



Research Article

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**A selective novel organic reagent diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) using for the direct and derivative spectrophotometric determination of lead (II) in presence of Micelar medium**

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**ABSTRACT**

*Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) is used as a novel chromogenic organic reagent for the determination of Lead (II) with specterophotometry. The novel chromogenic organic reagent Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) gave yellow color water soluble complex with Pb (II) in buffer (pH 4.0-5.0) medium. The complex shows maximum absorbance at 386 nm. The system obeyed beer's law in the concentration range of 0.270-2.79µg/ml. The optimum Lead (II) concentration range for accurate determination as evaluated from Ringbom plot was 0.482-2.642 µg/ml. The molar absorptivity and Sandell's sensitivity were  $1.875 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$  and  $0.0066 \text{ µg/cm}^2$  respectively. The Lead (II) forms M:L (1:1) color complex with DMAHBH and stability constant of the complex was found to be  $8.8 \times 10^6$ . Food, Soil and biological samples were analyzed for the determination of Lead (II) in the proposed method and obtained with good results.*

**Key words:** chromogenic organic reagent, derivative spectrophotometry, Lead (II), Food, Soil and Biological samples.

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**INTRODUCTION**

Lead is a ubiquitous pollutant in the ecosystem. Lead mining and smelting works and automobile exhausts, lead batteries, lead paints, manufacture industries of lead base alloys and automobile exhausts are the main causes of lead pollutants. The leaded dust settled on the plants and food stuff intended for human and animal consumption. Lead causes poisoning of living organism. It is a cumulative poison causing loss of appetite, constipation, abdominal pain, mental retardation, a blue line at the junction of teeth and gums and finally nervous disorders and brain damage. It also has effects on the hem-bio synthesis, blood pressure on kidney function.

Though a number of reagents are available for the spectrophotometric determination of lead, the well known dithiozone<sup>1</sup> method, which involves extraction, is often recommended because of its relative high sensitivity the dithiozone method, however, has some well known draw backs. The optimum pH range for extraction<sup>2-5</sup> of lead

from 7-10 the lead dithiozone complex solution are unstable in sun light several modifications of the dithiozone methods for the determination of lead have been made and applied for its petroleum products<sup>6</sup>, the food stuffs<sup>7,8</sup>, urine<sup>9</sup>, biological substances<sup>10</sup>, plant materials<sup>11,12</sup>, and water<sup>13,14</sup>.

various chromogenic organic reagents were reported for the spectrophotometric determination of the lead (II) at micro levels there several frequently adopted methods using analytical techniques such as AAS, ICP-AES, X-Ray fluorescence spectroscopy, voltametry, polarography, spectrophotometry and other techniques among them, spectrophotometric methods<sup>15-20</sup> are preferred because this very economical and high sensitivity.

### EXPERIMENTAL SECTION

Spectrophotometric measurements were made in a shimadzu 160 a microcomputer based UV-Visible spectrophotometer equipped with 1.0 cm quartz cells, an ELICO LI- 120 digital pH meter. All reagents used were of analytical reagent (AR) grade unless otherwise stated. All solutions were prepared with distilled water.

#### Reagent :

#### Synthesis of Diacetylmonoxime-3-amino-4-hydroxybenzoylhydrazone ( DMAHBH)

It was prepared by refluxing a mixture of Diacetylmonoxime(1.0111 g, 0.01 mole) and 3-Amino-4-hydroxybenzhydrazide (1.6717 g, 0.01 mole) in ethanol (15 ml) for 5 hours. On cooling the reaction mixture, a light yellowish crystalline product was separated out. The crystalline hydrazone was collected by filtration and washed several times with (20%) ethanol in water and dried in vacuum. The product was recrystallised with ethanol. Yield 79%, m.p. 220<sup>o</sup> C.

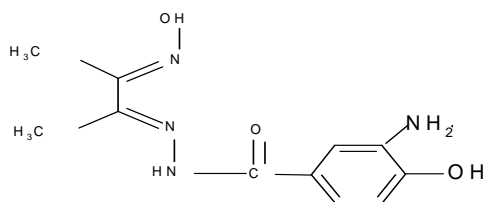


Fig. Structure of DMAHBH

#### Analytical properties of DMAHBH:

The reactions of some important metal ions were tested at different pH values. The characteristics of the most important complexes are summarized in Table 1.0. The samples were prepared in 10 ml standard volumetric flasks by adding 3 ml of buffer (pH 1.0-11), 0.5 ml of metal ion ( $1 \times 10^{-3}$  M) and 0.5 ml of ( $1 \times 10^{-2}$  M) DMAHBH solutions. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-800 nm range against reagent blank.

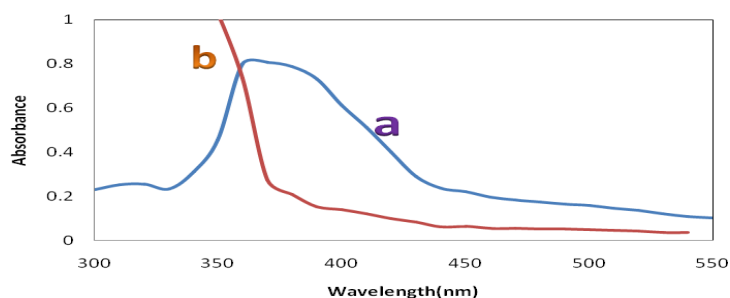
The data obtained from appropriate spectra which were derived in the presence of 10-fold molar excess of the reagent to metal ion. The pH values which facilitate the formation of different complexes were also included.

Table 1.0: Characteristics of DMAHBH complexes in solution

Metal ion	$\lambda_{\text{max}}$ (nm)	pH	Surfactant used	Colour of the complex
Os(VIII)	390	4.0	-	Bright yellow
Zr(IV)	388	4.0	-	Yellow
Cu(II)	412	9.0	-	Bright yellow
Lead	387	4.0	TritonX-100	Yellow
Cd	378	8.0-9.0	TritonX-100	yellow

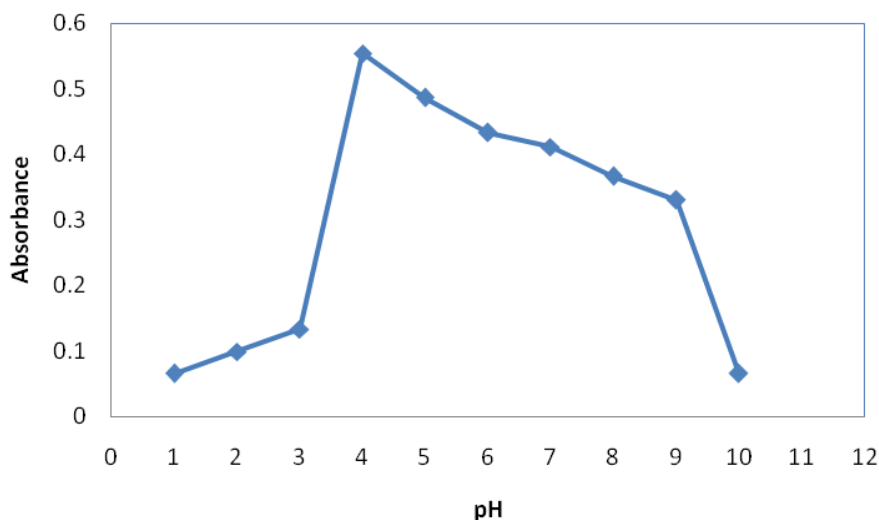
**RECOMMENDED PROCEDURE****Determination of Lead (II) (zero order).**

An aliquot of the solution containing 0.279-2.79 $\mu\text{g/ml}$  of Lead (II), 3 ml of buffer solution pH 1.0 to 10.0 and 0.5 ml of ( $1 \times 10^{-2}\text{M}$ ) DMAHBH reagent were taken in a 10ml standard volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 386 nm in a 1.0 cm cell again corresponding reagent blank prepared in the same way but without Lead (II) metal solution. The absorption spectra of DMAHBH and its Pb (II) complex under the optimum conditions are shown in fig. 2. The Pb (II)- DMAHBH complex shows the maximum absorbance at 386 nm, where as the reagent blank does not absorb appreciably.



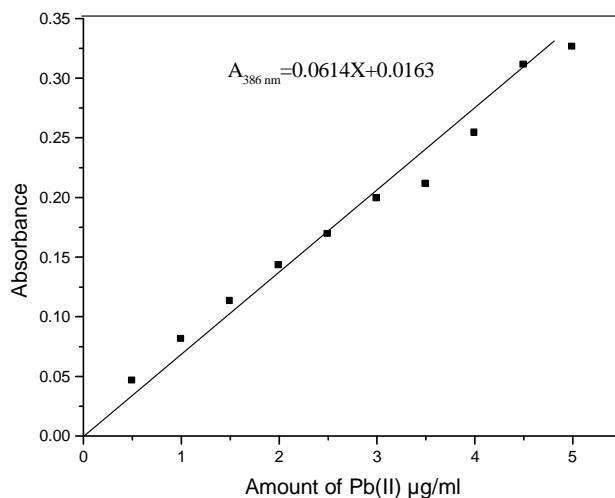
**Fig -1: Absorption spectra**  
(a). [Pb (II)- DMAHBH] complex Vs. reagent blank  
(b). DMAHBH Vs. buffer blank.

Effect of pH on the absorbance of the complex the study of the effect of pH on the color intensity of the reaction mixture showed that the maximum color was obtained in the pH range 4.0-5.0. Analytical studies were therefore, carried out at pH 4.0 Fig-2



**Fig-2: Effect of pH**

**Applicability of Beer's law** For the possible determination of Lead (II) at micro levels, the absorbance of the solutions containing different amounts of metal ion was measured. Calibration plot drawn between absorbance and amount of Lead (II) Fig 3 showed that Beer's law was obeyed in the concentration range 0.279-2.79 $\mu\text{g ml}^{-1}$  of Lead (II). The molar absorptivity and Sandall's sensitivity were  $1.875 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$  and 0.0066  $\mu\text{g/cm}^2$  respectively. The correlation coefficient of the calibration curve for experimental data was 0.997.



**Fig No.3: Absorbance Vs Amount of Pb (II) µg/ml**  
 [DMAHBH] =  $1 \times 10^{-2}$   
 pH = 4.0  
 Wavelength = 386 nm

## RESULTS DISCUSSION

Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) reagent is a blend of a carbonyl compound and a hydrazide. The reagent solution is stable for more than 24 hrs. in presence of buffer medium. The ligand presumably coordinates the metal ions to give a neutral water soluble complex.

### Determination of Lead (II) using DMAHBH:

Lead (II) reacts with DMAHBH in basic medium to give yellow coloured water-soluble complex. The colour reaction between Lead (II) and DMAHBH are instantaneous even at room temperature in the pH range 4.0 to 5.0. The absorbance of the yellow coloured species remains constant for two hours. The maximum colour intensity is observed at pH 4.0. A 10-fold molar excess of reagent is adequate for full colour development. The order of addition of buffer solution, metal ion and reagent has no adverse effect on the absorbance. The complex formation reaction between Lead (II) and DMAHBH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important physico-chemical and analytical characteristics of Lead (II) and DMAHBH are summarized in Table-2

**Table-2: Physico-chemical and analytical characteristics of [Pb (II) – DMAHBH] complex**

Characteristics	Results
$\lambda_{\max}$ (nm)	386
Colour	yellow
pH range (optimum)	4.0-5.0
Molar absorptivity ( $L \cdot mol^{-1} \cdot cm^{-1}$ )	$1.875 \times 10^4$
Sandell's sensitivity ( $\mu g \cdot cm^{-2}$ )	0.0066
Mole of reagent required per mole of metal ion for full colour development	10 - folds
Beer's law validity range ( $\mu g/ml$ )	0.279-2.79
Optimum concentration range ( $\mu g/ml$ )	0.482-2.642
Stability constant of the complex (Jobs method)	$8.8 \times 10^6$
Relative standard deviation (%)	0.1
Regression coefficient	0.996
Composition of complex (M:L) obtained in Job's and mole ratio method	1: 1

The first order derivative spectral graph was shown in fig no-4. This shows that the derivative amplitudes measured at 448 nm. First order was found to be proportional to the amount of Lead (II) respectively.

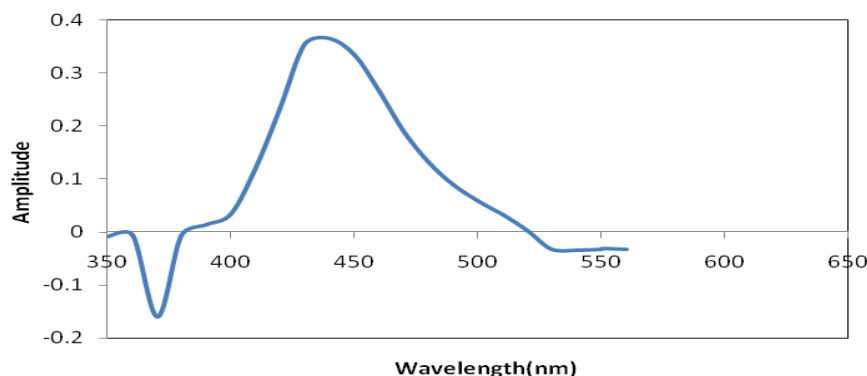


Fig no-4: First derivative spectra of [Pb (II)- DMAHBH] Vs reagent

### EFFECT OF FOREIGN IONS

The effect of foreign ions was studied with a view to examine the applicability of the method in presence of foreign ions. The interference of various foreign ions was studied with 1.554  $\mu\text{g/ml}$  of Lead (II) by adopting the following procedure.

Fixed amount of metal ion solution was taken in 10-ml volumetric flasks containing 3 ml of buffer solutions, required quantity of surfactant. Then appropriate amount of foreign ion was added to all the flasks except one. The reagent solution was added to all at the end. The contents were made up to the mark with distilled water. The absorbance of the complex in each flask was measured at a selected wavelength ( $\lambda_{\text{max}}$ ) against reagent blank. From this absorbance the tolerance limit of the foreign ion was determined. The amount of foreign ion which brings about a change in absorbance by  $\pm 2\%$  was taken as its tolerance limit.

Cations were added mostly as chlorides, sulphates or nitrates and the anions were added as sodium or potassium salts. Some of the cations interfering were masked by using adequate quantity of suitable masking agents.

Table-2: Tolerance limit of foreign ions in the determination of 1.554  $\mu\text{g/ml}$  of Lead (II)

Ion added	Tolerance limit ( $\mu\text{g/ml}$ )	Ion added	Tolerance limit ( $\mu\text{g/ml}$ )
Iodide	2032	Zr(IV)	165
Sulphate	513	Zn(II)	16
Urea	635	Bi(III)	43
Thiocyanide	199	Ni(II)	21
Bromide	831	Ce(IV)	36
Thiourea	654	Fe(III)	1.41, 1.6 <sup>a</sup>
Nitrate	1342	Cu(II)	1.16, <sup>b</sup>
Tetra borate	201	Ru(III)	1.93
Acetate	113	Ag(I)	9.11
Phosphate	165	Pt(IV)	7.32
Chlorides	331	Sb(II)	433
Tartarate	836	Sr(II)	31
Citrate	379	V(V)	133
Fluoride	436	Os(VIII)	6.32
Oxalate	372	Cd(II)	13
Thiosulphate	311	Co(II)	11
U(VI)	153	Al (III)	36
Sn(II)	47	Mo(VI)	26
La(III)	152	Cr(VI)	16
Ba(II)	188	Hg(II)	1.42
Na(I)	33	Mn(II)	46

<sup>a</sup> Masked with 81  $\mu\text{g/ml}$  of Fluoride

<sup>b</sup> Masked with 195  $\mu\text{g/ml}$  of Thiourea.

**APPLICATIONS**

The developed method was applied to the lead determination in several types of samples, such as bulked food sample and soil sample. The analytical results and recoveries for spiking with 1.50  $\mu\text{g g}^{-1}$  Lead is shown in Table 3. The recoveries of the spiked samples varied from 98 % to 101 % for lead, indicating that the low levels of lead present was determined with a comfortable degree of confidence.

**Table-3: Determination of Lead (II) in Bulked food and soil sample**

Sample	Determination of Pb (II) ( $\mu\text{g g}^{-1}$ )	Certified values( $\mu\text{g g}^{-1}$ )	RSD (%)	Recovery (%)
Bulked Food sample	1.30	1.32	3.0	98
Soil sample	1.62	1.61	2.8	101

**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. 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.

**Table-4: Determination of Pb (II) in Biological samples**

Sample	Composition	Concentration ( $\mu\text{g g}^{-1}$ )	
		Certified value	Found
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, 0.221; Co, 0.12; Mn, 7.00; Cu, 7.0 $\mu\text{g g}^{-1}$	0.8	0.76±0.04
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 $\mu\text{g g}^{-1}$	6.0	5.9±0.1
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 $\mu\text{g g}^{-1}$	105	104±1
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) $\mu\text{g g}^{-1}$	219	217±2

*\*average of best three determinations among five determinations*

**CONCLUSION**

In acidic medium, the Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) reacts with Lead (II) and imparts yellow color water soluble complex. The color reaction between Lead (II) and DMAHBH is instantaneous and the absorbance of the colored species remains constant for three hours. Order of addition of constituents (buffer, metal ion and reagent) has no adverse effect on the absorbance of the complex.

Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH) has been proven a sensitive and selective chromogenic organic reagent for the determination of Lead (II). Molar absorptivity of the color complex was  $1.875 \times 10^4 \text{ L.mole}^{-1} \text{ cm}^{-1}$ . The proposed method was especially sensitive and selective with respect to metals, which commonly seriously interfere with the determination of Copper and Iron performed by literature methods. The proposed method can be successfully applied to the determination of Lead (II) in food, soil and biological samples. This method was favorably compared with previously reported spectrophotometric methods.

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