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LIQUID – LIQUID EXTRACTION SPECTROPHOTOMETRIC DETERMINATION AND COMPARATIVE STUDY OF SOME METAL IONS WITH ORGANIC LIGAND

Patil Jayashree Shailesh
Department of Chemistry, J.S.M. College, Alibag, Raigad.

ABSTRACT:

The main reason for solvent extraction method is its usefulness among these separation techniques is because of its ease, simplicity, speed, wide scope, utilizing apparatus and requirement of only a separating funnel, application both to trace and macro level of metals. Separation of heavy metals from the environment can be possible by using this method[1-5].

Solvent extraction is considered to be one of the best methods of separation. It is based on transfer of a solute from one phase to another, which is immiscible with each other.

The spectrophotometric method is coupled with solvent extraction technique and used for the determination and comparative study of Sr(II) and Pb(II) using N,N'bis(O-hydroxy acetophenone) ethylene diimine(HAPED) as an analytical reagent[6-8]. This reagent is synthesized in the laboratory and characterized by NMR, IR, Mass and elemental analysis for its purity. This reagent forms a light pink colored stable complex with Strontium metal and light yellow colored stable complex with Lead metal, which can be quantitatively extracted into chloroform at pH 5.2 and pH 5.6 respectively. This Sr(II)-HAPED complex in chloroform exhibit intense absorption peak at 585nm and Pb(II) –HAPED complex in chloroform gave intense absorption peak at 535nm. Beer's law is obeyed in the range of 1 to 10 ppm of Strontium and Lead solution giving linear and reproducible graph[9].

The Molar absorptivity and Sandell's sensitivity are also calculated. However, the effect of reagent concentration, equilibrium stability and effect of interfering ions have been studied. The Stoichiometric ratio of complex of Strontium and Lead studied by Job's Continuous Variation method, Mole ratio and Slope ratio method have been studied and it is found to be metal and ligand ratio is 1:2. The proposed method is rapid, sensitive, reproducible, accurate and has been satisfactory applied for determination and separation of Sr(II) and Pb(II) in commercial mixtures, pharmaceutical samples and alloys[10-11].

KEYWORDS: *Sandell's Sensitivity, Molar absorptivity N,N'bis(O-hydroxy acetophenone) ethylene diimine (HAPED) reagent, Strontium(II), Lead(II), , Spectrophotometric determination.*

INTRODUCTION:

Spectrometry is essentially a trace-analytical technique and is one of the most powerful tools in chemical analysis. A wide variety of reagents have been proposed for the comparative study of Strontium and Lead and its spectrophotometric determination. Lead compounds are essential to life. Extractive methods [12-13] are highly sensitive but generally lacks in simplicity. Spectrophotometry is essentially a trace- analytical technique and is one of the most powerful tools in chemical analysis. A

wide variety of reagents have been proposed for the spectrophotometric determination of Strontium and Lead.

The extractive spectrophotometric analysis enables to separate desired metal ion, which is to be estimated in presence of other metal from samples. In the present work a novel analytical reagent N,N'bis''(O-hydroxy acetophenone) ethylene diimine (HAPED), was used for the extractive spectrophotometric determination of Strontium and Lead. The developed method can be employed for efficient determination of Strontium and Lead at microgram level. The results of analysis obtained were compared with those obtained by known methods[14-15].

MATERIALS AND METHODOLOGY

1. Instruments:

Shimadzu 2,100 UV-Visible spectrophotometer with 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH-meter was used for pH adjustment.

2. Synthesis of Reagent

The HAPED reagent was synthesised by O-hydroxy acetophenone and ethylene diamine in methanol in 2:1 molar proportions are mixed in round bottom flask. Shake the flask for 10 to 15 min. Immediately, dark-yellow-colour solid is obtained which is poured in ice-cold water. The solid obtained is separated by filtration and washed with cold water and the product is recrystallised from ethanol. The yield was about 90%. It is then characterised and used for extractive spectrophotometric determination of Sr(II) and Pb(II). A stock solution of HAPED reagent with concentration 0.1% was prepared in methanol. The scheme of reaction is shown in Figure 1.This is less hazardous synthesis as less amount of solvents are used in this method. Separation of metals can be takes place at very low concentration at micropgram or nanogram level. No sophisticated instruments are required for this method of analysis. Hence this type of research shows green chemistry approach.

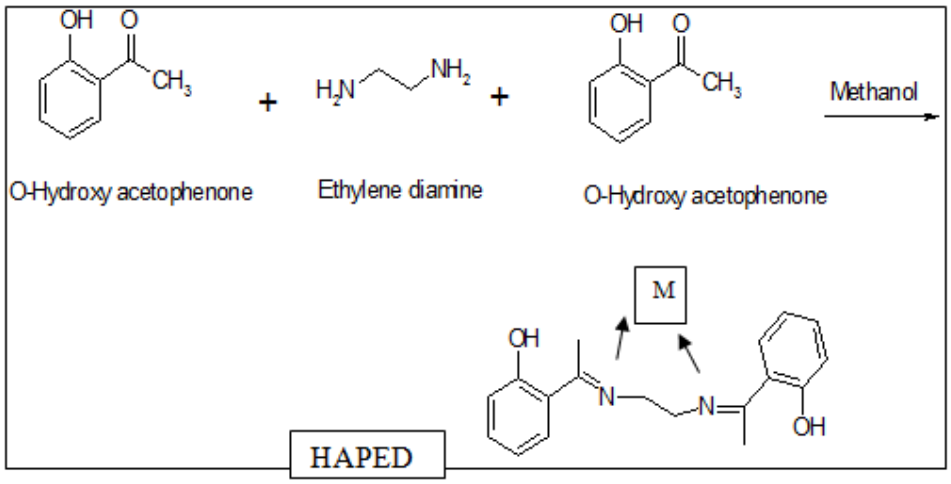


Figure-1:-Synthesis of reagent N,N"-bis (O-hydroxy -acetophenone) ethylene diimine (HAPED)

3. Preparation of stock solution

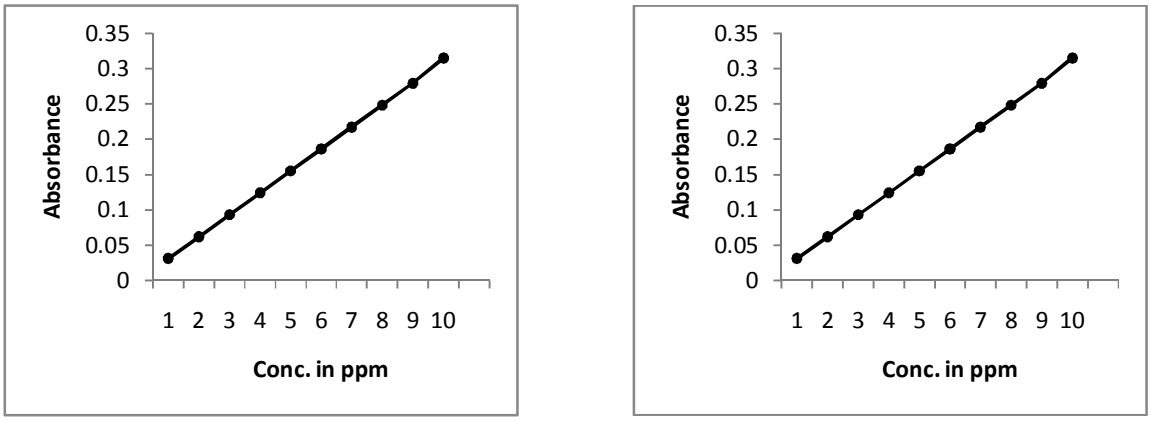
A weighed quantity of Strontium Nitrate and Lead Chloride was dissolved in double distilled water containing dilute Nitric acid and hydrochloric acid respectively and then diluted to desired volume by double distilled water. The solution was then standardized with titrimetric method method.

4. Recommended procedure

Mix 1-cm^3 aqueous solution containing 1-100mg of Strontium and Lead and 2 cm^3 of 0.1% methanolic solution of HAPED reagent in 25 cm^3 beaker. Adjust the pH of the solution to required value with buffer solution Make the final volume 10cm^3. Transfer the solution into 125 cm^3 separate funnel and equilibrate for 1min. with 10cm^3 chloroform. Allow the two phases to separate and measure the absorbance of organic phase containing the complex at 370 nm against reagent blank.

5. Preparation of calibration plot

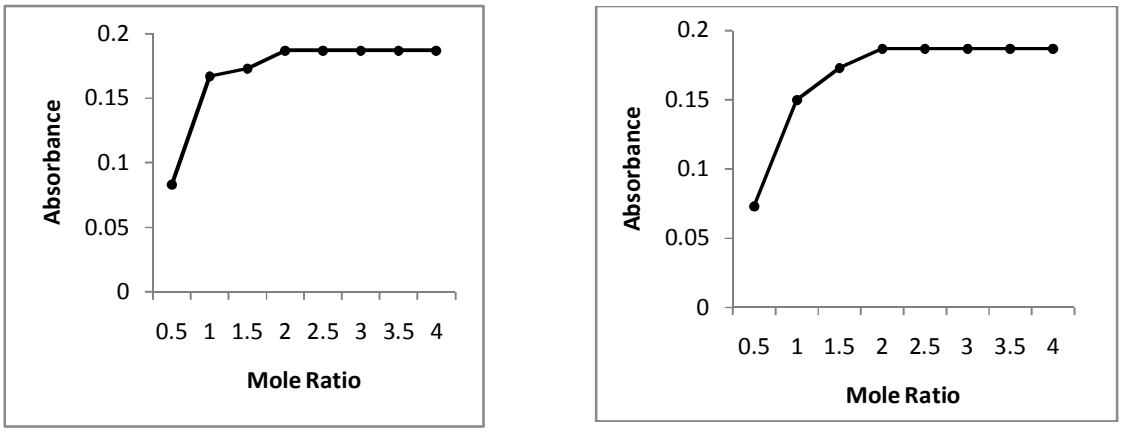
The calibration curve is prepared by taking known amount of Strontium and Lead which is described in the procedure. A graph of absorbance against concentration is shown in Figure 2. The concentration of the unknown Strontium and Lead solutions is determined from the calibration plot.



Figure,.2: Calibration plot for extractive spectrophotometric determination of Sr(II) and Pb(II) with chloroform.

6. Composition of the extracted species

The composition of the extracted species was determined by using the Job's continuous variation method and verified by mole ratio method and slope ratio method. These methods show that the composition of Sr(II) and Pb(II)- HAPED regent is 1: 2 which is represented in Figure 3.



Figure,3 Composition of the Extracted Sr(II) and Pb(II) - HAPED species by mole ratio method

7. Effect of foreign ions:

Various cations and anions were investigated to find the tolerance limit of these foreign ions in the extraction of Strontium (IV) and Lead(IV) presented in Table 2. The effect of diverse ions on the Strontium (IV) and Lead(IV) determination was studied, in presence of a definite amount of a foreign ion. The tolerance limit of the foreign ion was taken as the amount required causing an error of not more than 2% in recovery of Strontium(IV) and Lead(IV). The ions which interfere in the spectrophotometric determination of Strontium and Lead were masked by using appropriate masking agents presented in Table 3.

Table :1

Sr. No.	Different parameters Studied	Observation for Strontium(IV)	Observation for Lead(IV)
1	Solvent	Chloroform	Chloroform
2	pH	7.8	5.2
3	Equilibrium time	1 min.	1 min.
4	Stoichiometry M:L	1:2	1:2
5	95% confidence limit	±0.2752	±0.2560
6	Reagent Conc.	0.1%	0.1%
7	Volume of Rgt.	$2cm^3$	$2cm^3$
8	Average of 7 determination	9.60	9.50
9	Stability of the complex	35 h.	33 h.
10	Sandell sensitivity	0.0572-$\mu g/cm^2$	0.0376-$\mu g/cm^2$
11	Molar absorptivity	1,736.77 L/mol/cm	1,165.90 L/mol/cm

Table : 2 Effect of foreign ions

Sr. No.	Interfering ions	Tolerance limit
1	BrO_3^-, Br^-, NO_3^-, IO_3^-, SO_4^-, SO_3^-, CN^-, I^-, Cl^-,ClO_3^-, NO_2^-,	12
2	Tartrate, acetate	10
3	Oxalate , phosphate,	06
4	As(III), W(VI), Mg(II), Mo(VI), Cd(II),	09
5	Al(III), Bi(III), Ce(IV),Ca(II),	10
6	Na^+, Ag^+,K^+	05
7	Co(II), Fe(II), Cu(II), Ni(II), Cr(III)	Interfere strongly

Table-3: Effect of masking agent

Sr. No.	Interfering Ions	Masking Agents
1	Fe(III)	Sodium fluoride
2	Cr(III)	Ammonium acetate
3	Ni(II)	DMG
4	EDTA	Boiled with conc.HNO_3
5	CN^-	Boiled with conc.HNO_3 and formaldehyde
6	Cu(II)	Sodium sulphate

8. Comparison between reagents

Various reagents were investigated by the earlier researchers for removal of Sr(II) and Pb(II). The proposed reagent (HAPED) is found more superior as that of reported regents and are presented in Table 4.

Table 4: Comparison between regents

Sr./Ref.No.	Reagent	Remark
1	Diantipyryl-(p-chloro) phenylmethane	Beer's range 0-400 µg/25 cm^3
2	Piconaldehyde nicotinoyl hydrazone	Beer's Range 0.02-1.5ppm yellow-coloured complex with M:L ratio as 1:2
3	N,N'-diethylaniline	Require heating At 100ºC
4	Methylene green	Beer's range 0.2-30 cm^3
5	Ethylenebis(triphenyl phosphonium cation	Cr^{+3i}nterferes
6	5,5'-dithiodi(salicyclo hydroxamic acid	Beer's range 0.3-2.3 tetravalent Fe,Ti, Cu^{+2}, V^{+5i} interfere

9. Applications

The present method was applied for determination of amount of Sr(II) and Pb(II) in various samples of alloys, commercial mixtures, injection vial and tablets. The results obtained were in well agreement with the standard methods shown in Table -5. Every result is the average of independent determinations.

Table 5: Applications

Sr. No.	Sample	Standard method	Present method
1	Celesite ore	92.0 %	91.98 %
2	Strontianite	27.0 µg	26.970 µg
3	Manganese Ore	37 mg	36.85 mg
4	Sr(5) + Pd(5)	4.95 ppm	4.90 ppm
5	Sr(50) + Cd(50) + W(50)	50 ppm	49.95 ppm
6	Solder alloy	80.10%	80.06%
7	Galena	10.55%	10.45%
8	Pb(5) + Mn(5)	4.950ppm	4.945ppm
9	Pb(50) + Cd(50) + Cu(50)	50ppm	49.98ppm

The stability of Strontium and Lead complex is 46hr and 40hr. Represented as in figure:3. It is observed from this figure that a linear calibration curve was obtained in the range of 1-10 ppm Strontium and Lead. In this experiment the results of solvent extraction for removal of Sr(II) and Pb(II) by using as (HAPED) organic reagent are presented. Effect of various parameters like pH, absorbance, wavelength and validity of Beer's and Lambert's law. The absorption is observed maximum at wavelength 530 nm and 500nm. The equilibrium is attained within 1 min. The best results of solvent

extraction were obtained in aqueous phase at pH 5.2 and 5.6 whereas organic phase containing chloroform as solvent.

1. Effect of pH and absorbance

Chloroform is found to be the most suitable solvent which is carried maximum extraction which is shown in figure 5. 1 cm^3 aqueous solution contain 100 ppm Sr(II) and Pb(II) at different pH shaking with 2 cm^3 of 0.1% HAPED in chloroform, after separated a two layers measure the absorbance of organic phase at wavelength of 585nm and 535nm and pH of 5.2 and 5.6.

2 Selection of The Solvent

Different solvents were tried to determine the maximum extraction of Strontium and Lead. Chloroform was found to be most suitable solvent as it showed the maximum extraction. The extraction of Strontium varied from maximum to minimum for the solvent in the order of chloroform > n-butanol > xylene > diethyl ether > carbon Tetrachloride > ethyl Acetate > n-Hexane > nitrobenzene >cyclohexanone >methyl acetate which is shown in figure:4.

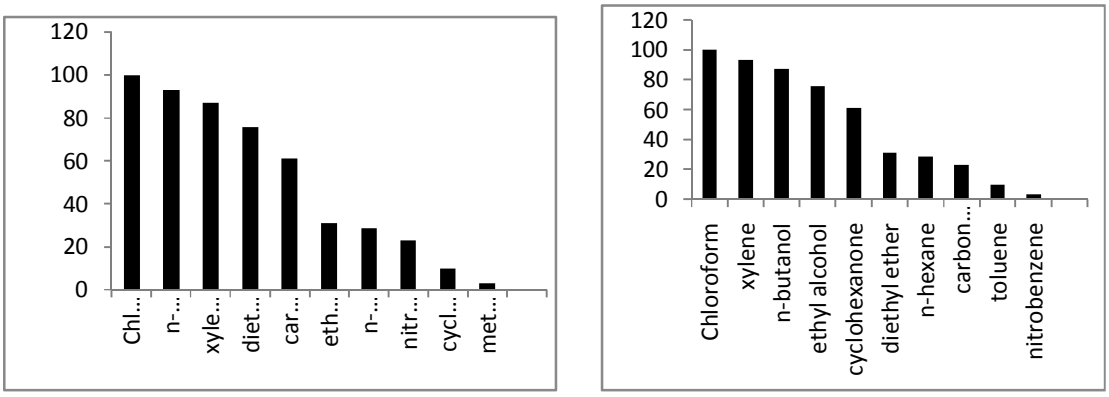


Figure :4 Effect of various solvents on Sr(II) and Lead(IV) : HAPED complex

3. Shaking time effect

1-cm^3 aqueous solution contain 100 ppm Sr(II)and Pb(II) at pH 5.2 and 5.6 after added 2 cm^3 of 0.1%HAPED in chloroform, shaking for different times (0-60) min. after separating the layers, measuring the absorbance of organic phase at wavelength of 585nm and 535nm.

4 Mole ratio method

Solution of 0.01M HAPED in chloroform used to extract 0.01M Sr(II) and Pb(II) from aqueous solution at optimum conditions, also determine absorbance of organic phase at wavelength of 585nm and 535nm respectively against chloroform, figure : 3 indicates that the ratio of Sr(II) and Pb(II) to complex was 1:2[Sr^{+2}: (HAPED) and Pb^{2+} (HAPED)].

4. CONCLUSION

The proposed method is more highly sensitive and selective than the reported methods for the extractive spectrophotometric determination of microgram amounts of Strontium and Lead. It has been successfully applied to the determination of Strontium and Lead at trace level in synthetic mixtures and alloys. It offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and suffers from less interference.

DECLARATION

"The facts and the views in the manuscripts are ours and I am totally responsible for authenticity, validity and originality". I undertake and agree that the manuscripts submitted to your journal have not been published elsewhere and have not been simultaneously submitted to other journals. I also declare that manuscript is my original work and we have not copied from anywhere else. There is no plagerism in my manuscripts.

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