

CHAPTER- 6

6.1 Summary

The main aim of the present investigation is synthesis of new ligand and characterization of Hydrazones and oxime hydrazones. Literature survey reveals that few hydrazones are used for the determination of Lead (II), Cadmium (II) Vanadium (V) and Copper (II). Based upon the fact the author has prepared Diacetylmonoxime-3-amino-4-hydroxybenzoylhydrazone(DMAHBH) and 3,5-Dimethoxy-4-hydroxy benzaldehyde isonicotinoyl hydrazone (DMHBIH). The structural confirmation of the above was done by IR, NMR and Mass Spectral data.

The above ligands were employed for the determination of Cadmium (II), Lead (II) Vanadium (II) and Copper (II) as Chromogenic reagent. The method is developed by using Spectrophotometer i.e., Direct, First and Second Order derivative technique. The developed methods were successfully employed for the determination of above metals in Alloys, Soil, Food, Tobacco, Water, Plant and biological samples. During the Investigation the following important observations are made.

The absorbance of the Complexes of Cadmium (II), Lead (II) Vanadium (V) and Copper (II) with DMAHBH and DMHBIH were observed. Lead (II)-DMHBIH Complex has shown maximum absorbance at 430nm in presence of Triton X-100 (5%), but maximum wavelength was observed in case of Lead (II)-DMHBIH. Copper (II)-DMAHBH forms stable complex without surfactant.

In the entire study, Phosphate Buffer Solutions (p^H 3.0-11.0) were employed for full color development of above metal complexes and observed that all the above metals gives Yellow colored metal complexes in presence of Triton X-100 (5%) (for Solubility and Stability) except Cd (II) –DMHBIH (CTAB is used)

A tenfold reagent solution is enough for complete Complexation (Full color development) and there is no adverse effect observed on changing the order of addition of Buffer, Metal, reagent and Surfactant. The formed metal complexes are stable for more than 2 to 3 hours.

Molar absorptivity and Sandell's Sensitivity of metal complexes of Cadmium (II), Lead (II) and Vanadium (V) are calculated and observed that Cadmium (II) – DMAHBH has shown maximum value i.e., 3.66×10^4 . Other parameters were also studied and data was incorporated

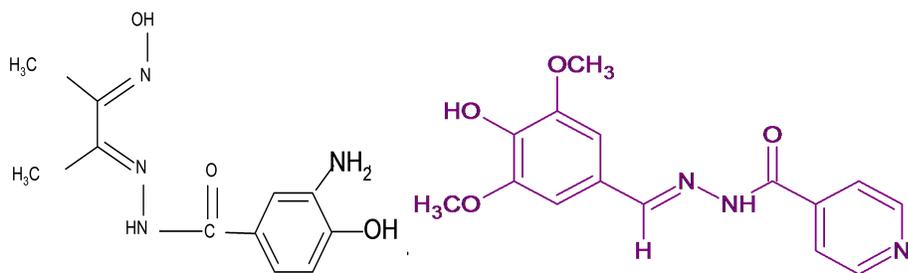
in **Table No: 6.1**. All the metals and ligands forms 1:1 complexes and the stability constants of the above complexes were calculated and incorporated in **Table No: 6.1**. Cd (II)-DMAHBH shows maximum stability constant 8.58×10^7 among the five developed systems.

Table.6.1: A detailed account of Physico-Chemical and analytical properties of metal complexes using DMAHBH and DMHBIH

CHARACTERISTICS	Cd(II) - DMAHBH	Pb(II) - DMAHBH	V(V) – DMAHBH	Cu (II)- DMAHBH	Cd(II) - DMHBIH	Pb(II) - DMHBIH
Maximum Absorbance (Zero order) (λ_{\max})	378	386	370	412	371	430
pH	8.0	4.0	9.0	9.0	4.0	9.0
Color of the Complex	Yellow	Yellow	Yellow	Bright Yellow	Yellow	Bright Yellow
First derivative (λ_{\max})	430	448	435	466	436	470
Second derivative (λ_{\max})	460	468	454	-----	468	539
Molar absorptivity (ϵ) l.mol ⁻¹ .cm ⁻¹	2.94×10^4	1.875×10^4	3.12×10^4	1.65×10^4	3.66×10^4	1.82×10^4
Sandell's sensitivity ($\mu\text{g.cm}^{-2}$)	0.0036	0.0066	0.0036	0.00606	0.0055	0.01302
Validity range ($\mu\text{g/ml}$)	0.5035-5.0535	0.279-2.79	0.243-2.438	0.3178-3.813	0.5035-5.0535	0.414-10.360
Optimum concentration range ($\mu\text{g/ml}$)	0.5035-5.0535	0.482-2.642	0.243-2.195	0.6355-3.4953	1.007-4.55	0.83-9.32
Composition (M:L)	1: 1	1: 1	1: 1	1:1	1: 1	1: 1
Stability constant (β)	8.58×10^7	8.8×10^6	6.42×10^7	7.15×10^5	2.06×10^7	8.99×10^6
R.S.D (%)	0.1	0.02	0.03	0.1	0.03	2.6

6.2 Conclusion

As per Literature survey Hydrazones and oximes are less exploited for the determination of Pb, Cd, V and Cu. The author synthesized new ligands Diacetylmonoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH), 3,5-Dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone (DMHBIH) and characterized them by Infra Red Spectrophotometer, Nuclear Magnetic Resonance Spectrophotometer, Mass Spectrometer. Based upon the spectral data the following structures are confirmed.



Structure of DMAHBH

Structure of DMHBIH

The above ligands are not used for the determination of Lead, Cadmium, Vanadium and Copper with DMAHBH, Cadmium and Lead with DMHBIH as per literature survey. The author successfully tested the formed yellow colored complexes of Cd, Pb and V in presence of Phosphate buffer solution (p^H 3-11) with the above ligands.

The effect of various surfactants on solubility and the absorbance of above complexes were studied and Triton X-100 (5%) has enhanced the solubility, stability, in case of Cd (II)-DMAHBH, CTAB was used. But Cu (II)-DMAHBH forms stable complex without any surfactant. The metal complexes such as Cd (II), Pb (II), V(V) and Cu (II) with DMAHBH and DMHBIH (Except V(V)-DMHBIH) obeys Beer's Law.

The interference ions such as anions and cations were systematically studied and masking agents like Fluoride, Phosphate and Thiourea etc are employed for masking of Iron, Copper etc for the determination of above complexes. The derivative spectrophotometric technique (1st & 2nd order) was successfully employed for the quantification of metal complexes.

The proposed direct and derivative spectrophotometric method for the determination of Cd (II), Pb (II), V (V) and Cu (II) was successfully applied in the following samples- Alloys, Soil, Biological Material, Food stuffs, Plant Material, Tobacco and Water.

6.3 Recommendations:

The newly synthesized organic ligand can be further employed for the determination of trace metal ions like Mercury (Hg), Zinc (Zn), Molybdenum (Mo), Antimony (Sb), Tin (Sn), Arsenic (As) etc in environmental and biological samples.