DIRECT AND DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF MERCURY (II) USING DIACETYLMONOXIME BENZOYLHYDRAZONE (DMBH)

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ABSTRACT: A simple and derivative spectrophotometric method has been developed for the determination of mercury (II) using Diacetylmonoxime benzoylhydrazone (DMBH). Mercury (II) forms an orange coloured water soluble complex with the reagent in basic medium (pH 10.5).The molar absorptivity and Sandell's sensitivity of coloured species are 2.01×10^4 L.mol^{-1} cm^{-1} and 0.0099 µg/cm^2 respectively. Beer's law is obeyed in the range 1.0029 – 12.0354 µg/ml of Hg (II) at λ_{max} 361 nm. The developed derivative spectrophotometric method was employed for the determination of mercury (II). This method has been satisfactorily applied for the determination of mercury (II) in different environmental water samples and biological samples.
Key words: Mercury (II), Diacetylmonoxime benzoylhydrazone (DMBH), derivative spectrophotometry.

INTRODUCTION

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al.[1]. Hydrazones are important class of known analytical reagents[2-7]. They react with many metal ions forming colour complexes and act as chelating agents. The present paper describes a new, very simple, rapid, sensitive and derivative spectrophotometric determination of mercury (II) is proposed. The method consists of the formation of orange coloured metal complex using Diacetyl monoxime Benzoyl Hydrazone (DMBH)-Figure-1 with Mercury (II) and the stability of the complex is presented.
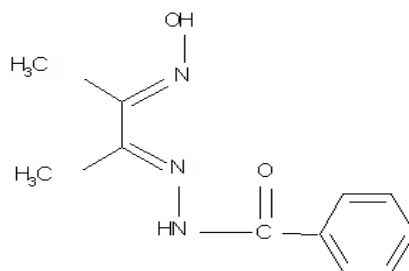

Figure.1. Structure of Diacetylmonoxime benzoylhydrazone (DMBH)

EXPERIMENTAL

A Shimadzu 160A, microcomputer based UV-VIS spectrophotometer equipped with 1.0cm quartz cells was used for all spectral measurements. The instrumental parameters are optimized and the best results were obtained with scan speed (2400) nm/min., slit width of 1nm and $\Delta\lambda=2$nm for first order derivative mode in the wavelength range 350-650nm. ELICO L1-120 digital pH meter was used for the pH adjustments.

All chemicals used were of A.R grade unless stated. All solutions were prepared with doubly distilled water. The standard mercury (II) solution (0.01M) was prepared by dissolving accurately weighed 0.2715 g of $HgCl_2$ in a few ml. of doubly distilled water and made up to the mark in a 100-ml of volumetric flask. The stock solution was standardised by using standard methods[8]. The working solutions were prepared by diluting the stock solution to an appropriate volume. Buffer solutions were prepared by using 0.1M HCl, 0.1M NaOH, 0.1M disodium hydrogen phosphate and 0.1M potassium dihydrogen phosphate. Solutions of various ions of suitable concentrations were prepared using AR grade chemicals.

The reagent Di acetyl monoxime Benzoyl Hydrazone(DMBH) was synthesized by refluxing equimolar amounts of Diacetylmonoxime and Benzhydrazide. In a 250 ml round bottomed flask hot methanolic solution of Diacetylmonoxime (1.011g, 0.01 mole) and hot methanolic solution of Benzhydrazide (1.3615g, 0.01mole) were mixed and refluxed using water condenser for 4 hours. On cooling the reaction mixture, a pale yellow coloured product separated out, which was collected by filtration and washed with double distilled water. The resulting hydrazone was recrystalized using 50% ethanol (yield 78%,%, mp 206-208^{0}C).

The reaction of some important metal ions were tested at different pH values. The samples were prepared in 10ml volumetric flasks by adding buffer solution 3.0 ml (pH 1-11), metal ion 0.5 ml of $1x10^{-3}$M and DMBH 0.5 ml of $1x10^{-2}$M solution. The mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-700nm range against reagent blank. The results are summarized in Table-1.

For the spectrophotometric determination of mercury (II), an aliquot of the solution containing 1.0029 to 12.0354 µg/ml of mercury (II), 3.0ml of buffer solution (pH 10.5), and 0.5ml of $1x10^{-2}$M DMBH reagent solution were taken in 10 ml volumetric flask and the solution was diluted up to the mark with doubly distilled water. The absorbance was read at 361nm in a 1.0cm cell against reagent blank prepared in the same way. The measured absorbance was used to compute the amount of mercury (II) from the predetermined calibration curve.

The first-order derivative spectrum was recorded with scan speed fast having a degree of freedom 9, in the wavelength range from 350-650nm. The derivative peak height was measured by peak-zero method at 417nm. The peak height was plotted against the amount of mercury (II) to obtain the calibration curve. The second order derivative spectrum of [Hg (II)-DMBH] system was recorded with reference to the reagent blank in a wavelength range 350-650nm.

RESULTS AND DISCUSSION

The reagent Diacetylmonoxime benzoylhydrazone (DMBH) was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMBH was not used for the spectrophotometric determination of mercury (II). The colour reactions of some important metal ions with DMBH are summarized in Table-1.In basic medium, the ligand presumably co-ordinates the metal ion as di-anion to give neutral complexes.

Table-1: Analytical Characteristics of Diacetylmonoximebenzoylhydrazone (DMBH)

Metal ion	pH	Colour	λ_{max} (nm)	Molar absorptivity (ε) (L.mol^{-1}cm^{-1})
Fe(II)	6.0	Yellow	360	1.25×10^4
Fe(III)	5.0	Yellow	368	1.16×10^4
Cd(II)	9.5	Yellow	348	1.60×10^4
Hg(II)	10.5	Yellow	361	$2.01 \times 10^{4*}$

*Present work

The absorption spectrum of DMBH and its mercury (II) complex under the optimum conditions are shown in Figure-2.The [Hg (II)-DMBH] complex shows the maximum absorbance at 361nm, where the reagent blank does not absorb appreciably.
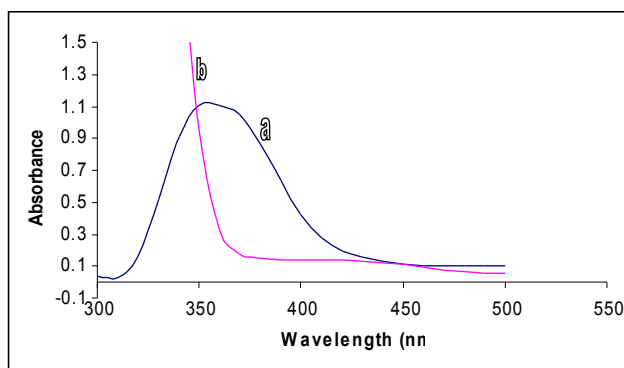
(a): [Hg(II)-DMBH] complex peak.
(b) : Reagent [DMBH] Vs DMF blank
Figure.2. Zero order Absorption spectra

Mercury (II) reacts with DMBH in basic buffer to give yellow coloured water soluble species. The colour reaction between mercury (II) and DMBH was instantaneous even at room temperature in pH range 9.0-11, the maximum colour intensity was observed at pH 10.5.

When the volume of reagent DMBH (1×10^{-2}M) was varied from 0.5ml to 4.0ml, the constant absorbance was obtained from 0.5 ml. Therefore 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 of [Hg (II)–DMBH] complex. Beer's law obeyed in the range 1.0029 to 12.0354 µg/ml. The molar absorptivity and Sandell's sensitivity of [Hg (II)-DMBH] 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 mercury (II) and DMBH complex are summarized in Table-2.

Table-2: Physico-Chemical and Analytical Characteristics of [Hg (II)-DMBH]

Characteristics	Results
Colour	Yellow
λ_{max}(nm)	361
p^H range (optimum)	9.0-11.0
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity(L.mol $^{-1}$cm^{-1}) (ε)	2.01×10^4
Sandell's sensitivity($\mu g/cm^2$)	0.0025
Beer's law validity range($\mu g/ml$)	1.0029 - 12.0354
Optimum concentration range($\mu g/ml$)	2.009-10.045
Composition of complex(M:L) obtained in Job's and mole ratio methods	1:1
Stability constant of the complex	6.44×10^5
Standard deviation	0.0001
Relative standard deviation (%)	0.02

Beers law was verified for zero order which gave a linear graph passing closer to the origin. It was shown in Figure-3
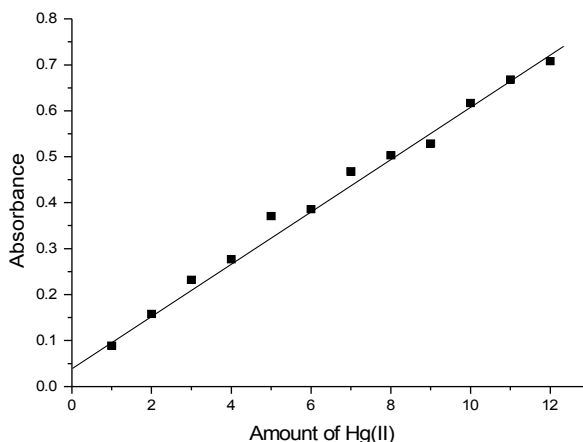
Figure.3. Zero order Beer's law spectrum of [Hg (II)-DMBH] complex

The first order derivative spectral graph was shown in Figure-4. This shows that the derivative amplitudes measured at 417nm for first order were found to be proportional to the amount of mercury (II).
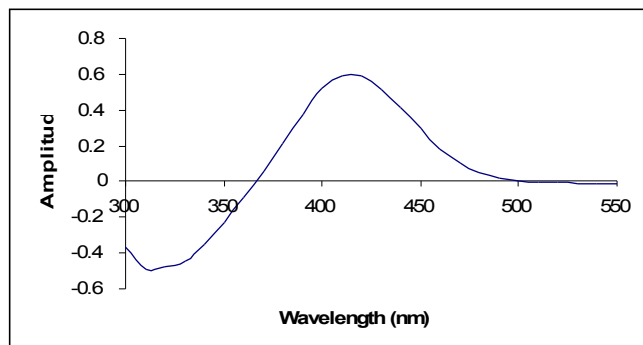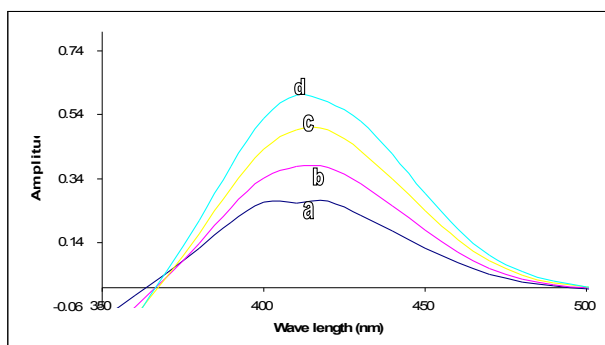
Figure.4. First order derivative spectra of [Hg (II)-DMBH] complex

Beers law was verified for first order for different amounts of mercury (II) and was shown in Figure-5.

a)   4.0118 µg/ml of Hg(II)   b) 6.0177 µg/ml of Hg(II)
c)   8.0236 µg/ml of Hg(II)   d) 10.0295 µg/ml of Hg(II)
Figure.5. Beer's law First order derivative spectra of [Hg (II)-DMBH] complex

The stoichiometry of the complex was found to be 1:1 (M: L) investigated by Job's continuous variation method and molar ratio method, with a stability constant 6.44×10^5.
The effect of various diverse ions in the determination of 2.5075 µg/ml mercury (II) and tolerance limit of foreign ions was studied 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, nitrate, thiosulphate, thiocyanide, bromide, sodium(I), calcium(II), bismuth(III), tungsten(VI). The tolerance limit values for many anions and cations are more in derivative method. The   interference of associated metal ion such as Iron (III) is decreased by adding masking agent Ascorbic acid.

Table-3. Tolerance limit of foreign ions in the determination of 5.01475 µg/ml mercury(II)

Ion added	Tolerance limit µg/mL	
	Zero order	D1
Urea	601	601
Ascorbic acid	440	440
Oxalate	440	440
Tartarate	330	330
Fluoride	285	285
Sdium tetraborate	168	168
citrate	113	113
Chloride	89	89
Bromide	80	80
Nitrate	06	06
W(VI)	92	92
Ce(IV)	14	14
Na(I)	12	12
Se(IV)	12	16
Ca(II)	06	06
Sb(III)	04	04
Fe(III)	0.84, 1.63[*]	0.84, 1.63[!]
Co(II)	0.6	0.6
Ni(II)	0.3	0.3

[*] Masked by 70 µg/ml of Ascorbic acid
[!] Masked by 70 µg/ml of Ascorbic acid

APPLICATIONS

The proposed method was applied for the determination of mercury (II) in soil samples, Vaccine samples and water samples.

Preparation of Soil samples: A 2g weight of soil, 5-7 ml of concentrated sulphuric acid and an excess of $KMnO_4$ are mixed in a conical flask equipped with a reflux condenser. The crystals of $KMnO_4$ are added slowly in small portions with continuous stirring. It is heated until vapours of $SO3$ are evolved. After cooling down, 10 ml of distilled water is added. The excess of $KMnO_4$ and manganese oxides are eliminated by adding H2O2. Iron is isolated as by precipitation as hydroxide. After filtration, the solution is transferred into 50 ml standard flask and made up to the mark with distilled water[9,11]. Aliquots of this solution were taken for analysis.

Preparation of Vaccine samples: Hepatitis B vaccine was taken in a 250 ml flask and to this 2 to 3 ml of nitric acid was added for dissolution and the sample was transferred in to a 100 ml standard flask. The solution was diluted up to the mark with distilled water. Suitable aliquots of this was taken for analysis.

Preparation of Water samples: Each water sample (250 ml) filtered with Whattman No.40 was mixed with 10 ml of concentrated nitric acid in a 500 ml distillation flask. The sample was digested in the presence of an excess of $KMnO_4$ solution according to the method recommended by Fifield et al.[10] . the solution was cooled and neutralized with dilute ammonium hydroxide solution. The digest was transferred into a 50 ml calibrated flask and diluted up to the mark with distilled water[9,10]. Aliquots of these solutions were taken for analysis. Results are described in table-4,5,6 and 7).

Table -4. Determination of mercury (II) in Soil samples.

Sample	Amount of mercury (II)* found(µg/ml)		Error (%)
	Dithiozone method	Present method	
Agricultural soil	0.41	0.40	+2.40
Urban soil	0.98	0.99	-1.02
Road side soil	1.62	1.63	-0.61

*average of best three determinations among five determinations

Table -5. Determination of mercury (II) in Vaccine samples.

Sample	Amount of mercury (II)* found(µg/ml)		Error (%)
	Dithiozone method	Present method	
Hepatitis B vaccine	0.25	0.26	-4.00

*average of best three determinations among five determinations

Table -6. Determination of mercury (II) in water samples.

Sample	Amount of mercury (II)* found(µg/ml)		Error (%)
	Dithiozone method	Present method	
Tap water	0.69	0.64	+7.20
Well water	0.84	0.85	-1.19
Laboratory water[a]	1.85	1.85	0.00
Waste water	3.29	3.26	+0.91
Drain water[b]	1.18	1.15	+2.54
River water[c]	0.61	0.59	+3.20
Sea water[d]	1.00	1.03	-3.00

*average of best three determinations among five determinations
[a] Laboratory water(Dept. of chemistry, JNTUA, Anantapur) ;
[b] Anantapur town drain water;
[c] Tungabhadra river water(Kurnool) and
[d] Bay of Bengal(Chennai).

Table -7. Determination of mercury (II)

S.No	Reagent	pH	λ_{max} (nm)	Molar absorptivity	Reference
1	Furfural-2-benzthiozolyl hydrazone (FBTH)	5.0	389	0.5×10^4	14
2	Diacetylmonoxime benzoylhydrazone (DMBH)	10.5	361	$2.01 \times 10^{4*}$	Present work

* present work

CONCLUSION

The present method using Diacetylmonoximebenzoylhydrazone (DMBH) as spectrophotometric reagent for the determination of mercury (II) in aqueous medium is sensitive and simple. Many of the methods involve either heating at a specific temperature[9-10] or extraction[11-12] of the reaction mixture. However heating at a specific temperature for a long time is laborious and time consuming. The determination of mercury (II) using DMBH is not laborious and there is no need of heating or extraction of the components. Further the reagent is easy to synthesize using available chemicals. More over the present method is simple, rapid, selective and more precise for the determination of mercury (II) [13].

ACKNOWLEDGEMENTS

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