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Extraction behaviour of 2-octylaminopyridine towards lead(II) from succinate media and its separation from other toxic metals

Chandrashekhar P. Mane, Mansing A. Anuse*

Analytical Chemistry Laboratory, Department of Chemistry,
Shivaji University, Kolhapur 416004, India

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Abstract

Liquid–liquid extraction of lead(II) from succinate media was carried out with 2-octylaminopyridine (2-OAP) in chloroform. Lead(II) was quantitatively extracted with 0.036 M 2-OAP in chloroform from 0.005–0.007 M sodium succinate when equilibrated for 5 min. Lead(II) from the organic phase was stripped with three 10 mL portions of 0.4 M acetic acid and determined titrimetrically with EDTA. The nature of extracted species was determined from the log–log plot. The optimum conditions have been evaluated based on a critical study of weak acid concentration, extractant concentration, period of equilibration and effect of diluents. The metal loading capacity of the reagent was found to be 8 mg of lead(II) with 10 mL 0.036 M of the extractant. The extraction of the lead(II) was carried out in presence of various ions to ascertain the tolerance limit of individual. Temperature dependence of the extraction equilibrium constants was examined to estimate the apparent thermodynamic functions (ΔH, ΔS and ΔG) for extraction reaction. Lead(II) was successfully separated from commonly associated metal ions such as Bi(III), Hg(II), Cr(VI), Cd(II), Zn(II), Al(III), Ca(II), Ba(II) and from binary and ternary mixtures. The method was extended for determination of lead(II) in real samples.

Keywords: Extraction; Lead(II); 2-OAP; Succinate media; Separation from toxic metals

1. Introduction

Lead is one of the most used metal in industry; being just surpassed by other metals as iron, copper, zinc and aluminium. The main application of lead and of its oxide (PbO) is producing electrical batteries for vehicles. Almost 80% of all the lead now used in the US is for the production of lead-acid batteries. Lead alloys are largely used in industry. The addition of a small percentage of arsenic or antimony, to the lead, increases its hardness and mechanical resistance, protecting it from abrasion. The calcium–lead and the tin–lead alloys are used in coating certain electrical cables. Current solder is a lead–tin alloy, in variable proportions in agreement with the requested melting point. The bismuth, cadmium or mercury addition can also affect the melting point of solder.

Lead based materials are facilitating the development of hyper fast computers and high definition TV, as well as cathode ray tubes used in viewing screens for television, computers and radar.

Because of its high density, capability and availability, lead is an outstanding material for radiation shielding. Major progress in medical field's use of radiation for imaging diagnostics such as CAT scans can be directly attributed to the use of sophisticated lead shielding to protect patients, healthcare professionals and the public.

Lead compounds such as tri- and tetrabasic lead sulphate and basic lead carbonate are used in both rigid and plasticized PVC to extend the temperature range at which they can be processed without degradation. Dibasic lead phosphate is used for protecting the articles from degradation by UV light when in service. Decorative lead crystal glass is one of the most attractive forms in which lead is used. Normally it is added in the form of lead oxide at 24–36%. Lead is also used in optical, ophthalmic, electric and radiation protection glasses.

Present day understanding of the effects of lead and its compounds are laborious because the poison is cumulative and its toxic effects are many and severe [1]. Whatsoever and that excessive amounts can be very harmful. However, although the

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* Corresponding author. Tel.: +91 231 2693487; fax: +91 231 2692333.
E-mail address: mansinganuse@yahoo.co.in (M.A. Anuse).

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Nomenclature

D	distribution ratio
$\%E$	percentage extraction
ΔG	free energy charge (kJ mol^{-1})
K_{ex}	extraction equilibrium constant
R	gas constant 8.314 J (4.186 cal)
$\%R$	percentage recovery
ΔS	entropy change (J mol^{-1} K^{-1})
T	absolute temperature
V_O	organic phase
V_W	aqueous phase

poisonous effects of lead were known even in ancient times, lead was used in ancient India to treat indigestion. The Egyptians also considered it therapeutic, an ingredient in plasters, for ulcers, and for the eyes. Lead acetate was generally considered to have cooling properties and used as a smoothing lotion. Medicinal ointments were believed to work much better if kept in lead containers. Lead also found application in dentistry.

Literature survey shows various solvent extraction methods for the separation and preconcentration of lead. A method was developed for the extraction of lead(II) from aqueous solution at pH 2.1–8.3 with cyanex 302 [1] in toluene as an extractant. The method was applicable for separation and determination of lead in alloys and environmental samples, however, extraction of lead(II) required higher concentration of extractants. A method was proposed for the extraction and separation of microgram amount of lead(II) from sodium salicylate solution with high molecular weight amines (HMWA) [2]. Lead(II) was stripped from the organic phase quantitatively with distilled water. Single phase solutions of water/ethanol/methyl isobutyl ketone (MIBK), when added to an excess of water, breakdown into two immiscible liquid layers and thenoyltrifluoro acetone, complex of lead was extracted into the organic layer [3]. A method for the trace analysis of lead(II) in natural waters was described by using dithizone in xylene as a complexing agent [4]. The procedure was used for the preconcentration of lead(II).

Lead(II) was separated by liquid–liquid extraction with HMWAs from mineral acid as well as weak acid media. HMWAs used are *N*-*n*-octylaniline [5], Trilaurylamine, Trilaurylammonium, tri-*n*-octylammonium and tri-*n*-hexyl ammonium chlorides [6], Alamine 336 [7], *n*-octylaniline [8], Adogen 364 [9]. Solvent extraction of lead(II) with *N*-*p*-alkyloxybenzoyl-*N*-phenyl-hydroxylamine [10] and *N*-cyclohexyl-*N*-nitrosohydroxylamine [11] were used. Extraction behaviour of lead(II) from alkaline media was investigated. Novel solvent extraction system for lead(II) was developed with dicyclohexano 18-crown-6 [12–14]. The method was extended for determination of lead in lead based alloys. Extraction of lead(II) with LIX 984 [15] dissolved in *n*-heptane was studied. The values of equilibrium constant for the extraction reactions are reported.

Organophosphorus and organothiophosphorus compounds have emerged as powerful extractant for many elements. Stepwise extraction of two lead(II) ions with a single molecule of calix (4) arene tetracarboxalic acid [16] and hexaaceto derivative of calix (6) arene [17] were used for extraction of lead(II) from weakly acidic media. The methods were applied for determination of lead(II) in real samples.

Bis(2,4,4-trimethylpentyl) phosphinodithioic acid (cyanex 301) [18] was reported as an effective extractant of lead(II) from aqueous hydrochloric acid solution. However, there was co-extraction of associated elements. Distribution equilibrium of lead(II) in the extraction with HDEHP and 2-ethylhexylphosphonic acid [19] in toluene from aqueous ammonium nitrate solutions were measured. Lead(II) and bismuth(II) were extracted and separated from each other by using mono octyl-*a*-anilinobenzyl phosphonic acid as an extractant [20]. The optimum pH value for extraction of bismuth(III) was 1.75 and for lead(II) it was 5.

n-Octylaniline has been used in our laboratory for quantitative extraction of lead(II) [21]. Pohlandt has synthesized *n*-octylaniline and reported its effectiveness as an extractant for some metals [22–26]. The extraction depends upon the method of preparation of the reagent. The 2-octylaminopyridine [27] is superior over *n*-octylaniline with respect to following reasons: (i) *n*-octylaniline is available commercially but it is more expensive, (ii) the synthesis of *n*-octylaniline by Pohlandt's method in laboratory is tedious and time consuming, (iii) 2-octylaminopyridine is a sensitive extractant as it requires low concentration for extraction of lead(II) (0.036 M) as compared with *n*-octylaniline (0.24 M), (iv) high molecular weight amines has little solubility in water as compared with secondary amine [28], (v) difficulty arises in phase separation when one can use toluene as a diluent for *n*-octylaniline, (vi) *n*-octylaniline is effective, only when it is freshly synthesized and used after distillation, otherwise during the extraction immediate solid phase formation takes place.

In view of all the above, separation and determination of lead has been receiving considerable attention by researchers. We report herein a simple and selective extraction procedure for lead(II) with 2-OAP. The method permits the separation of lead(II) from commonly associated metals and has been used to separate and determine lead(II) in alloys, ores and pharmaceutical samples.

2. Experimental

2.1. Apparatus and reagents

An Elico digital spectrophotometer model SL 171 with 1 cm quartz cells was used for absorbance measurements and a digital pH meter (model LI-120) was used to adjust the required pH of the solution.

A stock solution of lead(II) was prepared by dissolving 1.598 g of lead nitrate dried at 110 °C in 1 L of distilled water containing 5 mL of concentrated nitric acid. The solution was standardized titrimetrically [29] and contained 1000 μg mL^{-1} of lead(II). The extractant 2-octylaminopyridine (2-OAP) was synthesized by the method of Borshch and Petrukhin [27]. A solution of 2-OAP [0.75% (w/v) or 0.036 M] was prepared by dissolving the required quantity of dried 2-OAP in chloroform.

All the chemicals used were of analytical grade. Double distilled water was used throughout the experiment.

2.2. General extraction procedure

All distribution equilibria studies were carried out at 303 ± 1 K (except effect of temperature) with aqueous to organic ratio of 2.5:1. The concentration of sodium succinate in aqueous phase was kept constant at 0.005 M. The initial concentration of lead(II) in aqueous phase was 2 mg in 25 mL unless specified. The pH of the solution was adjusted to 10.0 by using dilute hydrochloric acid and sodium hydroxide. The solution was then transferred to a 125 mL separatory funnel. An aliquot of 10 mL of extractant in chloroform was equilibrated for 5 min with aqueous lead(II) solution. The two phases were allowed to settle and separate. The metal was stripped from the organic phase with three portions of 10 mL 0.4 M acetic acid. The metal in the aqueous phase was evaporated to almost dryness. The residue was extracted in 5 mL concentrated hydrochloric acid and again evaporated to almost dryness. The lead in the aqueous phase was determined titrimetrically with EDTA [29].

3. Results and discussion

3.1. Effect of pH

The effect of pH on the percentage extraction of lead(II) was studied in the pH range of 1–12 in the presence of weak organic acids such as sodium succinate (0.005 M), sodium malonate (0.007 M), sodium salicylate, sodium oxalate and L-ascorbic acid with 2-OAP in chloroform. The extraction of lead(II) was found to be quantitative in the pH range 9.7–11.0 with 0.036 M 2-OAP in chloroform (Fig. 1). Hence all extractions of lead(II) were carried out at pH 10 under similar experimental conditions.

3.2. Effect of reagent concentration

In order to optimize the reagent concentration, the extraction study of lead(II) was carried out by varying the reagent concentrations in the range of 0.00–0.048 M 2-OAP in chloroform while other parameters like pH period of equilibration, diluent and temperature were kept constant. Extraction was found to increase with increasing reagent concentration. The extraction of lead(II) was quantitative in the concentration range 0.024–0.048 M of 2-OAP (Table 1). Further increase in concentration decreases the extraction. The decrease in extraction is due to formation of stable ion-pair between 2-OAP and succinate. However, in recommended procedure 0.036 M 2-OAP in chloroform was used to ensure the complete extraction of metal ion.

3.3. Effect of weak organic acid concentration

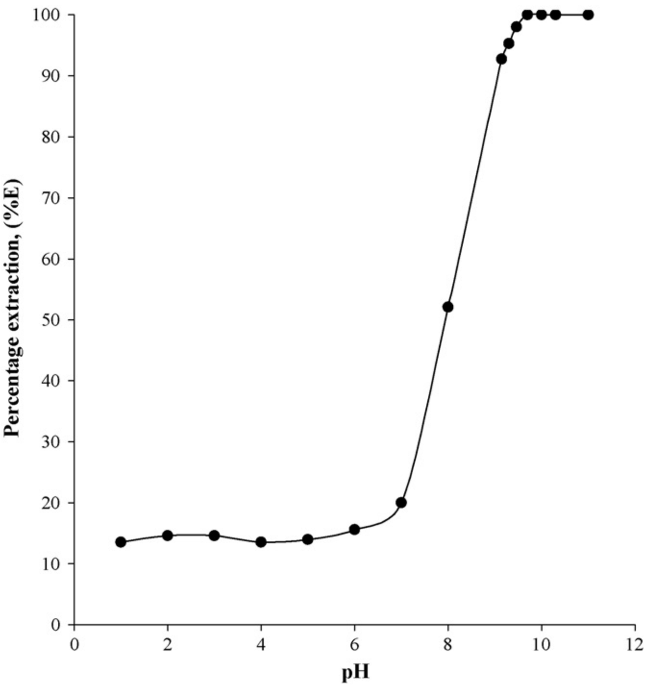

Fig. 1. Extraction behaviour of lead(II) as a function of pH from 0.005 M sodium succinate with 0.036 M 2-OAP.

The extraction of lead(II) was carried out in the presence of varying concentrations of weak acids such as sodium succinate, sodium malonate, sodium salicylate, sodium oxalate and L-ascorbic acid (Table 2) by keeping all the parameters constant. The extraction of lead(II) was found to be quantitative in the range of 0.005–0.007 M for sodium succinate and 0.007–0.009 M for sodium malonate. Therefore, 0.005 M concentration of sodium succinate was used throughout the experimental work as it required lower range of concentration compared with sodium malonate. The extraction of lead(II) was found to be incomplete in presence of sodium salicylate, sodium oxalate and L-ascorbic acid media.

3.4. Influence of various diluents

Various aromatic and aliphatic organic diluents such as benzene, toluene, xylene, carbon tetrachloride, chloroform, methyl

Table 1
Extraction of lead(II) as a function of reagent concentration

Reagent concentration (M)	Reagent concentration (%)	%E[a]	D[b]
0.0000	0	83.84	12.97
0.0048	0.1	85.86	15.22
0.0146	0.3	92.70	31.74
0.0243	0.5	100.00	∞
0.0339	0.7	100.00	∞
0.0436	0.9	100.00	∞
0.0485	1.0	100.00	∞
0.0727	1.5	97.98	121.26
0.0970	2.0	74.75	7.401
0.1213	2.5	74.75	7.401
0.2426	5	74.75	7.401
0.3395	7	74.75	7.401
0.4850	10	71.72	6.340

Lead(II), 2 mg; equilibration time, 5 min; pH 10.00; strippant, 0.4 M acetic acid (3 × 10 mL); sodium succinate, 0.005 M; aqueous:organic volume ratio, 25:10.

[a] Percentage extraction.

[b] Distribution ratio.

Table 2
Extraction of lead(II) as a function of organic acid concentration

Molarity of acid (M)	Sodium succinate		Sodium malonate		Sodium salicylate		Sodium oxalate		L-Ascorbic acid	
	%E[a]	D[b]	%E[a]	D[b]	%E[a]	D[b]	%E[a]	D[b]	%E[a]	D[b]
0.00	67.36	5.159	67.29	514	66.66	4.99	62.70	4.202	66.66	4.99
0.001	31.25	10.833	76.04	7.93	77.08	8.41	27.08	0.9284	31.25	0.992
0.002	85.41	14.635	77.08	8.40	88.54	19.32	29.16	1.029	37.5	1.2
0.003	88.54	19.315	73.95	7.096	92.70	31.74	32.29	1.192	37.5	1.2
0.004	95.83	51.45	82.29	11.61	92.70	31.74	20.83	0.6577	39.58	1.64
0.005	100	∞	87.5	87.5	82.29	11.61	12.5	0.357	52.08	2.72
0.006	100	∞	86.46	15.94	70.83	2.43	11.45	0.323	48.95	2.397
0.007	100	∞	100	∞	73.95	7.097	8.3	0.22	47.91	1.84
0.009	98.75	192.5	100	∞	70.83	2.43	12.5	0.357	37.5	1.2
0.01	95.83	57.45	94.79	45.48	70.83	2.43	9.3	0.256	32.29	1.19
0.03	94.79	45.48	93.75	37.5	70.83	2.43	12.5	0.357	20.83	0.659
0.05	93.75	37.5	93.75	37.5	70.83	2.43	12.5	0.357	20.83	0.659
0.07	93.75	37.5	69.79	5.775	70.83	2.43	12.5	0.357	20.83	0.659
0.09	92.70	31.74	65.62	4.771	70.83	2.43	12.5	0.357	20.83	0.659
0.1	81.25	10.833	64.58	4.558	70.83	2.43	12.5	0.357	20.83	0.659

Lead(II), 2 mg; equilibration time, 5 min; pH, 10.00; strippant, 0.4 M acetic acid (3 × 10 mL); extractant, 0.036 M 2-OAP in chloroform aqueous:organic volume ratio, 25:10.

[a] Percentage extraction.

[b] Distribution ratio.

isobutyl ketone (MIBK), *n*-butanol, amyl acetate, kerosene, amyl alcohol, 1,2-dichloroethane (Table 3) were employed for the extraction of lead(II) with 2-OAP. It was found that the extraction of lead(II) was found quantitative in chloroform. This is due to the high distribution of ion-pair complex in it and it provided better phase separation, while the other solvents were poor.

3.5. Nature of extracted species

Stoichiometry of the extracted species was determined from the experimental studies. The conventional slope analysis method was used for the determination of stoichiometry. It was observed that distribution ratio (D) of extraction was independent of lead(II) concentration, which is a clear indication that the extracted species is mononuclear in the whole range of the experimental study. The plot of $\log D_{\mathrm{Pb(II)}}$ versus $\log C_{[\text{2-OAP}]}$ at pH 8.0 and 8.5 and 0.005 M sodium succinate concentration was a linear graph with slopes of 1.71 and 1.80, respectively (Fig. 2), indicating that two ligands react with one mole of lead(II) ion, while the graph of $\log D_{[\mathrm{Pb(II)}]}$ versus $\log C_{[\text{succinate}]}$(Fig. 3) at pH 8.0 and 8.5 and 0.036 M 2-OAP concentration shows a linear plot with slope 2.24 and 2.13, respectively, indicating that two succinate ions are used in the reaction process.

Table 3
Extraction of lead(II) as a function of diluents

Solvent	Dielectric constant	%E[a]	D[b]
Benzene	2.28	73.95	7.097
Toluene	2.38	52.08	2.613
Xylene	2.30	66.66	4.998
Carbon tetrachloride	2.24	69.69	5.748
Chloroform	4.81	100.00	∞
Methyl isobutyl ketone	13.11	54.54	2.999
n-Butanol	17.80	66.66	4.998
Amyl acetate	4.80	18.18	0.046
Kerosene	1.8	59.59	3.686
Amyl alcohol	13.90	76.76	8.257
1,2-Dichloroethane	1.254	69.69	5.748

Lead(II), 2 mg; extractant, 0.036 M 2-OAP; pH 10.00; strippant, 0.4 M acetic acid (3 × 10 mL); sodium succinate, 0.005 M; aqueous:organic volume ratio, 25:10.

[a] Percentage extraction.

[b] Distribution ratio.

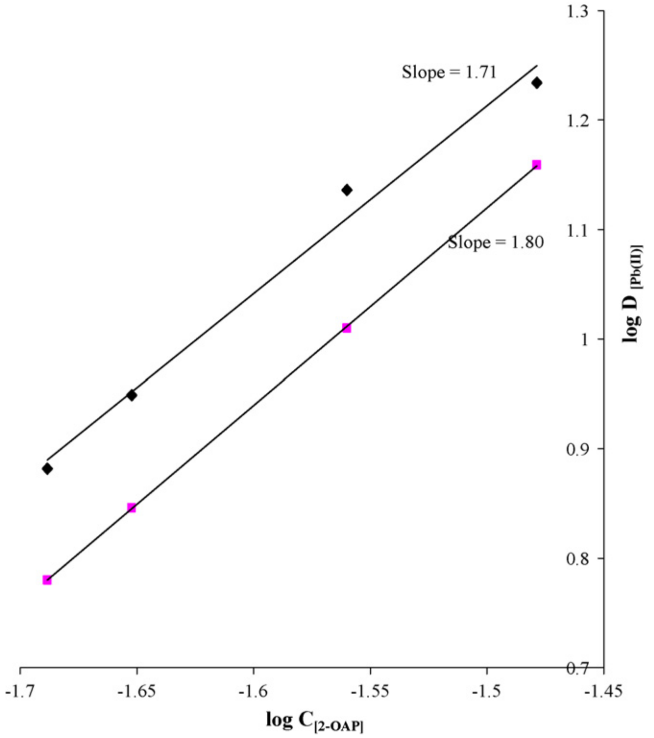

Fig. 2. log–log plot of distribution ratio $\log D_{[\mathrm{Pb(II)}]}$ versus $\log C_{[\text{2-OAP}]}$ at 0.005 M sodium succinate.

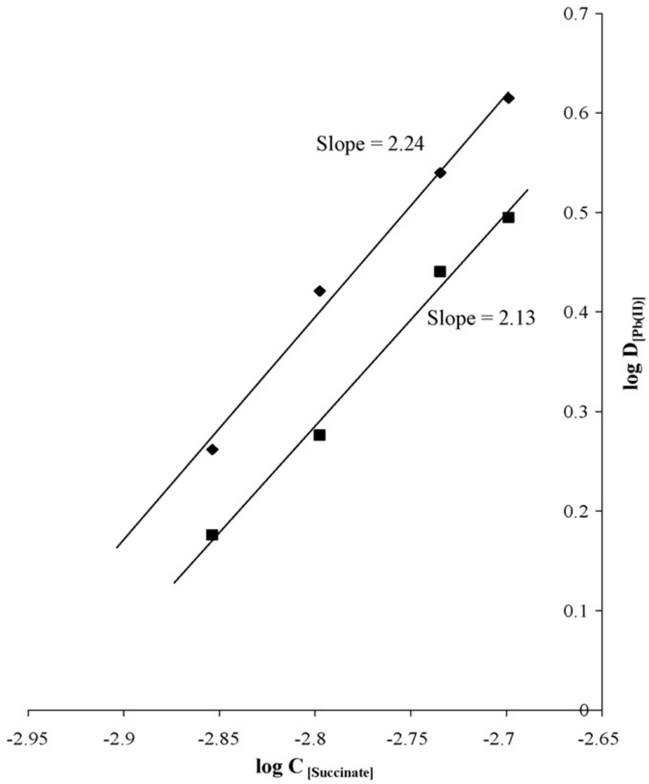

Fig. 3. log–log plot of distribution ratio $\log D_{[\mathrm{Pb(II)}]}$ versus $\log C_{[\mathrm{succinate}]}$ at 0.036 M 2-OAP.

2-Octylaminopyridine exists in diprotonated species only in higher hydrochloric acid concentration [27]. However, during extraction from weakly acidic solution, there is existence of monoprotonated form of the 2-OAP. It is known that the amino group nitrogen in the 2-OAP molecule has weak basic properties (secondary amino group). The basicity of the hetero nitrogen atom on contrary increases due to the ringstructure [28]. The addition of second proton to 2-OAP molecule is possible, evidently, in very acidic media. Hence as the extraction is carried out at pH 10.0 from weak organic acid (sodium succinate). There would be existence of monoprotonated species. The extraction of lead(II) from succinate media takes place via anion exchange mechanism [27]. Therefore, the probable extraction mechanism is given as,

$$\text{2-OAP}_{\text{org}} + \text{H}_{\text{aq}}{}^{+} \rightleftharpoons [\text{2-OAPH}^{+}]_{\text{org}} \tag{1}$$

$$\text{Pb(II)}^{+}2\text{succinate}^{2-} \rightleftharpoons [\text{Pb(succiante)}_2]_{\text{aq}}{}^{2-} \tag{2}$$

$$2[\text{2-OAPH}^{+}]_{\text{org}} + [\text{Pb(succiante)}_2]_{\text{aq}}{}^{2-} \rightleftharpoons [(\text{2-OAPH}^{+}]_2\text{Pb(succinate)}_2{}^{2-}]_{\text{org}} \tag{3}$$

3.6. *Effect of various stripping agents*

Lead(II) was stripped out from the loaded organic phase with different strength of acids and salts such as HCl, H_2SO_4, HNO_3, $HClO_4$, CH_3COOH, NaCl, $NaNO_3$ and NH_4Cl (Table 4). Lead(II) was stripped quantitatively with three 10 mL portions of acetic acid (0.4–0.5 M), nitric acid (0.3–0.6 M) and hydrochloric acid (0.5–0.6 M) from the organic phase. The use of other acid strengths did not result in complete stripping.

Bases such as NaOH, KOH and NH_3 proved to be completely ineffective in stripping lead(II) from the organic phase because extraction of lead(II) was from basic media (pH 10). Acetic acid was preferred than HNO_3 and HCl. Nitrates may cause interference in the further estimation procedure of lead(II) while hydrochloric acid causes more hazardous effect.

3.7. *Effect of equilibration time*

Lead(II) was equilibrated with 2-OAP in chloroform for periods between 15 s and 20 min. The extraction of lead(II) was found to be quantitative in the range 4–10 min. With further increase in shaking time, the percentage extraction decreased due to the dissociation of the ion-pair complex with more agitation.

3.8. *Effect of aqueous to organic volume ratio*

The results of contacting different volume ratios of organic to aqueous phase have been studied. The result indicate that a preferred aqueous/organic (A/O) phase ratio in this study was found to be 5:1 or less. This is evident from the sharp

Table 4
Extraction of lead(II) as a function of stripping agents

Molarity (M)	CH_3COOH (%*R*)[a]	HCl (%*R*)[a]	H_2SO_4 (%*R*)[a]	HNO_3 (%*R*)[a]	$HClO_4$ (%*R*)[a]	$NaNO_3$ (%*R*)[a]	NaCl (%*R*)[a]	NH_4Cl (%*R*)[a]
0.1	88.54	82.29	12.5	91.66	11.45	9.37	6.25	23.95
0.2	96.9	91.66	12.5	94.79	10.41	9.37	6.25	45.83
0.3	97.9	93.75	11.45	100.00	10.41	10.41	6.25	55.20
0.4	100.0	97.92	13.45	100.00	9.37	13.54	6.25	59.37
0.5	100.0	100.0	12.5	100.00	10.41	15.62	6.25	71.87
0.6	94.79	100.0	12.5	100.00	10.41	14.58	9.37	77.8
0.7	87.5	96.88	12.5	95.83	10.41	15.62	11.45	89.58
0.8	96.9	97.92	13.54	90.62	11.45	15.62	13.54	95.83
0.9	83.33	96.88	17.70	87.05	11.45	15.62	13.54	95.83
1.0	78.12	96.88	17.70	83.33	11.45	15.62	13.54	95.83

Lead(II), 2 mg; extractant, 0.036 M 2-OAP in chloroform; pH 10.00; equilibration time, 5 min; sodium succinate, 0.005 M; aqueous:organic volume ratio, 25:10.

[a] Percentage recovery.

increase in the separation efficiency as well as the distribution of lead(II) when phase ratio (A/O) changed from 20:1 to 5:1. This may simply be due to the unavailability of reagent for the metal extraction, so a crowding effect occurs at low phase ratio. However, in the recommended procedure the phase ratio is maintained as 2.5:1 so as to avoid the large consumption of sodium succinate.

3.9. Loading capacity of 2-OAP

The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal of various concentrations. For a 10 mL of 0.036 M solution of 2-OAP in chloroform at pH 10, 0.005 M sodium succinate concentration and a O/A of 2.5:1, the maximum loading capacity for lead(II) was found to be 8 mg at 303 K. This leads to the assumption that the ion-pair number is (molarity of extractant/molarity of metal) = 94.30.

3.10. Temperature effect

The extraction of lead(II) from aqueous solution adjusted to pH 10, using 10 mL of 0.036 M 2-OAP in chloroform, at varying temperature between 293 and 309.3 K, was studied. The change of extraction equilibrium constant (K_{ex}) with temperature is expressed by Van't Hoff equation

$$\frac{d(\log K_{ex})}{d}\left(\frac{1}{T}\right)=\frac{-\Delta H}{2.303R} \tag{4}$$

The plot of $\log K_{ex}$ versus $1000/T$ is linear with slope −5.02 (Fig. 4) and the enthalpy change of the extraction reaction was evaluated as $\Delta H = 96.23\ \mathrm{kJ\,mol^{-1}}$ which suggests that the reaction is endothermic.

The free energy ΔG and entropy ΔS were calculated from Eqs. (5) and (6). The values of ΔG are negative while the value of enthalpy is positive $96.23\ \mathrm{kJ\,mol^{-1}}$

$$\Delta G = -2.303RT\log K_{ex} \tag{5}$$

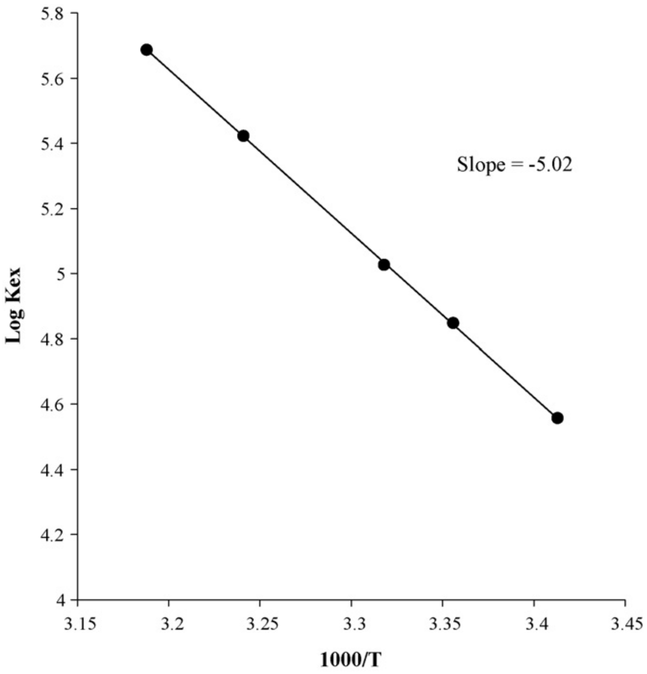

Fig. 4. Effect of temperature on the extraction of lead(II).

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{6}$$

The negative value of ΔG indicates the reaction is spontaneous. The positive enthalpy value indicate that the extraction of lead(II) with 2-OAP in chloroform is favourable with rise in temperature.

3.11. Effect of diverse ions

The effect of various foreign ions on the extraction of lead(II) with 10 mL of 0.036 M 2-OAP in chloroform at pH 10 from 0.005 M sodium succinate media was studied (Table 5). The tolerance limit was set not to cause more than ±2% error in the extraction of lead(II).

Table 5
Effect of diverse ion on the extraction of 2.0 mg of lead(II) at pH 10 in 0.005 M sodium succinate with 0.036 M 2-OAP dissolved in chloroform

Ion	Added as	Tolerance limit (mg)	Ion	Added as	Tolerance limit (mg)
Malonate	Sodium malonate	050.0	Ce(IV)	$Ce(SO_4)_2$	15.00
Salicylate	Sodium salicylate	050.0	Ba(II)	$BaCl_2{\cdot}2H_2O$	02.00
Acetate	Sodium acetate	100.00	Al(III)	$AlCl_3{\cdot}6H_2O$	05.00
Citrate	Citric acid	002.00	Ca(II)	$CaCl_2$	15.00
Ascorbate	Ascorbic acid	10.00	Ag(I)	$AgNO_3$	25.00
Thiosulphate	Sodium thiosulphate	25.00	Hg(II)	$HgCl_2$	15.00
Fluoride	Sodium fluoride	100.00	Y(III)	YCl_3	25.00
Tartrate	Sodium tartarate	005.00	Sr(II)	$Sr(NO_3)_2$	25.00
Oxalate	Sodium oxalate	002.00	U(VI)	$UO_2(NO_3)_2{\cdot}6H_2O$	15.00
Thiourea	Thiourea	025.00	Cu(II)	$CuSO_4{\cdot}5H_2O$	25.00
Iodide	Potassium iodide	50.00	In(III)	$InCl_3{\cdot}4H_2O$	02.00
Bromide	Potassium bromide	100.00	Ga(III)	$GaCl_3$	25.00
Thiocynate	Potassium thiocynate	100.00	Te(IV)	Na_2TeO_3	02.00
Nitrite	Sodium nitrite	100.00	Zn(II)	$ZnSO_4{\cdot}7H_2O$	02.00
Nitrate	Sodium nitrate	100.00			

Table 6
Separation of lead(II) from binary mixtures

Metal ion	Amount (mg)	Average % recovery[a]
Pb(II)	2	99.00
Th(IV)	2	99.6
Pb(II)	2	99.35
Bi(III)	1	100
Pb(II)	2	98.35
Hg(II)[b]	2	97.89
Pb(II)	2	99.32
Cr(VI)	1	97.54
Pb(II)	2	98.15
Cd(II)[c]	1	100
Pb(II)	2	98.99
Zn(II)	0.5	97.03
Pb(II)	2	99.74
Al(III)	1	98.14
Pb(II)	2	99.88
Ca(II)	0.5	96.85
Pb(II)	2	98.89
Ba(II)	1	98.50

[a] Average of six determinations.

[b] Hg^{2+} reduced to Hg^{+} by hydroxyl amine hydrochloride before extraction while for estimation of Hg, Hg^{+} can be oxidized to Hg^{2+} by bromine water.

[c] Masked by 50 mg SCN^{-}.

4. Applications

4.1. Separation of lead(II) from binary and ternary mixtures

Various metals showed different extents of extraction at different acid concentrations. In some cases, behaviour of lead(II)–2-OAP ion-pair complex towards stripping agent was observed to be different. Such differences were fully exploited for the selective separation of lead(II) from Th(IV), Bi(III), Hg(II), Cr(VI), Cd(II), Zn(II), Al(III), Ca(II) and Ba(II) (Tables 6 and 7).

Lead(II) was separated from a binary mixture of Cr(VI), Cd(II), Zn(II), Al(III), Ca(II) and Ba(II) by its extraction with 10 mL of 0.036 M 2-OAP in chloroform from 0.007 M sodium succinate. Under this condition the added metal ions remained quantitatively in aqueous phase. The aqueous phase is washed with 5 mL chloroform to remove traces of the reagent. Metal ions from aqueous phase were determined by standard methods [29,30]. The lead(II) was stripped from organic phase with 0.4 M acetic acid (3 × 10 mL) and estimated titrimetrically with 0.001 M EDTA.

Table 7
Separation and determination of cations from ternary mixtures

Metal ion	Amount (mg)	Average % recovery[a]
Pb(II)	2	99.40
Ca(II)	0.5	99.62
Th(IV)	2	98.77
Pb(II)	2	99.5
Ba(II)	1	99.61
Th(IV)	2	97.00
Pb(II)	2	99.71
Ca(II)	0.5	98.29
Bi(III)	1	100.00
Pb(II)	2	99.66
Ba(II)	1	98.64
Bi(III)	1	99.94
Pb(II)	2	99.89
Zn(II)	0.5	98.63
Bi(III)	1.0	99.94

[a] Average of six determinations.

Lead(II) was separated from Th(IV) and Bi(III) under the optimum condition of lead(II) by adjusting the pH 10 with ammonia and nitric acid. Thorium(IV) and bismuth(III) were coextracted with lead(II) in the organic phase. Lead(II) from the organic phase was back stripped with 0.4 M hydrochloric acid (3 × 10 mL) while under these conditions there is no back extraction of either Th(IV) or Bi(III) and lead(II) was determined as per the general procedure. Thorium(IV) was stripped by 0.01 M EDTA and acetate buffer solution (pH 4.7) (2 × 5 mL each) while bismuth(III) was back stripped with 0.1M EDTA solution (2 × 5 mL). Thorium(IV) and bismuth(III) from the aqueous phase were determined complexometrically [29,30].

Similarly lead(II) and mercury(II) were separated by extracting lead(II) from 0.007 M sodium succinate at pH 10.0 with 0.036 M 2-OAP in chloroform in the presence of 0.04 M hydroxylamine hydrochloride as a reducing agent to convert Hg(II) to Hg(I). It was found that under the optimum extraction conditions of lead(II) there was incomplete extraction of Hg(II) while quantitative extraction of Hg(I). Lead(II) was backstripped from the organic phase and determined as per the general procedure. While Hg(I) remained quantitatively in organic phase was converted into Hg(II) by addition of acidic bromine water (5 mL) with warming in water bath. Then it was back stripped with 2 M HCl (3 × 10 mL) and determined with EDTA [30].

A ternary mixture of Pb(II), Ca(II), Th(IV) and Pb(II), Ba(II), Th(IV) were resolved by following recommended procedure of lead(II). Under the optimum extraction condition of lead(II), thorium(IV) was quantitatively coextracted into organic phase along with lead(II). The separation of lead(II) from thorium(IV) can be achieved by the use of different strippants as given in binary mixture separation. Ca(II) or Ba(II) was remained unextracted in the aqueous phase which was determined by standard procedure [29,30].

Mixture of Pb(II), Ca(II), Bi(III) and Pb(II), Ba(II), Bi(III) were used for separation of individual metal ions. Bismuth(III) was quantitatively coextracted under the optimum conditions of lead(II). Lead(II) was back stripped as per the procedure while Bi(III) was back stripped with 0.1 M EDTA solution (2 × 5 mL). The aqueous phase containing Ca(II) or Ba(II) was washed with 5 mL chloroform to remove the traces of extractant. The aqueous phase was evaporated almost to dryness and metal ion content was determined [29,30].

Similarly lead(II) was separated from Zn(II) and Bi(III) from 0.007 M sodium succinate by adjusting pH 10 with 0.097 M 2-OAP in chloroform. Bismuth(III) was co-extracted quantitatively along with lead(II) while Zn(II) remained unextracted in aqueous phase. Lead(II) from the organic phase was back stripped with 0.4 M HCl (3 × 10 mL) and Bi(III) was then stripped with 0.1 M EDTA (2 × 5 mL) and determined by standard methods.

Table 8
Determination of lead(II) from real samples (alloys)

Alloy	Composition of alloy	Lead II taken (mg)	Lead II found (mg)	Recovery[a] (%)	R.S.D. (%)
Type metal alloy	80% Pb, 17% Sn, 3% Sb	2	1.9864	99.32	0.68
Solder alloy	40% Pb, 60% Sn	2	1.993	99.65	0.35
Bronze alloy	13.22% Pb, 3.15% Sn, 4.5% Zn, 78.3% Cu	2	1.9976	99.88	0.12
Gun metal alloy	Pb 2.31%, Cu 84.95%, Sn 4.89%	2	1.9942	99.71	0.29
Tin brass white metal alloy	Pb 3.18, Sn 82.2, Sb 9.45, Cu 4.58, As 1.15, Bi 0.1, Cd 0.14, Fe 0.024, Ni 0.17, Zn 0.04	0.400	0.399	99.99	0.01

[a] Average of six determinations

Table 9
Analysis of lead(II) from ore samples

Ore	Certified value (mg/gm)	Amount found by proposed method (mg/gm)	Recovery[a] (%)	R.S.D. (%)
Galena ore	220.00	217.954	99.07	0.93
Zinc ore concentrate no. 4	55.55	55.18	99.34	0.66

[a] Average of six determinations

Table 10
Analysis of lead(II) from ayurvedic medicines

Medicine	Amount of lead(II) found by AAS (mg/gm)	Amount of lead(II) found by proposed method (mg/gm)	Recovery[a] (%)	R.S.D. (%)
Menabon (Wishbon Pharmaceutical, Kolhapur)	10.4628	10.1970	99.46	0.54
Garbhapal Rasa (Shri Dhootpape-shwar Ltd., Mumbai)	59.536	59.137	99.33	0.67
Puspadhanwa (Shri Dhootpapeshwar Ltd., Mumbai)	6.915	6.789	99.18	0.82
Ekangavir Rasa (Zandu Vapi, Gujrat)	27.248	26.749	99.17	0.83
Nag Bhasma (Unjha Pharmacy Unjha 374170, India)	136.846	135.94	99.34	0.66

[a] Average of six determinations

4.2. Validity of the method

To study the applicability of the proposed method for real samples, the method was employed for analysis of lead(II) present in real samples such as alloys, ores and pharmaceutical samples.

Required quantity of the alloy sample was dissolved in 15 mL concentrated nitric acid the solution was evaporated to dryness. The procedure was repeated thrice, then it was extracted in 50–60 mL distilled water. The solution was evaporated till one fourth, filtered through Whatman filter paper number 1, the filtrate along with washing was collected in 100 mL volumetric flask and diluted up to the mark. An aliquot of diluted solution was taken for extraction and lead(II) determined, by the proposed method. The results of analysis are reported in Table 8.

Required quantity of ore sample was weighed in a clean, dry silica crucible and was heated up to 700 °C (till red hot) for 2 h to remove organic matter and volatile oxides and mass becomes porous. A fused mass of PbO produced was dissolved in 10 mL concentrated nitric acid solution. The solution was evaporated till almost dryness and repeated thrice. Then it was cooled and extracted with 50 mL distilled water, the solution was evaporated till one fourth, and filtered through Whatman filter paper 1. The filtrate along with washings was collected in 100 mL volumetric flask and diluted up to the mark. Aliquots of each sample were taken and the lead content was determined using proposed method. The results obtained with this method were compared with AAS method. The recovery of lead in these samples was found to be in good agreement with the theoretical values (Table 9).

4.3. Analysis of pharmaceutical samples

The proposed method was employed for the analysis of lead in pharmaceutical (ayurvedic) samples like Menabon, Garbhapal Rasa, Pushpadhanwa, Ekangavir Rasa, Nag Bhasma were treated with minimum amount of concentrated nitric acid, the solution was evaporated to moist dryness with the addition of concentrated nitric acid two times, cooled, diluted with distilled water, filtered to remove the residue and again diluted to 100 mL and analysed for lead content by the proposed method. The results obtained were in close agreement with those of the values obtained by the AAS method (Table 10).

5. Conclusion

The important features of the method described here are

(1) It permits selective separation of lead(II) from other toxic and associated metals such as Hg(II), Cd(II), Bi(III), Zn(II), Cr(VI), Th(IV), Al(III), Ba(II) and Ca(II).

(2) Low reagent concentration is required for quantitative recovery of lead(II).
(3) It is free from interference of a large number of foreign ions which are associated with lead(II) in its natural occurrence.
(4) 2-OAP extracts lead(II) in chloroform from sodium succinate media by anion exchange mechanism in which a complex of stoichiometric formula $[(\text{2-OAPH}^+]_2\ \text{Pb(succinate)}_2{}^{2-}]_{\text{org}}$ is formed.
(5) It is applicable to the analysis of lead(II) in synthetic mixtures, alloys, ayurvedic samples and minerals.
(6) The developed method is very simple, selective reproducible and rapid; requires less time for separation and determination.

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