

Derivative Spectrophotometric Determination of Mercury (II) Using Diacetyl Monoxime Isonicotinoyl Hydrazone (DMIH)

G.ChandraSekhar Reddy

Senior Lecturer in Chemistry, Govt.Polytechnic, Anantapur (A.P) and Research Scholar, Department of Chemistry, JNTU, Anantapur

N.Devanna & K.B. Chandrasekhar

Professor in Chemistry, Department of Chemistry, JNTU, Anantapur
E-mail: gadikotachandra@gmail.com; Chandrasekhar_kb@yahoo.co.in

Received: November 1, 2010 Accepted: November 19, 2010 doi:10.5539/ijc.v3n2p227

Abstract

Mercury (II) forms a yellow Coloured water soluble complex with Diacetyl Monoxime Isonicotinoyl hydrazone(DMIH) reagent in acidic buffer P^H 5.5 with λ_{max} at 351 nm. The molar absorptivity and sandell's sensitivity are $2.23 \times 10^4 \text{ L.mol}^{-1} \text{ cm}^{-1}$ and $0.00225 \mu\text{g/cm}^2$ respectively. The Beer's law validity range is 1.003 – 12.03 $\mu\text{g/mL}$. Mercury (II) forms (M:L) 1:1 complex with DMIH and stability constant of the complex is 6.692×10^6 . The derivative spectrophotometric determination of Hg (II) was carried out by measuring peak height method. The developed derivative spectrophotometric method was employed for the determination of Mercury (II) in synthetic samples of alloy. The effect of various diverse ions was also studied.

Keywords: Diacetyl Monoxime Isonicotinoyl hydrazone(DMIH), Derivative spectrophotometry, Mercury (II)

1. Introduction

Mercury is one of the serious environmental pollutants in any form. It is widely distributed in the environment due to industrial and agricultural activities. Mercury affect the human beings in several ways like vomiting, abdominal pain, damage to kidney, neurological disorder, enzyme inhibition, severe nausea etc. Mercury occurs in its compounds in +1 and +2 oxidation states. The Natural sources of mercury are scanty and scattered. Mercury causes MINAMITA disease, one of the most visible tragedies caused by water pollution.

The oximes and hydrazones are the most important spectrophotometric reagents for the determination of metal ions. Complex formation reactions are of great use in determining metal ions at the micro level or even nano gram level. In this context organic reagents occupy a better place over inorganic reagents because of their complexing ability with metal ions giving highly colored stable compounds. Among the large number of available organic reagents, the oximes and hydrazones became important spectrophotometric reagents for the determination of metal ions. The potential application of hydrazone derivatives for the spectrophotometric determination of metal ions was reviewed by Singh (1982) and others. Some hydrazone reagents (Pramanic, J, 1981; Chaudhry, 1991; Kawatkar, 1998) were used for the spectrophotometric determination of Mercury (II). In the light of good analytical characteristics of hydrazones, the author has developed a method for the spectrophotometric determination of Mercury (II) using an organic reagent namely Diacetyl Monoxime Isonicotinoyl hydrazone(DMIH). The author has reported the zero and first order derivative spectrophotometric determination of Mercury (II) in aqueous medium in this paper.

2. Experimental

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 P^H meter. All reagents used were of analytical reagent (AR) grade unless otherwise stated. All solutions were prepared with distilled water. The standard stock solution 0.01 M was prepared by dissolving 0.2715 g of fine A.R of Mercuric Chloride, HgCl_2 in doubly distilled water in a 100 mL standard flask.

The reagent Diacetyl Monoxime Isonicotinoyl Hydrazone(DMIH) was prepared by simple condensation of Diacetyl Monoxime and Isonicotinic hydrazide in 1:1 mole ratio and its structure is given in fig 1.

The reagent solution (0.01 M) was prepared by dissolving 0.22 grams of DMIH in 100 mL of dimethyl Formamide. The reagent is stable for 48 hours. Buffer solutions were prepared by mixing 1 M hydrochloric acid – 0.2 M sodium dihydrogen phosphate.

Reaction with metal ions: The reactions of some important metal ions were tested at different P^H values. The samples were prepared in 10 mL volumetric flasks by adding 3 mL of buffer P^H (1.0 – 11.0), 0.5 mL of metal ion (1×10^{-3} M) and 0.5 mL of DMIH (1×10^{-2} M) solutions. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 300 – 600 nm range against reagent blank. The results are summarized in Table -1

3. Recommended Procedure

3.1 Determination of Hg (II) (Zero order spectrophotometry)

An aliquot of the solution containing 1.003 – 12.036 $\mu\text{g/mL}$ of Hg (II), 3 mL of buffer solution of P^H 5.5 and 0.5 mL of 0.01 M DMIH reagent were taken in a 10 mL volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 351 nm in a 1.0 cm cell against reagent blank prepared in the same way but without Hg (II) metal solution. The measured absorbance was used to compute the amount of Hg (II) from the calibration plot

3.2 Determination of Hg (II) by first order derivative spectrophotometry

The first order derivative spectrum was recorded for the above solution of Hg (II) – DMIH with a scan speed having degrees of freedom 9 in a wavelength range 300 - 600nm. The derivative spectrum was measured by peak height (h) method at 400 nm. The peak height (h) at 400 nm is proportion to the concentration of Hg (II). Therefore the peak heights were measured at this wave length for the construction of calibration plots.

4. Results and Discussion

Diacetyl Monoxime Isonicotinoyl Hydrazone(DMIH) reagent can be easily prepared like any other Schiff base reagent. This new chromogenic reagent DMIH was not used for spectrophotometric determination of Hg (II) so far.

The reactions of some important metal ions with DMIH are summarized in table 1. The color reactions are mainly due to the complex formation of DMIH with divalent, trivalent, tetravalent and hexavalent metal ions like Hg(II), Ru(III), Au(III), Th (IV), Mo(VI) and U(VI) in acidic buffer medium to give intense colored complexes.

4.1 Determination of Hg (II) using DMIH

Hg (II) reacts with DMIH in acidic medium to give yellow colored water soluble complex. The color reaction of Hg (II) with DMIH is instantaneous even at room temperature in the P^H range 1.0-7.0.

The absorbance of the yellowish colored species remains constant for more than two hours. The maximum color intensity is observed at P^H 5.5.

It is observed that a 5 fold molar excess of reagent is more than sufficient for full color development. The order of addition of buffer solution, metal ion and reagent has no adverse effect on the absorbance. The complex formation reaction between Hg (II) and DMIH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Some of the important physico-Chemical and analytic characteristics of Hg (II) and DMIH are summarized in table -2

Derivative spectrophotometry is an important useful technique as it decreases the interference i.e increase the tolerance limit value of the foreign ions. Therefore it may be useful for the determination of metal ions having overlapped spectra. The proposed procedure has been used for the determination of Hg (II) and the zero order and first order derivative spectra of Hg (II) Complex of DMIH are given in Fig 2 and 3 respectively.

4.2 Effect of diverse ions

The effect of various diverse ions in the determination of Hg (II) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of foreign ions was taken as the amount of foreign ion required to cause an error of $\pm 2\%$ in the absorbance or amplitude the results are given in table - 3. The data obtained in the derivative method is also incorporated.

Applications: The proposed method was applied for determination of Hg (II) in various synthetic samples of alloy and river water samples. Metal ions like Cu(II), Pb (II), Mn(II), Ni(II), Bi(II), Sn(II) and Cd(II) are generally associated with Hg (II) in commercial samples. The present method can be applied for the determination of Hg (II) in some synthetic alloys containing large amounts of Fe(II), Fe(III), Pb (II) Mn(II), Ni(II), Bi(II), Sn(II) and Cd(II).

4.3 Recommended Procedure

Known aliquots of the sample solution were taken in a 10 mL volumetric flask containing buffer solution of 3 mL with 5.5 P^H and 0.5 mL of DMIH (1X 10⁻² M) solution. The contents were made up to the mark with distilled water. The absorbance was measured at 351 nm against the corresponding reagent blank. The results were presented in Table- 4

5. Conclusions

The present method using DMIH as a spectrophotometric reagent for the determination of Mercury (II) in aqueous medium is sensitive and simple. The determination of Hg(II) using DMIH is not laborious and there is no need of heating the components or extraction. Further the reagent is easy to synthesize using available chemicals. Moreover the present method is simple, rapid, reasonably sensitive and selective for the determination of Mercury(II). This method is compared with some previously reported spectrophotometric methods⁵⁻⁹ for the determination of mercury (II) presented in table – 5.

Acknowledgement

The authors are thankful to the Jawaharlal Nehru Technological University, Anantapur for providing research facilities to carry out the present work.

References

- Chaudhry S.P and Shome S.C J. (1991). *Indian Chem.Soc.* 68. 430.
 Guo, Zhongxian, Fen Xi Huaxne. (1996). 24(1) 65.
 Kamburova M. (1995). *Chem.Anal.*,(worsaw) 40(5) 791.
 Kawatkar. S.G and Manoli.P.S. (1998). *Acta cien. Indica*, 24 C, 109.
 Pramanic. J, Ghosh. J.P, Mazumdar. M and Das. H.S J. (1981). *Indian Chem.Soc.*, 58.235.
 Saran, R., Sardana, A.K. and Ramanaiah, G.V. (1994). *Indian J.Chem.Technol.*, 1(4) 258.
 Singh R.B., Jain. p and Singh. R.P. (1982). *Talanta*, 29.77.
 Tang Jin, Ting and ChaiJun, Fenxi Shiyanshi. (1999). 18(5) 50.
 Yang, Minghua, Zhang, Yunta, Zhao. (2001). *Guidan Guangdong Weiliang Yuansu Kexue* 8(4) 56.

Table 1. Analytical Characteristics of Diacetyl Monoxime Isonocotinoylhydrozone(DMIH)

Sl No	Metal Ion	P ^H	λ_{\max} (nm)	Molor absorptivity (L.mol ⁻¹ cm ⁻¹) X10 ⁴
1	Ru (III)	4.5	346	1.4
2	Hg (II)	5.5	351	2.23
3	U(VI)	3.25	364	1.63
4	Th(IV)	5.0	352	2.265
5	Au(III)	4.5	361	1.5
6	Mo(VI)	5	346	1.93

Table 2. Some of Physico- Chemical and analytical characteristics of Hg(II) –DMIH Complex

Characteristics	Results
λ_{\max} (nm)	351
P ^H Range(Optimum)	5.0-6.0
Mole of reagent required per mole of metal ion for full colour development	5 folds
Molar absorptivity (L.mol ⁻¹ cm ⁻¹)	2.23 X10 ⁴
Sandell's sensitivity($\mu\text{g}/\text{Cm}^2$)	0.00225
Beer's law validity range ($\mu\text{g} / \text{mL}$)	1.003 – 12.036
Optimum Concentration Range ($\mu\text{g} / \text{mL}$)	2.006 – 10.03
Composition of complex (M:L) obtained in job's and mole ratio method	1:1
Stability Constant of the complex	6.692 X10 ⁶
Standard Deviation	0.0002
Relative Standard Deviation	0.0307

Table 3. Tolerance limit of Foreign Ions in the determination of 5.015 $\mu\text{g} / \text{mL}$ Hg(II)

Ion Added	Tolerance Limit($\mu\text{g} / \text{mL}$)		Ion Added	Tolerance Limit($\mu\text{g} / \text{mL}$)	
	Zero Order	First Derivative		Zero Order	First Derivative
Urea	30	60	Sn ⁺²	118.7	118.7
Sulphate	96	96	Bi ⁺³	208.98	104.5
Phosphate	95	95	Ba ⁺²	137.3	137.3
Nitrate	62	93	Zn ⁺²	65.4	91.56
Acetate	59	88.5	Zr ⁺⁴	136.8	136.8
Oxalate	134	134	U ⁺⁶	238	357
Thio Urea	114	114	W ⁺⁶	183.8	183.8
Tartarate	141	141	# Al ⁺³	40.47	26.98
Ascorbic Acid	176	176	Ag ⁺	107.9	161.85
Fluoride	19	28.5	Ca ⁺²	40	40
Iodide	126.9	126.9	Ni ⁺²	88.5	88.5
Bromide	79.9	79.9	Pd ⁺²	106.4	159.6
Chloride	35.5	53.25	V ⁺⁵	50.9	76.35
Mo ⁺⁶	95.9	95.9	Sr ⁺²	87.6	87.6
Mn ⁺²	54.9	54.9	Sb ⁺³	121.8	121.8

Masked with thio urea (114 $\mu\text{g} / \text{mL}$)

Table 4. Estimation of Mercury (II) ($\mu\text{g} / \text{mL}$) in synthetic alloy samples

Sample ($\mu\text{g} / \text{mL}$)	Amount of Hg(II) ($\mu\text{g} / \text{mL}$)		
	Added	Found *	Error (%)
Sn(II) 40 Fe(II) 6	10.0	10.2	+ 2.0
Bi(III) – (03) Pb(II) –(02)	8.0	8.4	+5.0
Cu(II) (02) Fe(III) (04)	8.0	7.6	-5.0
Cd(II) (2) Sn(II) (40)	8.0	7.8	-2.5

- Average of best three determinations among five determinations

Table 5.

Reagent	λ_{max} (nm)	pH	Molar absorptivity ($\text{L}\cdot\text{mol}^{-1}\text{cm}^{-1}$)	Extraction/ Heating	Beers Law Validity Range	Ref
5-(2-Carboxy Phenyl) azo- 8-Quinololinol	-	4.4-6.5	6.05	Aqueous	0.3-0.18	5
T.V,2,5-diphenyl-3-(1-Naphthyl- Tetrazolium chloride)	-	-	1×10^6	Extraction	-	6
2-Hydroxy-3-Carboxy-5-Sulpho Benzene diazo amino azobenzene	522	10-10.5	1.63×10^5	-	0-1.0	7
4,4-Biazobenzenediazo amino benzene	515	-	1.8×10^5	Aqueous	0-1.2 $\mu\text{g}/25\text{mL}$	8
1-4-Nitrophenyl-3-5-Nitro-2-Pyridyl triazine	438, 525	11.2	2.1×10^5	-	0-280 $\mu\text{g}/\text{mL}$	9
Diacetyl monoxime Isonicotinoyl hydrazone(DMIH)	351	5.5	2.23×10^4	Aqueous	1.003-12.36 $\mu\text{g} / \text{mL}$	Present Work

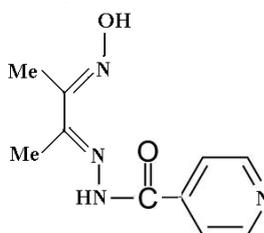


Figure 1. Structure of Diacetyl Monoxime Isonicotinoyl Hydrazone(DMIH)

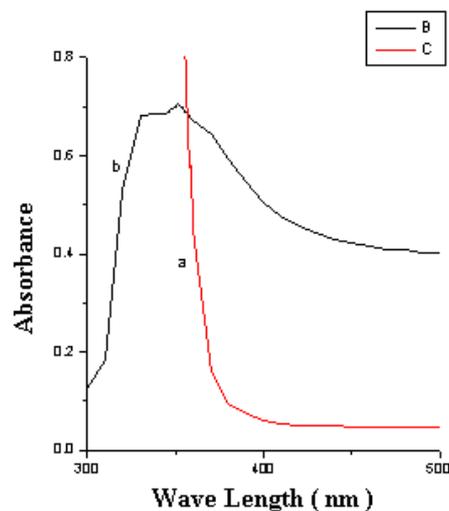


Figure 2. Zero order absorption spectra of (a) reagent DMIH 1×10^{-2} M vs Water blank at P^H 5.5 (b) Hg (II) – DMIH complex vs reagent blank at $P^H=5.5$, Hg(II) = 1×10^{-3} M; DMIH= 1×10^{-2} M

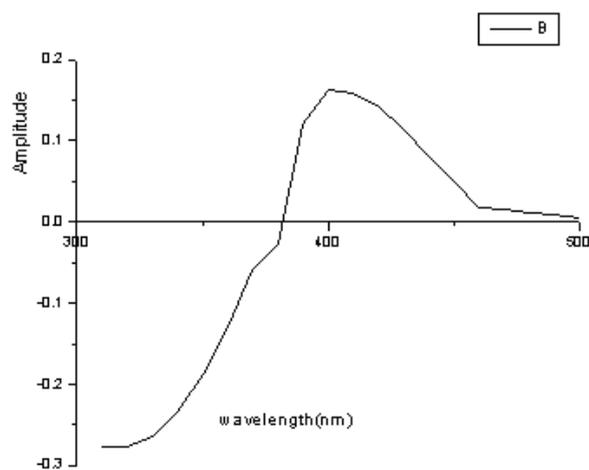


Figure 3. First Order Derivative Spectrum of Hg (II) – DMIH Complex Vs Reagent Blank at $P^H = 5.5$, Hg (II) = 1×10^{-3} M, DMIH = 1×10^{-2} M