Derivative Spectrophotometric Determination of Lead(II) using Diacetylmonoxime-4-hydroxybenzoylhydrazone

G. Narender Reddy†, K.B. Chandrasekhar*, N. Devanna and K.N. Jayaveera
Department of Chemistry, Jawaharlal Nehru Technological University
College of Engineering (Autonomous), Anantapur-515 002, India
E-mail: chandrasekhar_kb@yahoo.co.in

Diacetylmonoxime-4-hydroxybenzoylhydrazone (DM-4-HBH) used as an analytical reagent for lead(II). This reagent gives bright yellow coloured water soluble complex in basic buffer solution. The maximum absorbance is observed at pH 10. The molar absorptivity and sandell's sensitivity of Pb(II) λ_{max} at 440 nm was found to be 1.71×10^4 L mol^{-1} cm^{-1} and 0.01208 $\mu g/cm^2$. Beer's law validity range 0.414-10.360 μg mL^{-1}. Pb(II) forms 1:1 complex with DM-4-HBH and stability constant of the complex was 9.88×10^5. The first order derivative method has been developed. The derivative amplitude was measured by peak height method and shows maximum amplitude at 484 nm in basic buffer medium. The developed first order derivative spectrophotometric method was used for the determination of Pb(II) in synthetic alloy samples.

Key Words: Diacetylmonoxime-4-hydroxybenzoylhydra-zone, Derivative spectrophotometry, Pb(II) determination.

INTRODUCTION

Oximes and hydrazones are the two important classes of known analytical reagents. The potential analytical applications of hydrazone derivatives have been reviewed by Singh *et al.*[1]. In the light of analytical potentialities of oximes and hydrazones. Herein, the analytical properties of reagents containing both functional groups *viz.*, oximes and hydrazones are reported. Diacetylmonoxime-4-hydroxy benzoylhydrazone (DM-4-HBH) was synthesized and employed for the spectrophotometric determination of Pb(II). Derivative spectrophotometry is a useful approach for the determination of the concentration of single components in mixtures with overlapping spectra as it may eliminate interferences. Derivative spectro-photometric methods for determination of metal ions[2-4] are not exploited much.

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†Government Polytechnic, Anantapur-515 002, India.

EXPERIMENTAL

Spectrophotometric measurements were made in an Schimadzu 160A microcomputer based UV-Visible spectrophotometer equipped with 1 cm quartz cells, an ELICO LI-120 digital pH meter was used for pH adjustments and afcoset electronic balance was used for weighing.

All reagents used were of AR 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 (Pb(NO$_3$)$_2$, LR SD Fine) in distilled water in a 250 mL standard flask.

The reagent diacetylmonoxime-4-hydroxy benzoylhydrazone (DM-4-HBH) was prepared by simple condensation of 1 mole of diacetylmonoxime with 1 mole of 4-hydroxy benzoylhydrazide (Fig. 1).
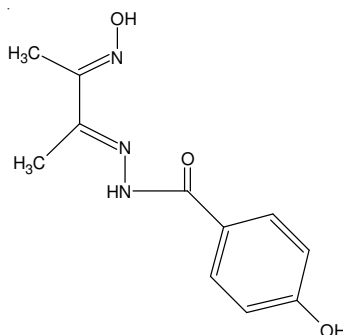

Fig 1. Structure of Diacetylmonoxime-4-hydroxy benzoylhydrazone

The reagent solution (0.01 M) was prepared by dissolving 0.236 g of DM-4-HBH in 100 mL of dimethyl formamide. The reagent solution is stable for 48 h. Buffer solutions were prepared by 1 M HCl, 1 M sodium acetate (pH 0.5-3.5); 0.2 M acetic acid, 0.2 M sodium acetate (pH 4.0-7.0); 2 M ammonium chloride, 2 M ammonium hydroxide (pH 7.5-12.0).

Reaction with metal ions: The reactions of some important metal ions were tested at different pH values. The samples were prepared in 10 mL volumetric flasks by adding 5 mL of buffer (pH, 1.0- 11.0), 0.5 mL of metal ion (1 × 10^{-3} M) and 0.5 mL of 1 × 10^{-2} M DM-4-HBH solutions. The solution mixture was diluted up to the mark with DMF. The absorbance was measured in 350-600 nm range against reagent blank. The results are summarized in Table-1.

Recommended procedure

Determination of Pb(II) (zero order spectrophotometry): An aliquot of the solution containing 0.414-10.36 μg/mL of Pb(II), 3 mL of buffer solution (2 M ammonium chloride, 2 M ammonium hydroxide) pH 10.0 and 0.5 mL of 1 × 10^{-3} M DM-4-HBH reagent were taken in a 10 mL

volumetric flask and the solution was diluted up to the mark with DMF. The absorbance of the solution was recorded at 440 nm in a 1.0 cm cell against corresponding reagent blank prepared in the same way but without Pb(II) metal solution. The measured absorbance was used to compute the amount of Pb(II) from the calibration plot.

TABLE-1
ANALYTICAL CHARECTERISTICS OF
DIACETYLMONOXIME-4-HYDROXY BENZOYLHYDRAZONE

Metal ion	pH	λ_{max} (nm)	Molar absorptivity (L mol^{-1} cm^{-1}) $\times 10^4$
Pb(II)	10.00	440	1.71
Cd(II)	10.75	412	3.27
Co(II)	10.25	414	2.00

The peak hight was plotted against the amount Pb(II) to obtain the calibration curve (Fig. 2).
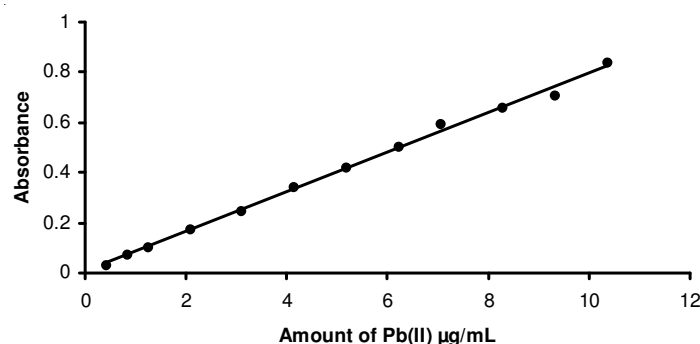

Fig. 2.   Absorbance *vs.* amount of Pb(II) (mg/mL); pH 10.0, [DM-4-HBH] = 5 × 10^{-5} M, wavelength 440 nm

Determination of Pb(II) by first order derivative spectrophotometry: For the above solution of Pb(II)-DM-4-HBH first order derivative spectrum was recorded, with a scan speed having degrees of freedom 9 in a wavelength range 300 to 650 nm. The derivative spectrum was measured by peak height (h) method at 484 nm. The peak height (h) at 484 nm is proportional to the concentration of Pb(II). Therefore, the peak heights were measured at this wavelength for the construction of calibration plots.

Determination of Pb(II) by second order derivative spectrophotometry: The second order derivative spectra of Pb(II)-DM-4-HBH system recorded in a wavelength range 300-650 nm shows maximum amplitude at 506 nm. Therefore the amplitude at this wavelength was measured for the construction of calibration plots.

RESULTS AND DISCUSSION

Diacetylmonoxime-4-hydroxy benzoylhydrazone (DM-4-HBH) reagent is a blend of two functional groups *viz.*, oxime and hydrazones. The reagent solution is stable for 48 h. In basic medium, the ligand presumably coordinates the metal ions as di-anion to give a neutral complexes.

Determination of Pb(II) using DM-4-HBH: Pb(II) reacts with DM-4-HBH in basic medium to give bright yellow coloured water-soluble complex. The colour reaction between Pb(II) and DM-4-HBH are instantaneous even at room temperature in the pH range 8.0-12.0. The absorbance of the bright yellow coloured species remains constant for more than 2 h. 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 metal ion, reagent and buffer solution has no adverse effect on the absorbance. The complex formation reaction between Pb(II) and DM-4-HBH 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 Pb(II) and DM-4-HBH are summarized in Table-2.

TABLE-2
PHYSICO-CHEMICAL AND ANALYTICAL
CHARACTERISTICS OF Pb(II)-DM-4-HBH COMPLEX

Characteristics	Results
λ_{max} (nm)	440
pH range (optimum)	9.5-10.5
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity (L mol^{-1} cm^{-1})	1.71×10^4
Sandell's sensitivity ($\mu g/cm^2$)	0.01208
Beer's law validity range ($\mu g/mL$)	0.414 to 10.360
Optimum concentration range ($\mu g/mL$)	0.83 to 9.32
Composition of complex (M:L) obtained in jobs and mole ratio method	1:1
Stability constant of the complex	9.88×10^5
Standard deviation in the determination of 2.072 $\mu g/mL$ of Pb(II) for ten determinations	0.000026
Relative standard deviation (%)	0.014

Derivative spectrophotometry is a useful technique, in the sense that, it decreases the interference *i.e.*, increase the tolerance limit value of the foreign ions and may be advantageously used for the determination of metal ions having overlapping spectra. The recommended procedure has been employed for the determination of Pb(II). The zero order, first order and second order derivative spectra of Pb(II) complex of DM-4-HBH are given in Figs. 3-5, respectively.
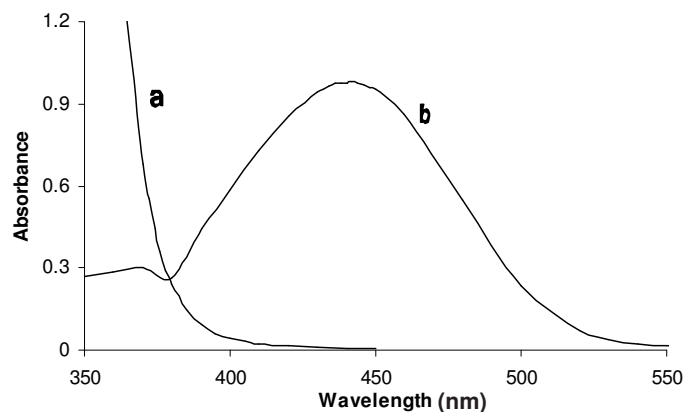
Fig. 3.   Zero order absorption spectra of Pb(II)-DM-4-HBH complex
a) Reagent DM-4-HBH 5×10^{-4} M *vs.* water blank at pH = 10.0.
b) Absorption spectra of Pb(II)-DM-4-HBH complex *vs.* reagent blank
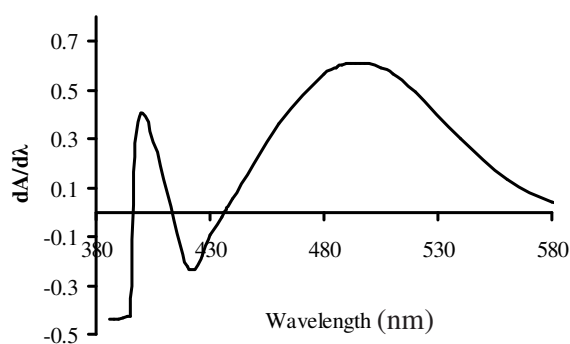at pH = 10.0, Pb(II) = 5×10^{-5} M, DM-4-HBH = 5×10^{-4} M

Fig. 4.   First order derivative spectra of Pb(II)-DM-4-HBH complex *vs.* reagent
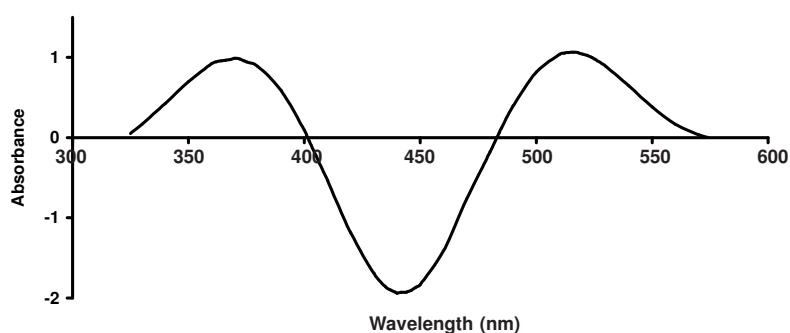as blank at pH = 10.0, Pb(II) = 5×10^{-5} M, DM-4-HBH = 5×10^{-4} M

Fig. 5.   Second order derivative spectra of Pb(II)-DM-4-HBH complex *vs.*
reagent as blank at pH = 10.0, Pb(II) = 5×10^{-5} M, DM-4-HBH =
5×10^{-4} M

Effect of diverse ions (interference): The effect of various diverse ions in the determination of 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 tolerance limit value of diverse ions in the determination of 5.18 µg/mL of Pb(II) are given in Table-3. The interference of associated metal ions such as Fe(III) and Cu(II) is decreased with masking agents fluoride and thiourea, respectively. It was noticed that all the ions that do not interfere in the zero order determination of Pb(II) given in above also do not interfere in the first and second order derivative spectrophotometric determination of Pb(II). Further, their tolerance limits were in generally higher than those in the zero order determination of Pb(II).

TABLE-3
TOLERENCE LIMIT OF FOREIGN IONS IN THE DETERMINATION
OF 5.18 µg/mL OF LEAD(II)

Ion added	Tolerance limit (µg/mL)	Ion added	Tolerance limit (µg/mL)
I^-	1269.0	W^{6+}	46.00
$S_2O_3^{2-}$	1122.0	Sb^{3+}	31.00
SO_4^{2-}	961.0	Pd^{2+}	27.00
$C_2O_4^{2-}$	881.0	Hg^{2+}	16.00
Br^-	799.0	Mo^{6+}	15.00
H_2NCSNH_2	762.0	Al^{3+}	7.00
$B_4O_7^{2-}$	620.0	Zn^{2+}	4.00
H_2NCONH_2	691.0	Sn^{2+}	5.00
CH_3COO^-	591.0	Cr^{6+}	4.00
SCN^-	581.0	Ni^{2+}	3.00
$C_6H_5O_7^{3-}$	379.0	Mn^{2+}	2.00
Cl^-	355.0	V^{5+}	0.26
$C_4H_4O_6^{2-}$	193.0	$Fe^{3+}*$	0.70
F^-	190.0	$Cu^{2+}**$	0.66
PO_4^{3-}	5.0	–	–

*Masked with 160 µg/mL of fluoride.
**Masked with 762 µg/mL of thiourea.

Applications: The proposed method has been applied for the determination of Pb(II) in synthetic alloy samples by employing the recommended procedure.

Analysis of synthetic alloy sample: A 0.5 g sample of the synthetic alloy was digested in 15 mL of 2:1 ratio mixture off conc. HCl and conc. HNO_3. It was heated until it is dissolved and final volume reduced to 5 mL.

5 mL of HCl (5 M) was added to the above and filtered. Then the filtrate was collected in a 25 mL volumetric flask and made up to the mark. Pb(II) in this solution was determined by the recommended procedure from a pre-determined calibration plot, the results obtained are presented in Table-4.

TABLE-4
ESTIMATION OF Pb(II) (μg/mL) IN SYNTHETIC ALLOY SAMPLES

Sample	Amount of Pb(II) (μg/mL)		Error (%)
	Amount added	Amount found*	
Lead-tin alloy† for printed circuit boards	48.00	48.50	+1.0416
Mineral cylinder‡	34.00	33.60	-1.1760

*Average of best three determinations among five determinations.
†Sn 44 %; In 5 %; Cu 2.5 % Te 0.5 %; remaining Pb.
‡Sn 21-26 %; Sb 7-13 %; Ag > 0.6% ; S 24 %; Fe 3 %; In 0.054 %; Si in traces; Pb 34 %.

Conclusion

From the above discussion, it can be concluded that DM-4-HBH is a potential reagent for the derivative spectrophotometric determination of Pb(II). The reagent is easy to synthesize using available chemicals. Moreover, the present method is simple, rapid, reasonably sensitive and selective for the determination of Pb(II) without the need of heating or extraction. The above method is comparable with other recently reported spectrophotometric methods for the determination of Pb(II)[5,6].

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