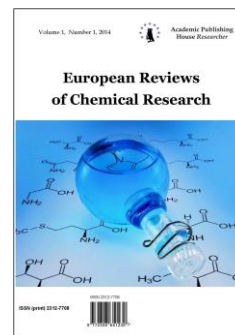


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### A Sensitive and Selective Chromogenic Organic Reagent 4-hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (HDMBHBH) for the Direct and Derivative Spectrophotometric Determination of Lead (II)

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#### Abstract

4-hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (HDMBHBH) is used as a novel chromogenic organic reagent for the determination of Lead (II) using spectrophotometry. The novel chromogenic organic reagent 4-hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (HDMBHBH) gave yellow coloured water soluble complex with Pb (II) in basic buffer (pH = 10.0) medium. The colour complex shows maximum absorbance at 386 nm. The system obeyed Beer's law in the concentration range of 0.518–5.18 µg/ml. The optimum Lead (II) concentration range for accurate determination as evaluated from Ringbom plot was 1.036–4.662 µg/ml. The molar absorptivity and Sandell's sensitivity were  $2.66 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  and  $0.0077 \text{ µg/cm}^2$  respectively. The Lead (II) forms 1:1 colour complex with HDMBHBH and stability constant of the complex was found to be  $3.42 \times 10^6$ . The present developed method was successfully applied for the determination of Lead (II) in biological samples.

**Keywords:** novel chromogenic organic reagent; derivative spectrophotometry; lead (II); biological samples.

#### Introduction

Generally, lead compounds are toxic for animals. Throughout most of human history, lead was used for a wide variety of applications with little or no appreciation of the serious health hazards it poses. Today, physiologists understand that the human body is able to excrete about 2

milligrams of lead efficiently each day but excess of that can cause serious health problems. That is why lead compounds are not used in pesticides or insecticides.

Hence, the analytical methods are required with highest possible sensitivity and selectivity. One of the techniques which is simple and readily in reach of developing and developed countries is photometry. This is a nondestructive technique and it is useful for the determination of trace amounts of metal ions in different kinds of samples such as alloys, biological and industrial materials and wastes.

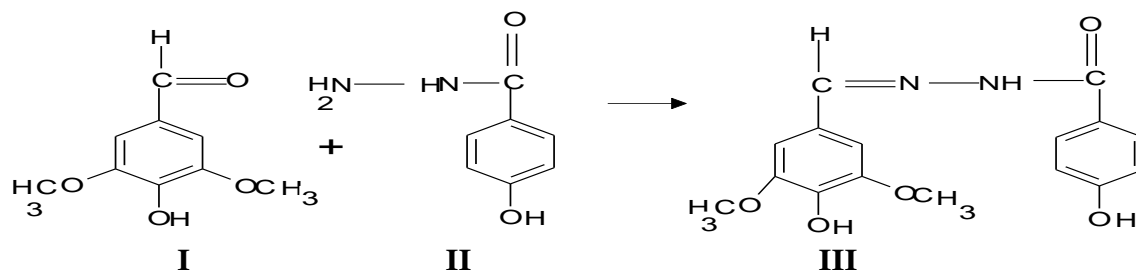
### Experimental study

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, characterization and analytical properties of 4-hydroxy 3,5-dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone (HDMBHBH)**

It is prepared by refluxing 1.82 g of 4-hydroxy 3,5-dimethoxy benzaldehyde and 1.52 g of 4-hydroxy benzhydrazide in 25 ml of carbinol for about 4 hours. The contents are allowed to cool and the product is separated by filtration. The crude product (yield 80 %) obtained ( $C_{16}H_{16}N_2O_5$ ) is recrystallized twice from hot methanol. Pure light greenish coloured crystals of 4-hydroxy 3,5-dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone (HDMBHBH) (III) (m.p. 292–294 °C) are obtained (see the scheme below).



**I** = 4-Hydroxy 3,5-dimethoxy benzaldehyde

**II** = 4-Hydroxybenzhydrazide

**III** = 4-Hydroxy 3,5-dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone (HDMBHBH)

The reagent 4-hydroxy-3,5-dimethoxybenzaldehyde-4-hydroxy benzoyl hydrazone (HDMBHBH) was characterized with the help of Infrared,  $^1\text{H-NMR}$  and mass spectral data and the structure was confirmed by the spectral data.

### 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. The samples were prepared in 10 ml standard volumetric flasks by adding 3 ml of buffer (pH = 1.0–11.0), 0.5 ml of metal ion ( $1 \times 10^{-3}$  M) and 0.5 ml of ( $1 \times 10^{-2}$  M) HDMBHBH 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: Characteristics of *HDMBHBH* complexes in solution

Metal ion	$\lambda_{\max}$ (nm)	pH	Surfactant used	Colour of the complex
Pb(II)	386	9.0–10.0	Triton-X	Yellow
Au(III)	400	3.0–5.0	Triton-X	Brown
V(V)	392	3.0–5.0	Triton-X	Yellow

### Recommended procedure

#### Determination of Lead (II) (zero order)

An aliquot of the solution containing 0.3178 to 3.813  $\mu\text{g/ml}$  of Lead (II), 3 ml of buffer solution pH = 8.0 to 10.0 and 0.5 ml of ( $1 \times 10^{-2}$  M) HDMBHBH reagent were taken in a 10 ml standard volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 412 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 HDMBHBH and its Pb (II) complex under the optimum conditions are shown in Figure 2. The [Pb(II)–HDMBHBH] complex shows the maximum absorbance at 412 nm, whereas the reagent blank does not absorb appreciably.

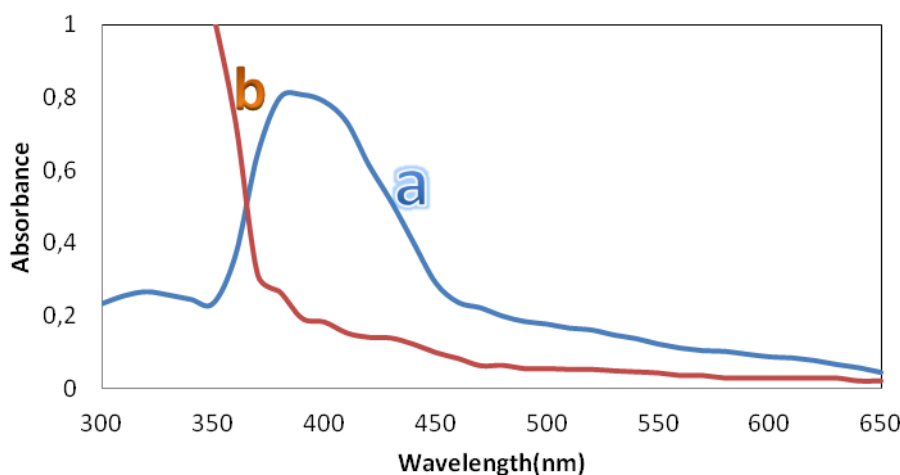


Figure 2: Absorption spectra:  
 (a). [Pb(II)–HDMBHBH] complex Vs. reagent blank;  
 (b). HDMBHBH Vs. buffer blank.

### Results and discussion

#### 4-hydroxy 3,5-dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone (HDMBHBH)

4-hydroxy 3,5-dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone (HDMBHBH) reagent is a blend of a carbonyl compound and a hydrazide. The reagent solution is stable for more than 24 hrs in presence of the buffer medium. The ligand presumably coordinates the metal ions to give a neutral water soluble complex.

#### Determination of Lead (II) using HDMBHBH

Copper (II) reacts with HDMBHBH in basic medium to give yellow coloured water-soluble complex. The colour reactions between Lead (II) and HDMBHBH are instantaneous even at room

temperature in the pH range 8.0 to 10.0. The absorbance of the bright yellow coloured species remains constant for five hours. The maximum colour intensity is observed at pH = 10.0. 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 HDMBHBH 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 HDMBHBH are summarized in Table 2.

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

Characteristics	Results
$\lambda_{\max}$ (nm)	386
colour	yellow
pH range (optimum)	9.0 to 10.0
Mole of reagent required per mole of metal ion for full colour development	10-folds
Molar absorptivity ( $L \cdot mol^{-1} \cdot cm^{-1}$ )	$2.66 \times 10^4$
Sandell's sensitivity ( $\mu g \cdot cm^{-2}$ )	0.0077
Beer's law validity range ( $\mu g/ml$ )	0.518–5.18
Optimum concentration range ( $\mu g/ml$ )	1.036–4.662
Composition of complex (M:L) obtained in Job's and mole ratio method	1 : 1
Stability constant of the complex (jobs method)	$3.42 \times 10^6$
Relative standard deviation (%)	0.02
Regression coefficient	0.999

The system [Pb(II)–HDMBHBH] obeys Beers law and the calibrated values were presented in Figure 3.

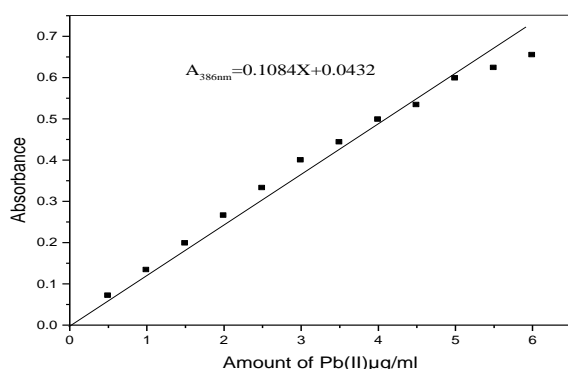


Figure 3: Absorbance Vs Amount of Pb (II)  $\mu g/ml$ :  
[HDMBHBH] =  $1 \times 10^{-2}$ ; pH = 9.0; wavelength = 418 nm

The first order derivative spectral graph was shown in Figure 4. This shows that the derivative amplitude is measured at 418 nm. First order was found to be proportional to the amount of Lead (II) respectively.

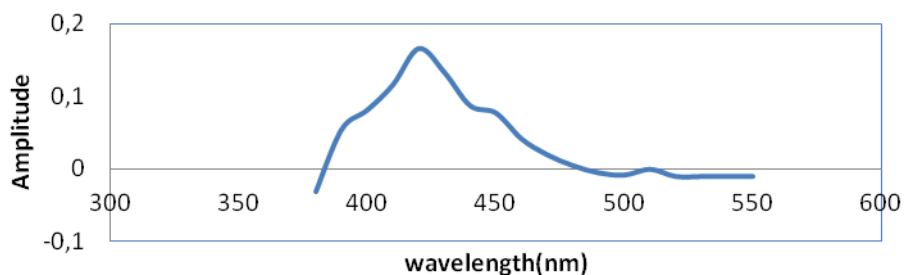


Figure 4: First derivative spectra of [Pb(II)-HDMBHBH] Vs reagent

### ***Effect of foreign ions***

Derivative spectrophotometry is a very useful technique in the sense that it decreases the interference, i.e., increases the tolerance limit value of foreign ions of metal ions having overlapping spectra. The recommended procedures have been employed for the spectrophotometric determination of Lead (II). The effect of various diverse ions in the determination of Lead (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  $\pm 2\%$  in the absorbance or amplitude. The experimental results are given in Table 3.

Table 3: Tolerance limit of foreign ions in the determination of 5.18  $\mu\text{g/ml}$  of Lead (II)

<b>Ion added</b>	<b>Tolerance limit (<math>\mu\text{g/ml}</math>)</b>	<b>Ion added</b>	<b>Tolerance limit (<math>\mu\text{g/ml}</math>)</b>
Iodide	2187	Zr(IV)	216
Sulphate	559	Zn(II)	20
Urea	723	Bi(III)	58
Thiocyanide	183	Ni(II)	33
Bromide	959	Ce(IV)	42
Thiourea	797	Fe(III)	1.6, 1.9 <sup>a</sup>
Nitrate	1678	Cu(II)	1.7, 2.5 <sup>b</sup>
Tetra borate	249	Ru(III)	2.6
Acetate	167	Ag(I)	12
Phosphate	293	Pt(IV)	11
Chlorides	249	Sb(II)	476
Tartarate	744	Sr(II)	25
Citrate	379	V(V)	116
Fluoride	577	Os(VIII)	8
Oxalate	269	Cd(II)	22
Thiosulphate	356	Co(II)	25
U(VI)	198	Al (III)	42
Sn(II)	47	Mo(VI)	20
La(III)	152	Cr(VI)	28
Ba(II)	267	Hg(II)	1.5, 1.3 <sup>c</sup>
Na(I)	45	Mn(II)	55

'a' masked with 76  $\mu\text{g/ml}$  of Fluoride

'b' masked with 345  $\mu\text{g/ml}$  of Thiourea

'c' masked with 315  $\mu\text{g/ml}$  of Ascorbic acid.

**Applications:****Determination of Lead (II) in biological samples**

The accuracy and applicability of the proposed method has been applied to the determination of lead in tea leaves, human hair and pond sediment by National Institute for Environment Studies (NIES). 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 up to 100 ml with water in a calibrated flask. 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 obtained are presented in Table 4.

Table 4: Determination of Lead (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	5.7±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 $\mu\text{g g}^{-1}$	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); Mo, (6.4); Ce, (3.1); Th, (0.35); Sm, (0.20); Eu, (0.05); Lu, (0.02) $\mu\text{g g}^{-1}$	219±9	217±2

\*Average of the best three determinations among five determinations

**Conclusion**

In basic medium, 4-hydroxy 3,5-dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone (HDMBHBH) reacts with Lead (II) and imparts yellow coloration water soluble complex. The colour reaction between Lead (II) and HDMBHBH is instantaneous and the absorbance of the coloured species remains constant for 3 hr. Order of addition of constituents (buffer, metal ion and reagent) has no adverse effect on the absorbance of the complex.

4-hydroxy 3,5-dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone (HDMBHBH) has been proven to be a sensitive and selective chromogenic organic reagent for the determination of Lead (II). Molar absorptivity of the colour complex was  $1.65 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$ . The proposed method was especially sensitive and selective with respect to metals, which commonly seriously interfere with the determination of Lead (II) performed by literature methods. The proposed method can be successfully applied for the determination of Lead (II) in biological samples. This method was favorably compared with previously reported spectrophotometric methods.

### Acknowledgement

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### **Чувствительный и селективный хромогенный органический реагент 4-гидрокси-3,5-диметокси бензальдегид-4-гидрокси бензоил гидразон (HDMВНВН) для прямого и производного спектрофотометрического определения свинца (II)**

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**Аннотация.** 4-гидрокси-3,5-диметокси бензальдегид-4-гидрокси бензоил гидразон (HDMВНВН) используется в качестве нового хромогенного органического реагента для определения свинца (II) с использованием спектрофотометрии. Новый хромогенный органический реагент 4-гидрокси-3,5-диметокси бензальдегид-4-гидрокси бензоил гидразон (HDMВНВН) дал водорастворимый комплекс с Pb (II) желтого цвета в основном буферном растворе (pH = 10,0) среднего. Цвет комплекс показывает максимальную оптическую плотность при 386 нм. Система подчиняется закону Бера в интервале концентраций 0.518–5.18 µg/мл. Молярный коэффициент поглощения и чувствительность

составили  $2.66 \times 10^4$  л·моль<sup>-1</sup>·см<sup>-1</sup> и 0.0077 мкг/см<sup>2</sup> соответственно. Свинец (II) формирует комплекс I:I с HDMBHBN и константа устойчивости комплекса составляет  $3.42 \times 10^6$ . Разработанный метод был успешно применен для определения свинца (II) в биологических пробах.

**Ключевые слова:** новый хромогенный органический реагент; спектрофотометрия; свинец (II); биологические образцы.