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Spectrophotometric Determination of Trace Lead in Biological Samples by using 2,4-di Methoxy benzaldehyde isonicotinoyl Hydrazone (DMBIH)

Ramakrishna Reddy. K*, Devanna. N, Chandrasekhar. K.B

Department of Chemistry, JNTUA, College of Engineering, Anantapur, A.P, India.

Abstract

A rapid, simple, sensitive and selective spectrophotometric method has been developed for the determination of Lead (II) using newly synthesized Chromogenic reagent 2, 4-Dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH). Lead (II) forms bright yellow coloured water soluble complex with DMBIH in the pH range 8.0-10.0. The maximum absorbance was observed at pH 9.0. The molar absorptivity and sandell's sensitivity of Pb (II) at λ_{max} 396 nm was found to be 3.1372×10^4 L.mole^{-1}.cm^{-1} and 0.005 μg / cm^2. Beer's law validity range 0.4596-5.5152 μg/ml. Pb (II) forms 1:1 complex with DMBIH and stability constant of the complex was found to be 3.57×10^6. The first and second order derivative method has been developed. The derivative amplitudes were measured by peak height method and shows maximum amplitudes at 425 nm and 445 nm respectively in alkali buffer medium. The developed method was used for the determination of Pb (II) in biological samples.
Keywords: Lead (II), Derivative Spectrophotometry, 2,4-Dimethoxy benzaldehyde isonicotinoylhydrazone (DMBIH) and Biological samples.

Contents

Corresponding author
Ramakrishna Reddy. K
E-mail: reddykotanka@yahoo.com
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1. Introduction

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al[1]. Hydrazones are important class of known analytical reagents. Due to analytical potentialities of hydrazones herein we report the synthesis, characterization and analytical properties of the reagent 2,4-Dimethoxybenzaldehyde isonicotynoyl hydrzone (DMBIH). Lead is the most important element, which affect the physical properties of steel, alloys and high purity metals. It is highly toxic to man, animals, and causes environmental disease when released in the atmosphere. Very low concentrations of this metal are normally present in various matrices such as plants, soils, food and water. Therefore, it is very important from an analytical point of view to develop sensitive, selective, rapid and economical methods for its quantitative determination when present in trace amounts. A survey of the literature reveals that lead may be determined spectrophotometrically after extraction of its complexes into various organic solvents [2, 3]. Although, these methods are simple and economical but are not sufficiently sensitive and selective. The preconcentration factor is much less as compared to the present method. Graphite furnace atomic absorption spectroscopy, neutron activation analysis, inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectrometry and direct current plasma atomic emission spectrometry may be used for the

determination of lead at trace level but these instruments are expensive, day-to-day maintenance is high and they are not free from various types of inherent interferences [4-9].

Derivative spectrophotometry offers the advantages of increased selectivity and sensitivity compared with normal spectrophotometry [10-17]. Spectrophotometers equipped with suitable derivative units enable not only the derivative spectra of the first and second orders to be obtained but also higher orders.The increased selectivity in derivative spectrophotometry results from the fact that bands, which overlap in normal absorption spectra, appear as separated bands in the derivative spectra. Derivative spectrophotometry can increase the sensitivity owing to the amplification of derivative signals and lowering of noise, improvements in selectivity and in sensitivity are easier to obtain in instances where the bands in the normal absorption spectra are fairly sharp [18, 19]. Sodium tetra phenyl borate (TPB) and its derivatives have been used in the estimation of alkali and univalent metal ions [20-22].

2. Materials and Methods

Apparatus

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction and the recorder was a computer controlled thermal graphic printer with a cathode ray tube and one degree of freedom in the wavelength range 300 – 800 nm.

Reagents

Preparation of 2, 4-Dimethoxybenzaldehyde isonicotinoylhdrazone

All reagents used were of A.R grade unless otherwise stated. All solutions were prepared with distilled water. The standard Pb (II) solution (0.1 M) was prepared by dissolving 8.28 g of Lead nitrate in 250 ml distilled water. The reagent DMBIH is prepared by the Sah and Daniels procedure. 1.6617 gm of 2,4-Dimethoxybenzaldehyde and 1.3714 gm of Isonicotynoylhydrazide were dissolved in sufficient volume of methanol and the mixture is refluxed for four hours. The contents are allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{16}O_4N_2$). The resultant product is recrystallised twice from hot methanol. Pure light greenish crystals of 2,4-dimethoxybenzaldehydeisonicotinoylhydrazone (DMBIH) (m.p. 234-236°C.) was obtained. IR and NMR spectral studies characterized the compound. The mass spectrum shows that molecular ion peak at m/z 286 (M+1). The structure of DMBIH was confirmed based upon IR, NMR and mass spectral data.
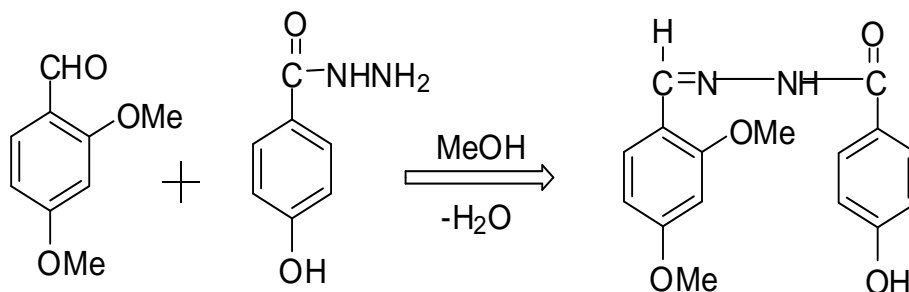

Fig1. Structure of 2,4-Dimethoxybenzaldehydeisonicotinoylhydrazone

3. Results and Discussion

The reagent 2,4-Dimethoxybenzaldehydeisonicotinoylhydrazone (DMBIH) was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMBIH was used for the spectrophotometric method for determination of the Pb (II). The absorption spectra of DMBIH and its Pb (II) complex under the optimum conditions are shown in Figure 2. The Pb (II)-DMBIH complex shows the maximum absorbance at 396 nm, where the reagent blank does not absorb appreciably.

Lead (II) reacts with DMBIH in basic buffer to give yellow coloured water-soluble Complex. The colour reaction between Lead (II) and DMBIH was instantaneous even at room temperature in pH range 8.0-10.0, the maximum colour intensity was observed at pH 9.0. The absorbance of lead (II)-DMBIH remains constant for more than 24 hours. The effect of various surfactants such as Triton X-100 (5%), sodium dodecyl benzene sulphonate (SDBS) and Cetyl trimethyl ammonium bromide (CTAB) on the absorption profiles of the system has been investigated. In presence of SDBS (5%) surfactant the complex is more stable and exhibited maximum absorbance. The results were shown in table 1.

Table 1: Effect of SDBS on the absorbance of metal complex

[Pb (II)]	=	2.5×10^{-5}M
[DMBIH]	=	2.5×10^{-4}M
pH	=	9.0
Wavelength	=	396 nm
SDBS (5%)	=	0.5ml

SDBS	Absorbance
0.5	0.725
0.8	0.724
1.0	0.725
1.5	0.724
2.0	0.723
2.5	0.724
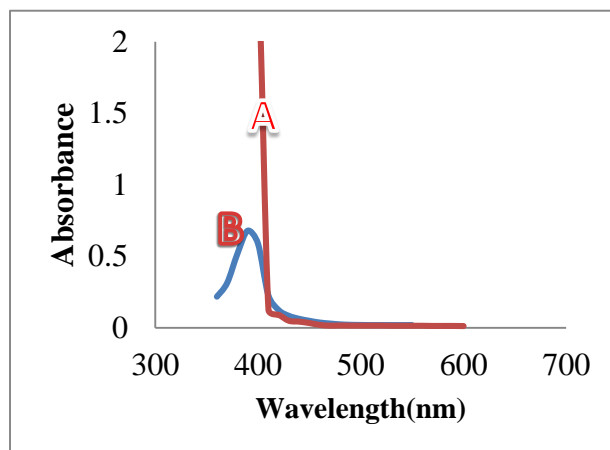
Fig 2. Absorption spectra of (A). Reagent (DMBIH) vs buffer blank, (B). [Hg (II)-DMBIH] Complex, Pb (II) = 0.5 mL of 2.5×10^{-5} M, DMBIH = 0.5 mL of 2.5×10^{-4} M, pH = 9.0, SDBS (5%) = 0.5 ml

When varying the volume of reagent DMBIH (2.5×10^{-4} M) from 0.5 ml to   4.0 ml, the constant absorbance was obtained from 0.5 ml. Therefore 10-fold molar excess of reagent is adequate for full colour development. The excess of reagent has no adverse effect on the absorbance of the complex. The order of addition of buffer solution, metal ion, and reagent has no adverse effect on the absorbance of Pb (II)-DMBIH complex. Beer's law was obeyed in the range 0.4596-5.5152µg/ml. The optimum concentration range of Pb (II)-DMBIH complex was 0.9192-4.596 µg/ml. The molar absorpitivity and Sandell's sensitivity of Pb (II)-DMBIH complex was obtained from the Beer's law. The linear regression analysis of absorbance at λ_{max} of the complex against metal ion (µg/ml) shows a good linear fit. The various important analytical characteristics of Pb (II) and DMBIH complex are summarized in Table 2.

Table 2. Physico-Chemical and analytical characteristics of   [Pb (II)-DMBIH] complex

Characteristics	Results
Colour	Yellow
λ_{max}(nm)	396
p^H range (optimum)	8.0 – 10.0
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity(L.mol $^{-1}$cm^{-1}) (ϵ)	3.1372×10^4
Sandell's sensitivity(µg cm^{-2})	0.005
Beer's law validity range(µg/ml)	0.4596-5.5152
Optimum concentration range(µg/ml)	0.9192-4.596
Composition of complex(M:L) obtained in Job's and mole ratio methods	1:1
Stability constant of the complex	3.57×10^6
Standard deviation for ten determinations	0.002
Relative standard deviation (%)	0.2

The first order and second order derivative spectral graphs shown in Figure.3 and 4 respectively. This shows that, the derivative amplitudes measured at λ_{max} 425 nm for first order and 445 nm for second order were found to be proportional to the amount of Lead (II).
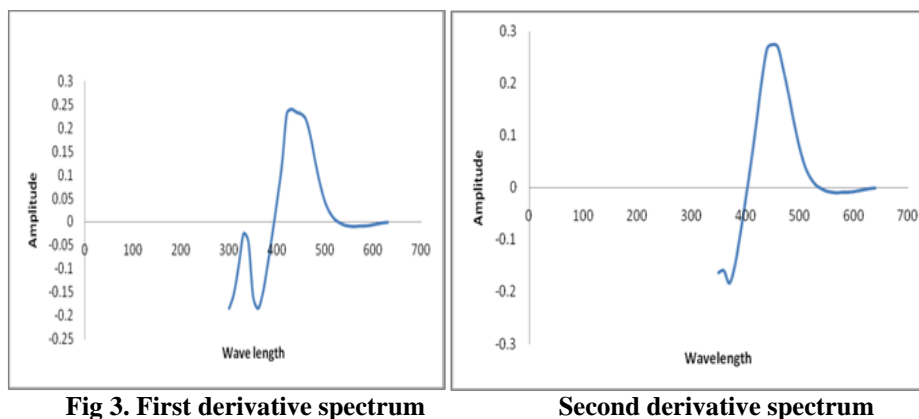

Fig 3. First derivative spectrum   Second derivative spectrum

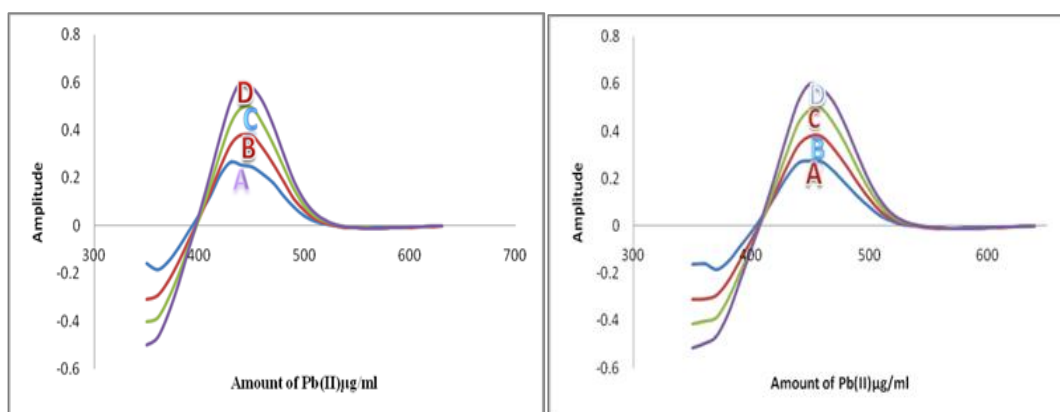[Pb (II)] = 2.5 x 10^{-5} M, [DMBIH] = 2.5 x 10^{-4} M, pH = 9.0SDBS (5%) = 0.5 ml

Fig 4. First order derivative spectrum   Second order derivative spectrum

Pb (II) (μg/ml) = A) 2.072; B) 3.108; C) 4.144; D) 5.180, [DMBIH]= 5 x10^{-4} M, pH = 9.0, SDBS (5%) = 0.5 ml

The stoichiometry of the complex was found to be 1: 1 (metal: ligand) investigated by job's continuous variation method and molar ratio method, with a stability constant 3.57 x10^6. The effect of various diverse ions in the determination of of 2.59 μg/ml Pb (II) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ± 2% in the absorbance or amplitude. The results are given in Table 3. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess, such as iodide, bromide,acetate, thiocyanide, tartarate, tetraborate and chloride, Strontium (I), Manganese (II), Barium (II), Zn (II), Bi (III) and Lanthanum (III). The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as iron (III) and Cu (II) are decreased by adding masking agents fluoride and thiourea.

Table 3. Tolerance limit of foreign ions in the determination of 2.59 μg/ml of Pb (II)

Ion added	Tolerance limit μg/ml	Ion added	Tolerance limit μg/ml
Bromide	3196	Bi^{+3}	104
Iodide	2542	Co^{2+}	90
Urea	1560	Zn^{2+}	84
Chloride	1164	Ca^{2+}	75
Tetraborate	990	Sn^{2+}	72
Sulphate	950	Zr^{4+}	68
Oxalate	889	Ni^{2+}	62
Nitrate	630	U^{6+}	60

Acetate	595	Ag^+	58
Thiocyanide	587	Mo^{6+}	54
Phosphate	482	As^{3+}	53
Ascorbic acid	179	Sb^{3+}	49
Tartarate	155	Cr^{3+}	45
Thiourea	120	Al^{3+}	35
Fluoride	98	Hg^{2+}	11
Ba^{2+}	222	Pd^{2+}	10
La^{3+}	194	Ru^{3+}	8
Sr^{2+}	185	Cu^{2+}	2.66 ,6.27*
Mn^{+2}	116	Fe^{3+}	4.62,9.2 **

* Masked with 545 µg/ml of Thiourea, **Masked with 276 µg/ml of Fluoride.

Applications

Determination of Pb (II) in Biological samples:

The accuracy and applicability of the proposed method has been applied to the determination of lead in National Institute for Environmental Studies (NIES) No.1 tea leaves; No.2 Human Hair ; No.3 Pond sediment.A 0.1 g sample was taken in a beaker and dissolved in concentrated nitric acid (∼5 ml) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100 ml with water in a calibrated flask.NIES, No.4 Vehicle Exhaust Particulates (1 g) was dissolved in 18 ml of concentrated nitric acid, 18 ml of concentrated perchloric acid and 2 ml of concentrated hydrofluoric acid in a 100 ml Teflon beaker, evaporated to a small volume, filtered through a filter paper and made up to 100 ml with distilled water. An aliquot (10–50 ml) of the sample solution was taken individually and lead was determined by the general procedure. The results are presented in Table 4.

Table 4. Determination of Pb (II) in Biological samples

Sample	Composition	Concentration ($\mu g\ g^{-1}$)		
		Certified value	Found	
			D1	D2
NIES, No.1 Tea Leaves	Zn, 33; Cd, 0.030; Sb, 0.014; Ni, 6.5; Cr, 0.15; Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, 15.5; Sr, 3.7; Ca, 3200; Cs, 0.22l; Co, 0.12; Mn, 7.00; Cu, 7.0 µg g^{-1}	0.8	0.76±0.04	0.77±0.03
NIES, No.2 Human Hair	Zn, 169; Cd, 0.20; Sb, 0.07; Ni, 1.8; Al, 240; Fe, 225; Mg, 208; Hg, 4.4; K, 34; Rb, 0.19; Sc, 0.05; Se, 1.4; Na, 26; Sr, 2.3; Ti, 3.2; Ca, 728; Cr, 1.4; Ba, 2.2; Cu, 16.3; Co, 0.10 µg g^{-1}	6.0	5.6±0.4	5.7±0.3
NIES, No.3 Pond Sediment	Fe, 6.53±0.35; Al, 10.6±0.5; Ca, 0.81; K, 0.68; Na, 0.57% Zn, 343; Cu, 210; Cr, 75; Ni, 40; Cd, 0.82; Co, 27; As, 12 µg g^{-1}	105	107±2	109 ±4
NIES, No.4 Vehicle Exhaust Particulates	K, 0.115±0.008; Ca, 0.53±0.02; Mg, 0.101±0.005; Al, 0.33±0.02; Na, 0.92±0.008; Zn, 0.104±0.005%; Sr, 89±3; Co, 3.3±0.3; Cu, 67±3.5; Cd, 1.1±0.1; As, 2.6±0.2; Cr, 25.5±1.5; V, 17±2; Sb, 6.0±0.4; Ni, 18.5±1.5; Cs, (0.24); Rb, (4.6); Sc, (0.055); La, (1.2); Br, (56); Ag, (0.2); Se, (1.3); Mo, (6.4); Ce, (3.1); Th, (0.35); Sm, (0.20); Eu, (0.05); Lu, (0.02) µg g^{-1}	219±9	215±4	217±2

*average of best three determinations among five determinations

4. Acknowledgements

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