

Separation of divalent lead from ayurvedic (herbal) medicines and alloys using extraction chromatography

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A selective, sensitive, less expensive and more precise method has been developed for the separation of lead(II) using *N-n*-octylaniline (liquid anion exchanger) coated silica gel as stationary phase. The quantitative extraction of lead(II) is found with 0.087 mol/L⁻¹ *N-n*-octylaniline and 0.007 - 0.15 mol/L⁻¹ ascorbic acid at pH 9.0. The extracted lead(II) has been eluted from the column with 0.5 mol/L⁻¹ hydrochloric acid and analyzed by spectrophotometric method. The probable composition of the extracted species is deduced from log-log plots and extracted species is found to be [2RR'NH₂⁺.Pb(C₆H₇O₆)₄²⁻]_(org.). The optimum extraction conditions are evaluated from a critical study of effects of pH, ascorbic acid concentration, *N-n*-octylaniline concentration and elution time. The proposed method is found simple and efficient as it avoids large number of cation and anion interferences. Lead(II) is successfully separated from binary mixtures with bismuth(III), gold(III) and osmium(VIII). The method is also extended for separation of lead(II) from ayurvedic medicine and synthetic mixtures corresponding to alloys.

Keywords: Alloys, Ayurvedic medicine, Extraction chromatography, Lead(II), *N-n*-octylaniline

Lead is a toxic and relatively rare element (10⁻³ wt%), but is well known for its technical importance. Lead and its compounds constitute one of the most important industrial health hazards and also the major soil contaminant. It has low reactivity and solubility and due to this reason lead poisoning occurs in many cases, where lead is dispersed, like sanding lead based paint, long term exposure in the case of pewter tableware. Even in trace level, it decreases enzymatic and kidney function and causes neuromuscular difficulties¹. Obviously, trace level separation of metallic toxicant lead(II) poses a challenging problem to the analytical chemists.

The most widely used techniques for the separation and preconcentration of trace level of lead(II) includes reverse osmosis², liquid-liquid extraction^{3,4}, coprecipitation^{5,6}, ion-exchange⁷, adsorption^{8,9}, cloud point extraction¹⁰, electrochemical deposition¹¹ and solid phase extraction (SPE)¹²⁻¹⁴. Solid phase extraction is an effective alternative, when the metals are in large volumes of relatively low concentrations. Extraction chromatographic separation of lead(II) was carried out with Versatic 911¹⁵ and Versatic10¹⁶

(liquid cation exchangers) coated on silanised silica gel from acetate buffer media. The effect of pH on R_f values in ion exchange paper chromatography has been studied. The method was used for separation of lead(II) from synthetic multi-component mixtures, industrial waste and standard alloy samples using its preconcentration on the column. Lead can be separated by extraction chromatography using bis (2-ethyl hexyl) phosphoric acid coated on silica gel as a stationary phase in 0.01 mol/L⁻¹ hydrochloric acid¹⁷. Modified silica gel by thiosalicylic acid was used as a reagent for extraction and concentration of lead ions from aquatic samples and determined with FAAS¹⁸. To desorb the lead ions, 4.0 mol/L⁻¹ nitric acid is required. 4-propyl-2-thiouracil¹⁹ coated on activated charcoal was preconcentrate copper(II), nickel(II), cobalt(II) and lead(II). These metals were simultaneously determined by AAS but separation was not achieved. The separation of lead(II) from cadmium(II), bismuth(III), indium(III) and vanadium(V) was carried out with 60% acetone from a column of AG50W-X8 cation-exchange resin²⁰ by taking advantage of difference in their stripping agents. Extraction of lead, nickel, zinc and copper was carried out with hexamethylenammonium hexamethylenedithiocarbamate (HMA-HMDC) and reversed-phase liquid

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chromatography using Cosmosil 5 C-18, (4.6×250 mm) column. This method was used to determine these metals from citrus leaves and rice flour²¹.

Uranium(VI) and lead(II) were extracted from sodium salicylate solution with high molecular-weight amines, viz. aliquat 336, TOA, TIOA, amberlite LA-1 or amberlite LA-2 in xylene²². This method permits separation of uranium and lead from binary mixtures with commonly associated metal ions and from air samples. Cyanex 302²³ was used as an extractant for solvent extraction of lead(II) in phosphoric acid media. In this method, extraction of lead was strongly dependent on phosphoric acid concentration. 2-Octylaminopyridine²⁴ was used as an extractant for solvent extraction separation of lead(II) in sodium succinate media at pH 10. Though lead(II) is separated from other toxic metals, excess reagent gives adverse effect on extraction which requires multiple stripping and minimum equilibration time of 4 min. Tributyl phosphine oxide²⁵ was used for solvent extraction of lead(II) from salicylate media. The method was applied for separation of lead(II) and copper(II) from various samples. Lead(II) was quantitatively extracted with tributyl phosphate²⁶ in 3.0 mol/L hydrochloric acid but method suffers from high reagent concentration (30%) and it requires lithium chloride (2 mol/L⁻¹) as a salting out agent.

The extensive use of organic solvents is no longer desirable as these are expensive and harmful to the environment and health. A number of methods have been developed which are solvent free or low solvent consumption methods. Among these, solid phase extraction reduces the limitations of liquid-liquid extraction (LLE). Recently in our laboratory *N-n*-octylaniline was applied for solid phase extraction of aluminium(III)²⁷, copper(II)²⁸, gold(III)²⁹, palladium(II)³⁰, ruthenium(III)³¹ and manganese(II)³². In the present work, extraction of lead(II) was achieved from ascorbic acid media with *N-n*-octylaniline (liquid anion exchanger) coated on silica gel as a stationary phase. Lead(II) was quantitatively extracted from 0.01 mol/L⁻¹ ascorbic acid at pH 9.0 and eluted with 0.5 mol/L⁻¹ hydrochloric acid. The method is applied for separation of lead(II) from binary mixtures, ayurvedic (herbal) medicine and synthetic mixtures corresponding to alloys.

Experimental Procedure

Apparatus

An Elico spectrophotometer model SL-159 with 10 mm path length quartz cell and a control

hydrodynamic pH meter were used to measure absorbance and adjust the required pH.

Reagents

All the chemicals used were of analytical grade. Double distilled water was used throughout the experimental work. A stock solution of lead(II) was prepared by dissolving 0.39937g of lead(II)nitrate [Pb(NO₃)₂] (make Qualigens) in 250 mL of distilled water and standardized using gravimetric method³³. A working solution containing 50 µg mL⁻¹ lead(II) was prepared by further dilution.

Ascorbic acid (Vitamin C) and hydrochloric acid were provided by Merck India Ltd. and 4-(2-pyridylazo) resorcinol disodium salt (PAR) by S.D. Fine Chem. Ltd. Other standard solutions of different metal ions used for the study of effect of foreign ions on the extraction were prepared by dissolving their corresponding salts in dilute hydrochloric acid. The solutions of anions were prepared by dissolving respective sodium salts in distilled water. The *N-n*-octylaniline was prepared by the method reported by Gardlund³⁴ and its dilutions were prepared in chloroform.

Preparation of anion exchange material

A portion of 5.0 g silicated silica gel³⁵ was soaked with 0.087 mol L⁻¹ *N-n*-octylaniline which was previously equilibrated with ascorbic acid (0.01 mol/L⁻¹) at pH 9.0 for 10 min, the solvent was evaporated to get nearly dried gel using rotary vacuum evaporator. The slurry of *N-n*-octylaniline coated silica gel in distilled water was prepared by centrifugation at 2000 r min⁻¹. Then the coated silica gel was packed into chromatographic column to give a 6.0 cm bed height. The bed was covered with a glass wool plug.

General procedure for extraction and estimation of lead(II)

An aliquot solution containing 100 µg lead(II) was made up to 25.0 mL by adjusting the concentration of ascorbic acid to 0.01 mol/L⁻¹ and pH 9.0. It was passed through the column containing 0.087 mol/L⁻¹ *N-n*-octylaniline coated on silica gel at a flow rate of 1.0 ml min⁻¹. After extraction, lead(II) was eluted with 25 mL (0.5 mol/L⁻¹) hydrochloric acid and determined by spectrophotometric method³⁶.

Results and Discussion

Effect of ascorbic acid concentration on extraction of lead(II)

Hundred microgram (100.0 g) lead(II) in 25.0 mL aqueous solution was extracted by varying ascorbic acid concentration from 0.001 mol/L⁻¹ to 0.70 mol/L⁻¹

with 0.087 mol/L⁻¹ N-*n*-octylaniline as the stationary phase on silica gel. The percentage extraction of lead(II) initially increases with increase in ascorbic acid concentration, becomes quantitative at 0.007-0.15 mol/L⁻¹ and then decreases (Fig. 1). Hence, all the extractions were carried out at 0.01 mol/L⁻¹ ascorbic acid at pH 9.

Effect of pH on extraction of lead(II)

The extraction of lead(II) was studied in a pH range 4.5-12 (Table 1). Metal ion was quantitatively extracted in 0.01 mol/L⁻¹ ascorbic acid media at the pH range 5-10. This shows that the equilibrium at pH range 5-10 is favorable for the formation of ion-pair complex from ascorbic acid medium. Hence, all the extractions were carried out at pH 9.

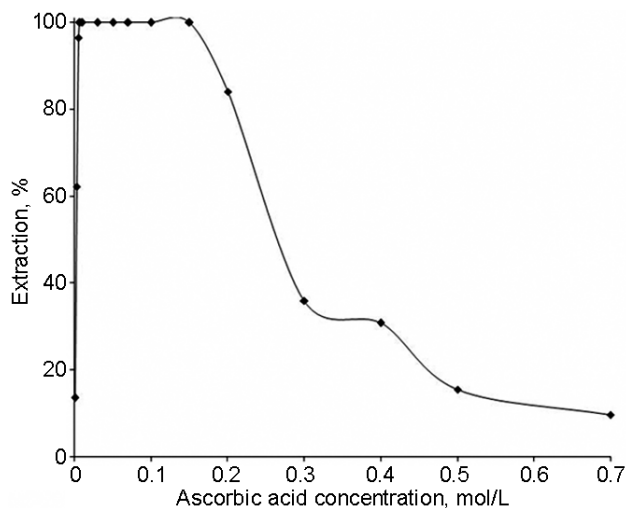


Fig. 1—Extraction of lead(II) as a function of ascorbic acid concentration

Table 1—Extraction behavior of lead(II) as a function of pH [Pb(II) 100 µg; ascorbic acid 0.01 mol L⁻¹; eluent 0.5 mol L⁻¹ hydrochloric acid; N-*n*- octylaniline 0.087 mol L⁻¹ and flow rate 1.0 mL min⁻¹]

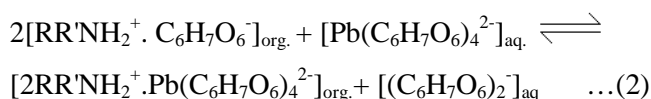
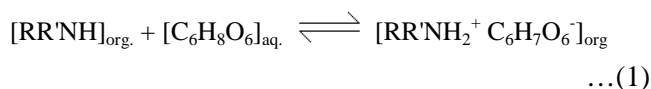
pH	Percentage extraction (%E)	Distribution coefficient (K _d)
4.5	42.0	0.72
4.75	75.9	3.15
5	99.9	999.0
6	99.9	999.0
7	99.9	999.0
8	99.9	999.0
9	99.9	999.0
10	99.9	999.0
11	89.6	8.62
12	44.7	0.81

Effect of flow rate on percentage extraction of lead(II)

The effect of flow rate on percentage extraction of lead(II) has been studied from 0.5 mL min⁻¹ to 4.0 mL min⁻¹. It is observed that the increase in flow rate is inversely proportional to percentage extraction. Therefore, normal flow rate is kept 1.0 mL min⁻¹ for further extraction studies.

Effect of N-*n*-octylaniline concentration on extraction of Pb(II)

The concentration of N-*n*-octylaniline varies from 0.022 mol/L⁻¹ to 0.109 mol/L⁻¹ over ascorbic acid concentration 0.005-0.05 mol/L⁻¹ at 1.0 mL min⁻¹ flow rate for lead(II). It is found that for quantitative extraction of lead(II), 0.087 mol/L⁻¹ N-*n*-octylaniline is sufficient in 0.01-0.05 mol/L⁻¹ ascorbic acid media. An increase in N-*n*-octylaniline concentration increases the percentage extraction of lead(II). Log-log plot of N-*n*-octylaniline concentration versus log of distribution coefficient (Fig. 2) at 0.005-0.007 mol/L⁻¹ of ascorbic acid gives slopes 2.3 and 2.4 respectively. The probable composition of metal to amine ratio is calculated as 1:2. It indicates that the probable extracted species is [2RR'NH₂⁺. Pb(C₆H₇O₆)₄²⁻]_{org}. The extraction mechanism can be explained as follows:



where R = -C₆H₅ R' = -CH₂(CH₂)₆CH₃

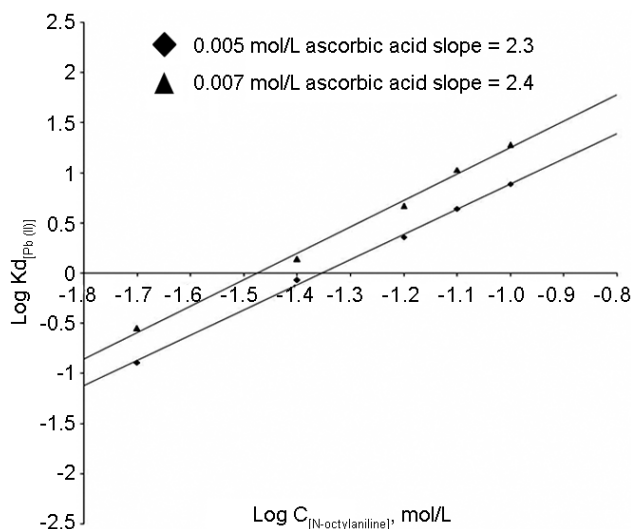


Fig. 2—Log-log plot of distribution coefficient versus N-*n*-octylaniline concentration at 0.005 and 0.007 mol L⁻¹ ascorbic acid

Effect of eluting agent

The elution study of lead(II) was carried out using hydrochloric acid (0.05-5.0 mol/L⁻¹), sulphuric acid (0.1-2.5 mol/L⁻¹), perchloric acid (0.05-6.0 mol/L⁻¹), hydrobromic acid (0.1-3.0 mol/L⁻¹), nitric acid (0.1-3.0 mol/L⁻¹), sodium hydroxide (0.1-3.0 mol/L⁻¹) and ammonia (0.1-2.5 mol/L⁻¹). The elution of lead(II) is found quantitatively from column in 0.5 mol/L⁻¹ hydrochloric acid. Maximum elution of lead(II) is observed in sulphuric acid 99.9%, perchloric acid 99.9%, hydrobromic acid 99.9% and nitric acid 99.3%. In sodium hydroxide and ammonia there is no elution of metal ion. Hydrochloric acid is used for elution of lead(II) in further study.

Effect of foreign ions

Various amounts of foreign ions have been added to a fixed amount of lead(II) (100 µg) to study the effect of interference according to the recommended procedure. The tolerance limit is set at the amount required to cause ± 1.5% error in the recovery of

lead(II) (Table 2). It is observed that the method is free from interference for large number of cations and anions. The cations showing interferences in the method are uranium(VI), zinc(II), iron(III) and mercury(II).

Applications**Analysis of lead(II) from synthetic mixtures corresponding to alloys**

Validity of the method is confirmed by applying it for the separation of lead(II) from synthetic mixtures corresponding to alloys. However, the real samples are not available at the working place, which forces us to use synthetic mixtures corresponding to the composition of alloys. The composition of alloys has been prepared for sealing alloy, wood-metal alloy, lead-bismuth alloy, bismuth solder alloy and solder alloy in laboratory and the proposed method has been applied for the separation of lead(II) (Table 3). The results obtained are in good agreement with the certified values.

Table 2—Effect of foreign ions
[Pb(II) 100 µg; ascorbic acid 0.01 mol L⁻¹; pH 9.0; eluent 0.5 mol L⁻¹ hydrochloric acid; N-n- octylaniline concentration 0.087 mol L⁻¹ and flow rate 1.0 mL min⁻¹]

Foreign ion	Added	Tolerance limit µg, lead(II)	Foreign ion	Added	Tolerance limit, µg lead(II)
Sb(III)	Sb ₂ O ₃	300	W(IV)	Na ₂ WO ₄ ·2H ₂ O	300
Cr(VI)	K ₂ Cr ₂ O ₇	300	In(III)	InCl ₃	150
Cu(II)	CuSO ₄ ·5H ₂ O	50	Ni(II)	NiCl ₂ ·6H ₂ O	300
Mn(II)	MnCl ₂ ·6H ₂ O	50	Ir(III)	IrCl ₃ ·xH ₂ O	300
V(V)	V ₂ O ₅	50	Fe(II)	FeSO ₄ ·7H ₂ O	50
Tl(III)	TlNO ₃	100	Bi(III)	Bi(NO ₃) ₃	300
Cd(II)	3CdSO ₄ ·8H ₂ O	50	Os(VIII)	O ₅ O ₄	100
Sn(II)	SnCl ₂	200	Rh(III)	RhCl ₃ ·xH ₂ O	300
Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄ ·2H ₂ O	300	Ru(III)	RuCl ₃ ·xH ₂ O	300
Ag(I)	AgNO ₃	300	EDTA	EDTA(Disodium salt)	100
Mg(II)	MgCl ₂ ·6H ₂ O	300	Tartrate	C ₆ H ₆ O ₆	300
Co(II)	CoCl ₂ ·6H ₂ O	50	Malonate	CH ₂ (COONa) ₂	300
Ti(IV)	TiO ₂	300	Oxalate	(COOH) ₂ ·2H ₂ O	300
Ga(III)	GaCl ₃	300	Succinate	(CH ₂ COONa) ₂ ·6H ₂ O	300
Al(III)	AlCl ₃	200	Citrate	C ₆ H ₈ O ₇ ·H ₂ O	300
Au(III)	HAuClO ₄ ·H ₂ O	100	Thiourea	SN ₂ H ₄ C	200

Table 3—Analysis of lead(II) from synthetic mixtures corresponding to alloys
[Ascorbic acid 0.01 mol L⁻¹; pH 9.0; eluent 0.5 mol L⁻¹ hydrochloric acid; N-n-octylaniline concentration 0.087 mol L⁻¹ and flow rate 1.0 mL min⁻¹]

Alloy sample composition	Pb(II) taken, µg	Pb(II) found, µg	Mean (n=3)	Recovery, % (n=3)	Confidence limit	RSD, % (n=3)
Sealing alloy (Bi 58; Pb 36; Sb 6)	100.0	99.5, 99.4, 99.6	99.5	99.5	99.47 – 99.53	0.10
Wood metal alloy (Bi 50; Pb 26; Sn 13.3; Cd 10)	100.0	99.5, 99.3, 99.6	99.5	99.5	99.46 – 99.54	0.15
Lead bismuth alloy (Pb 84.6; Bi 15.4)	100.0	99.4, 99.5, 99.5	99.5	99.5	99.49 – 99.52	0.06
Bismuth solder alloy (Bi 27.5; Pb 27.5 Sn 45)	100.0	99.6, 99.7, 99.6	99.6	99.6	99.56 – 99.64	0.15
Solder alloy (Pb 40 ; Sn 60)	100.0	99.7, 99.7, 99.6	99.7	99.7	99.69 – 99.72	0.06

Table 4—Separation of lead(II) from binary mixtures
[N-n-octylaniline 0.087 mol L⁻¹; eluent 25 ml 0.5 mol L⁻¹ hydrochloric acid; ascorbic acid 0.01 mol L⁻¹;
pH 9.0 and flow rate 1.0 mL min⁻¹]

Mixture*	Chromogenic ligand	Taken, µg	Found, µg	Recovery, %	Confidence limit	RSD, %
Pb(II) + Bi(III)	PAR	100.0	99.66	99.7	99.60 – 99.72	0.22
	KI	100.0	99.58	99.6	99.53 – 99.63	0.21
Pb(II) + Au(III)	PAR	100.0	99.71	99.7	99.64 – 99.78	0.26
	SnCl ₂	100.0	99.51	99.5	99.43 – 99.59	0.30
Pb(II) + Os(VIII)	PAR	100.0	99.78	99.8	99.72 – 99.84	0.23
	Thiourea	100.0	99.80	99.8	99.76 – 99.84	0.14

* Lead(II) gets extracted; and bismuth(III), gold(III) and osmium(VIII) remain in aqueous phase.

Table 5—Separation of lead(II) from ayurvedic (herbal) medicine (n=3)
[Ascorbic acid 0.01 mol L⁻¹; pH 9.0; eluent 0.5 mol L⁻¹ hydrochloric acid; N-n-octylaniline concentration 0.087 mol L⁻¹ and
flow rate 1.0 mL min⁻¹]

Pharmaceutical sample	Pb(II)		Recovery, %	Confidence limit	% RSD
	Added, µg	Found, µg			
Nag Bhasma (Batch No. 2109) [Koral Pharmaceuticals]	100.0	99.43	99.4	99.30 – 99.56	0.52
Ekgangweer Ras (Batch No. 165) [Shree baidyanath Ayurved Bhavan Pvt. Ltd.]	280.0	278.0	99.3	277.94 – 278.06	0.36
Garbhupal Ras (Lot No. 52 GM10) [Shree Bhuvaneshwari Aushadhashram Gondal]	80.0	79.5	99.4	79.45 – 79.56	0.19
Tribang Bhasma (S.Y.S.) (Batch No. 106), [Shree Akshar Pharmaceuticals Pvt. Ltd.]	247	245.4	99.4	245.37 – 245.43	0.20

Separation of lead(II) from binary mixtures

Synthetic binary mixtures of lead(II) with bismuth(III), gold(III) and osmium(VIII) were prepared. The separations of these mixtures were carried out using the proposed method. The results are reported in Table 4.

Separation of lead(II) from ayurvedic samples

The ayurvedic samples like Nag Bhasma, Ekgangweer Ras, Garbhupal Ras, Tribang Bhasma containing lead(II) were prepared as solutions by wet digestion³⁷ method. The solution was filtered and then diluted to 50 ml and analysed for lead content by the proposed method. The results are found in good agreement with the certified values (Table 5).

Conclusion

Method is simple, rapid and reproducible. Extraction of lead(II) requires low concentration of N-n-octylaniline. Method is free from large number of foreign ions. The method gives separation of lead(II) from alloys, viz. sealing alloys, wood metal alloy, lead bismuth alloy, bismuth solder alloy and solder alloy. It permits separation of lead(II) from ayurvedic samples and associated metals, viz. bismuth(III), gold(III) and osmium(VIII).

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