μg) quantita-

Table 1. Optimum Conditions for Extraction of Lead

[Pb]	[Salicylate]/M	Triphenylphosphine oxide (5% in toluene)	pH
1—4 mg	9.0×10^{-3}—1.0×10^{-2}	10 ml	6.0—6.7
25—100 μg	9.0×10^{-3}—1.0×10^{-2}	5 ml	6.0—6.7

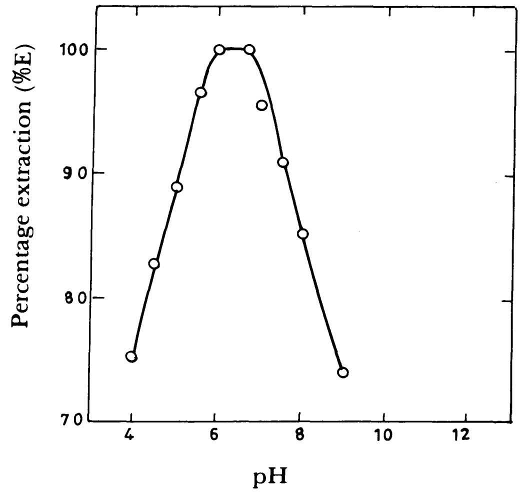

Fig. 1. Extraction behavior of lead salicylate in to triphenylphosphine oxide as a function of pH.
Pb=1 mg; [TPPO]=10 ml of 5% in toluene; [sodium salicylate]=0.01 M; shaking time=90 s.

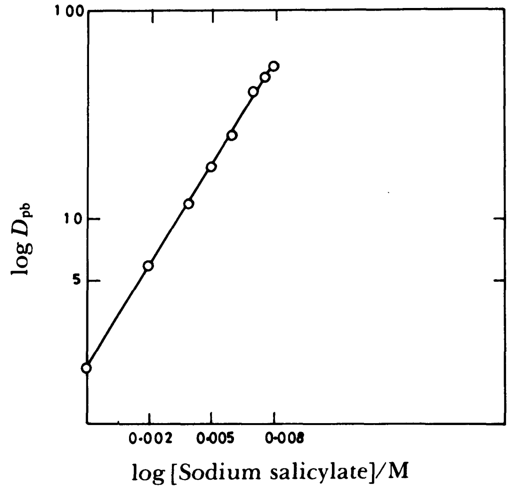

Fig. 3. Distribution ratio of lead(II) as a function of sodium salicylate concentration.
Pb=1 mg; [TPPO]=10 ml of 5% in toluene; pH=6.5; shaking time=90 s.

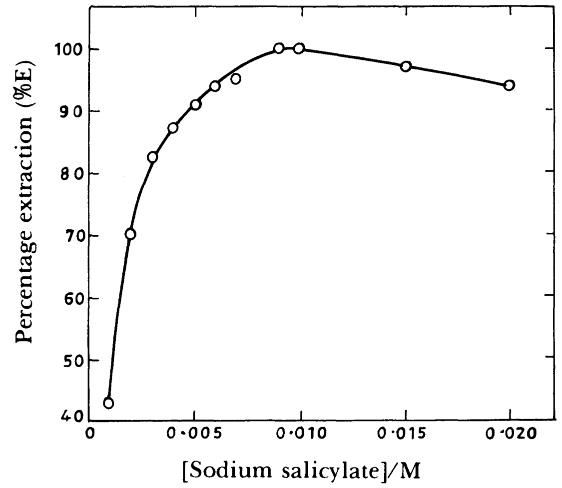

Fig. 2. Extraction behavior of lead salicylate into triphenylphosphine oxide as a function of sodium salicylate concentration.
Pb=1 mg; [TPPO]=10 ml of 5% in toluene; pH=6.5; shaking time=90 s.

Table 2. Distribution Ratio of Pb(II) as a Function of Sodium Salicylate Concentration
Pb=1 mg; extractant=10 ml of 5% triphenylphosphine oxide solution in toluene; pH 6.5.

[Sodium salicylate]/M	%E	*D*
1.0×10^{-3}	43.3	1.91
2.0×10^{-3}	70.2	5.87
3.0×10^{-3}	82.5	11.78
4.0×10^{-3}	87.7	17.77
5.0×10^{-3}	90.9	24.97
6.0×10^{-3}	94.0	39.17
8.0×10^{-3}	95.5	53.05
9.0×10^{-3}—1.0×10^{-2}	100.0	∞

Slope of the plot of $\log D_{Pb}$ vs. $\log C=1.63$.

tive extraction of lead is obtained using 5 ml of 5% triphenylphosphine oxide solution. The optimum extraction conditions are reported in Table 1 and illustrated in Figs. 1 and 2.

Nature of Extracted Species. The log-log plots of distribution ratio versus salicylate concentraion, at fixed pH and triphenylphosphine oxide concentration, (Fig. 3 and Table 2) and versus triphenylphosphine oxide concentration, at fixed pH and sodium salicylate concentration (Fig. 4 and Tabel 3) indicate a molar ratio of 1:2 with respect to both salicylate ion and triphenylphosphine oxide. Hence, the probable extracted species is, $Pb(Sal)_2\cdot2TPPO$ where Sal stands for salicylate ion and TPPO stands for triphenylphosphine oxide. Thus, the probable extraction mechanism can be expressed as:

$$Pb(H_2O)_2^{2+} + 2(HOC_6H_4COO)^- + 2TPPO \rightleftharpoons$$

$$Pb(HOC_6H_4COO)_2\cdot2TPPO + 2H_2O$$

Extracted species

The extraction may be due to the solvation of lead salicylate by triphenylphosphine oxide molecules.

Effect of Foreign Ions. A number of ions were tested for the interference in the extraction of lead. The study showed that for the extraction and photometric estimation of 50 μg of lead, a large number of cations and anions did not interfer (as shown by less than 1% error in analytical recovery of lead). However, ions such as uranium(VI), thorium(IV), and oxalate did offer interference. The results of the study of interfering ions is reported in Table 4.

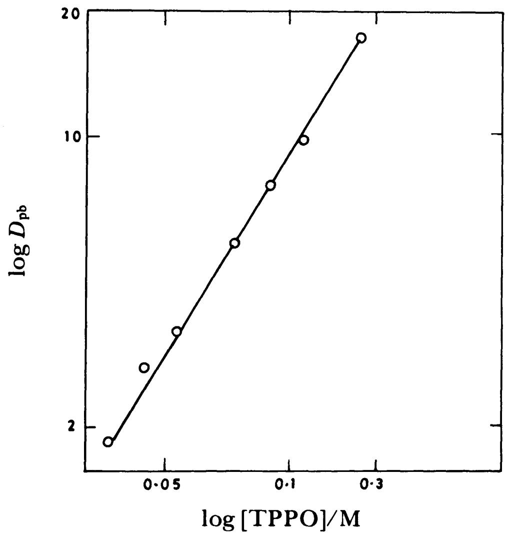

Fig. 4. Distribution ratio of Pb(II) as a function of triphenylphosphine oxide concentration.
Pb=1 mg; [sodium salicylate]=1.0×10^{-2} M; pH=6.5; shaking time=90 s.

Table 3. Distribution Ratio of Pb(II) as a Function of Triphenylphosphine Oxide Concentration
Pb=1 mg; Extractant=10 ml of triphenylphosphine oxide solution in toluene; [Sodium salicylate]=0.01 M; pH=6.5

[TPPO]/%	%E	*D*
1.0	42.7	1.86
1.25	53.0	2.82
1.5	58.1	3.47
2.0	69.2	5.61
2.5	75.6	7.75
3.0	80.0	10.00
4.0	87.7	17.82
5.0	100.0	∞

Slope of the plot of log D_{Pb} vs. log C=1.7.

Separation of Lead from Chromium(VI), Iron(III), Antimony(III), Copper(II), Nickel(II), and Mercury(II). Ions such as chromium(VI) , iron(III), antimony(III), copper(II), and nickel(II) are not extracted into triphenylphosphine oxide under the optimum extraction conditions of lead. Hence, it is possible to separate lead from these elements in their binary mixtures. The unextracted ions were detemined spectrophotometrically using known methods while lead is estimated spectrophotometrically using PAR as described in the general procedure.

Under the extraction conditions of lead, mercury shows partial extraction. However, by selective stripping of lead with distilled water, which does not backstrip mercury, the two ions can be quantitatively separated from each other. The partially extracted mercury is backstripped with acetate buffer (pH 4.7); combined with the major portion of unextracted mercury and estimated complexometrically.[29]

The recovery of lead and the added ions is ≥99.0%. The results of the separation of binary mixtures is reported in Table 5.

Analytical Applications. 1. Analysis of Alloys. 0.5 g of each of two different standard alloys containing lead, were weighed accurately. Then, 10 ml of concentrated nitric acid was added to each of them and were evaporated to dryness. The residue was taken up with dilute nitric acid (4 M) and the precipitate of metastannic acid was filtered off. The filtrate was diluted to 50 ml and an aliquot of this solution was used for the extraction and estimation of lead using the proposed method.

2. Analysis of Gasoline. 25 ml of Gasoline containing tetraethyllead was evaporated slowly on a water bath (≃80 °C) to remove all the volatile liquids. To the oily residue, 3 ml of concentrated nitric acid was added, slowly, with due care, in order to convert organolead to lead nitrate. This was heated on a water bath for 20 minutes. After cooling, the oily part was removed by extracting it with benzene while the lead

Table 4. Effect of Possible Interfering Ions on the Extraction of 50 μg of Lead(II)[a]

Tolerance limit/μg	Foreign ions
1000	As(III), Sb(III), Ca(II), Fe(III), Cr(VI), Mn(II), Hg(II), Mg(II), F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}, SCN^-, $S_2O_3^{2-}$
750	Zr(IV), Al(III)
500	Ag(I), Ba(II), Sr(II), Pd(II), Au(III), Te(IV), V(V)
250	Se(IV), ascorbate
100	Ni(II), Co(II), Bi(III)
50	Cu(II), Pt(IV), PO_4^{3-}
Ions not tolerated	U(VI), Th(IV), Oxalate

a) Spectrophotometric estimation.

Table 5. Separation of Pb(II) from Cr(VI), Fe(III), Ni(II), Cu(II), and Hg(II) in Their Synthetic Binary Mixtures

Sr. No.	Composition/μg	Recovery of Pb(II)[a]/%	Relative error/%	Recovery of added ion/%	Relative error/%	Estimation procedure for added ions and their references
1.	Pb(II), 50; Sb(III), 100	99.8	0.2	99.8	0.2	Photometrically with KI (30)
2.	Pb(II), 50; Sb(III), 250	99.9	0.1	99.8	0.2	Photometrically with KI (30)
3.	Pb(II), 50; Cr((VI), 10	99.7	0.3	99.0	1.0	Photometrically with diphenyl carbazide (31)
4.	Pb(II), 50; Cr(VI), 20	99.5	0.5	99.2	0.8	Photometrically with diphenyl carbazide (31)
5.	Pb(II), 50; Fe(III), 50	99.7	0.3	99.3	0.7	Photometrically with 1,10-phenanthroline (30)
6.	Pb(II), 50; Fe(III), 100	99.6	0.4	99.4	0.6	Photometrically with 1,10-phenanthroline (30)
7.	Pb(II), 50; Ni(II), 50	99.2	0.8	99.5	0.5	Photometrically with dimethyl glyoxime (30)
8.	Pb(II), 50; Cu(II), 25	99.5	0.5	99.1	0.9	Photometrically with PAN (32)
9.	Pb(II), 50; Hg(II), 1000	99.1	0.9	99.0	1.0	Complexometrically with EDTA (29)

a) Mean of 6 determinations.

Table 6. Analysis of Lead in Real Samples

Sr. No.	Sample	Lead content (Certified)	Results found by the proposed method	
			Spectrophoto metrically[a]	By AAS
1.	Tin base white metal (179/2)[b]	3.18%	3.10%	3.08%
2.	White metal (8d)[b]	3.26%	3.21%	3.22%
3.	Gasoline	—	5.33 ppm	5.31 ppm
4.	Air-borne particulate samples			
	(a) Tilaknagar area	—	2.36 μg m^3	2.35 μg m^3
	(b) Khar area (I)	—	0.36 μg m^3	0.36 μg m^3
	(c) Khar area (II)	—	0.52 μg m^3	0.52 μg m^3
	(d) Khar area (III)	—	1.03 μg m^3	1.03 μg m^3
	(e) Parel area	—	0.68 μg m^3	0.70 μg m^3

a) Mean of 6 results. b) British Standard Alloys.

nitrate formed in situ was estimated by recommended procedure.

3. Analysis of Air-Borne Particulates. Filter paper strips containing adsorbed lead particles from polluted air samples were supplied by Air Pollution Monitoring and Research Laboratory, Municipal Corporation of Greater Bombey, Khar. The samples belonged to different subrban areas of Bombay such as Parel, Khar, and Tilaknagar. The separation and determination of lead in these glasswool filter papers (containing adsorbed air particulates) were done as follows:

Sample filter paper strips (8 sq cm area) were digested with 10 ml of 50% nitric acid for about 15 minutes. This was then diluted with distilled water to 15 ml volume and filtered to remove the insoluble glasswool filter paper residue and other dust particles. The filtrate was used for the extration and estimation of lead by the proposed method.

The results of the above sample analysis are reported in Table 6. All the samples were also analyzed for comparison of results, using Atomic Absorption Spectrophotometer. The results so obtained were in good agreement with each other.

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References

1) T. N. Tweeten and J. W. Knoeck, *Anal. Chem.*, **48**, 64 (1976).

2) B. I. Petrov, M. I Degtev, and V. P. Zhivopestev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **20**, 681 (1977).

3) Y. Akama, H. Naka, T. Nakai, and F. Kawamura, *Bunseki Kgaku*, **27**, 680 (1978).

4) M. V. R. Murti and S. M. Khopkar, *J. Indian Chem. Soc.*, **55**, 735 (1978).

5) I. Yasoo, T. Tsuzuki, and K. Inoue, *Hokkaidoritsu*

Eisei Kenkyushoho, **30**, 98 (1980).

6) A. Atonso, M. Gallego, and M. Valcarcel, *Bunseki Kagaku,* **32**, E-387 (1985).

7) J. Wang, *Huaxe Tongbao,* **7**, 37 (1986).

8) V. V. Mudshingikar and V. M. Shinde, *Indian J. Chem., Sect. A,* **23**, 539 (1984).

9) S. B. Akki and S. M. Khopkar, *Bull. Chem. Soc. Jpn.,* **45**, 167 (1972).

10) A. A. Yadav and S. M. Khopkar, *Talanta,* **18**, 833 (1971).

11) A. Sanz-Medel, D. Blanco Gomis, E. Fuente, and S. Arribas Jimeno, *Talanta,* **31**, 515 (1984)

12) V. V. Yashin, M. B. Korshunov, and M. T. Tolmachova, *Zh. Anal. Khim.,* **40**, 469 (1985).

13) J. W. O'Laughlin and T. P. O'Brion, *Talanta,* **22**, 587 (1975).

14) R. Pietsch, *Anal. Chim. Acta,* **115**, 379 (1980).

15) U. S. Ray, *Indian J. Chem., Sect. A,* **21**, 444 (1982).

16) U. S. Ray, and S. C. Modak, *J. Indian Chem. Soc.,* **61**, 245 (1984).

17) J. Chwastowoska, E. Kosiarska, and G. Maciejko, *Chem. Anal. (Warsaw),* **22**, 927 (1977).

18) R. Pietsch and P. T. Gilani, *Anal. Chim. Acta,* **75**, 385 (1975).

19) E. Uhlemann, B. Maack, and M. Raab, *Anal. Chim. Acta,* **116**, 403 (1980).

20) S. Werner, *Z. Chem.,* **20**, 383 (1980).

21) T. Suzuki and T. Sotobayashi, *Jpn. Analyst,* **12**, 910 (1964).

22) P. S. Patil and V. M. Shinde, *Sepn. Sci. Technol.,* **14**, 247 (1979).

23) B. Yu. Spivakov, V. I. Lebede, V. M. Shkinus, N. P. Krivenkova, T. S. Plotnikova, I. P. Kharlamev, and Yu. A. Zolotov, *Z. Anelit. Khim.,* **31**, 757 (1976).

24) G. K. de Jong, W. T. Kok, and U. A. T. Brinkman, *J. Chromatogr.,* **135**, 249 (1977).

25) C. W. McDonald, M. M. Mahayni, and M. Konjo, *Sepn. Sci. Technol.,* **135**, 429 (1978).

26) S. P. Rao, R. R. Reddy, and J. Jagdamba, *Acta Cienc. Indica (Ser.) Chem.,* **9**, 235 (1983).

27) A. I. Vogel, "A Text book of Quantitative Inorganic Analysis," 3rd ed, Longmans, London (1961), p. 443.

28) N. M. Malakhova, N. L. Olenovich, and N. I. Kotelnaya, *Zh. Anal. Khim.,* **35**, 475 (1980).

29) F. J. Welcher, "The Analytical Uses of EDTA," ed by D. Van Nostrand, New York (1961), p. 164.

30) Z. Marczenko, "Spectrophotometric Determination of Elements," Wydawnictwa-Nauko-Techniczne and Ellis Harwood Publisher (1976), pp. 127, 311, 372.

31) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed, Interscience, New York (1961), p. 397.

32) B. F. Pease and M. B. Williams, *Anal. Chem.,* **31**, 1044 (1959).