

CHAPTER I.

INTRODUCTION

INTRODUCTION

Organic reagents are used in all branches of analytical chemistry and technology. Organic reagents find many important applications in the analytical chemistry of inorganic and organic species. They are used for masking, separating, detecting, and concentrating elements as well as for their determination. The extensive use of organic reagents is attributed to their advantages over ordinary inorganic reagents.¹

The commonly used organic reagents are α -nitroso- β -naphthol, dimethylglyoxime, dithizone, alizarin, α -benzoinoxime (cupron) sodium diethyl dithiocarbamate, cupferron. α -Nitroso- β -naphthol may be regarded as a first synthetic organic reagent applied in quantitative analysis. It was suggested by Ilinskii and Knorre² in 1885 for the precipitation of cobalt and its gravimetric determination. The real development in the field of organic reagents started only in 1905 when Tschugaeff³ reported dimethylglyoxime as a selective precipitant for nickel. Dithizone was reported by Fischer⁴ in 1925 for the detection and determination of various trace metals. Since then several thousand papers, large number of reviews and monographs⁵⁻⁴⁶ have been published on the application of organic reagents in inorganic analysis.

Organic reagents are being synthesized today with a view to increase selectivity and sensitivity of the reagents, to find specific conditions of reactions (pH, reagent concentration, application of masking complexing agents, etc.), acid

resistant organic reagents, and reagent suitable for automotive analysis with a remote control of the process, etc. It reacts with a limited number of ions and allow the determination of even negligibly small amounts of ions as compared with inorganic reagents. This concept was introduced and developed by Feigl and others.¹⁹ High specificity of organic reagents allow the detection of individual ions in composite mixtures without their preliminary separation. To achieve the degree of selectivity, desired in analytical work, it is necessary to exploit differences in two or more physical or chemical properties. Some of the more common properties that are used in this way include :-

- [I] The production of a characteristic colour. This may be-
 - (A) For the direct spectrophotometric estimation of the species giving rise to the colour.
 - (B) For detecting end point, e.g. by means of an indicator in acid-base or oxidation reduction titrations, or by absorption of an indicator on to a precipitate.

- [II] Difference in solubility. This may be made the basis of a gravimetric method or used volumetrically, or trace constituents may be separated by coprecipitation.

- [III] The use of "masking" reagents to prevent a species other than the one being studied from participating in a reaction.

- [IV] Differences in distribution between solvents at controlled pH values.
- [V] Differences in ion exchange and chromatographic behaviour.
- [VI] Differences in volatility.
- [VII] Oxidation or reduction to other valence states.

All these properties of organic species can be profoundly modified by the use of suitable organic reagents.

Organic reagents can not be rigidly classified. Some may act as a reducing agents and some others as oxidizing agents. But, in general it is divided into two classes i.e. first those that form heteropolar or electrovalent salts and second are which form chelates. The reagents of second class contain a group with replaceable hydrogen atom ($-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{SH}$, $-\text{OH}$, etc.) in addition to a functional group of basic character such as $-\text{NH}_2$, $=\text{N}-\text{H}$, $>\text{O}$ with which the reacting metal is co-ordinated to form a five or six membered ring.

It reacts with metal ions and gives a variety of compounds: simple and complex salts, inner complexes (cheletes), absorption products. These reactions mostly involve oxidation-reduction processes. The reaction product formed, commonly develop intense colour and thus increases the sensitivity of colour tests, which allow their application in photometric analysis. The character of interaction of organic reagents with inorganic ions, is dependable on the position of

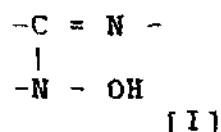
elements in the periodic system and on the structure of molecules of organic reagents. The compounds produced when a substance contains two or more donor groups combining with a metal so that two or more rings are formed, are termed as chelates. The term chelate was suggested by Morgan and Drew⁴⁷ in 1920. They are characterized by high stability, weak electrolytic dissociation, intense colour, poor solubility in water, high solubility in some organic solvents.

The complex forming properties of organic compounds have long been used for their characterization. The binary and ternary complexes or mixed ligand complexes are formed when metal ion reacts with two or more different ligands. A number of monobasic and bidentate chelating agents like oxine, PBHA, dithizone, etc. have been reported for the extraction-spectrophotometric determination of traces of various metal ions e.g. Ni(II), Co(II), Pd(II), Mn(II), etc. in the presence of other anions or neutral ligands.⁴⁸⁻⁶⁰ The use of mixed ligands have several advantages as under :-

- (1) The sensitivity and specificity of reactions are enhanced.
- (2) The degree of extraction of metal is increased.
- (3) The hydrophilic nature of the complex is minimised.
- (4) In some cases the hydrolysis of metal is prohibited.
- (5) The high colour intensity of the complex permit the spectrophotometric determination of metals.

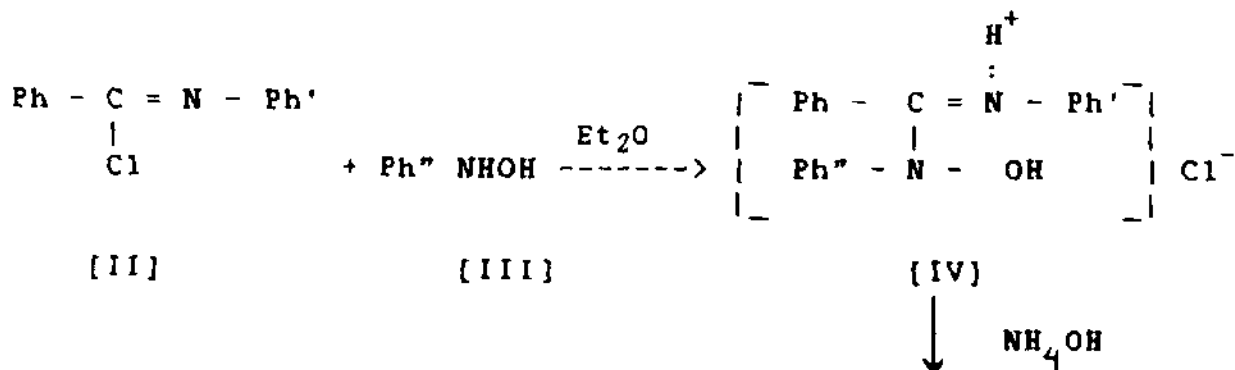
HYDROXYAMIDINES AS ANALYTICAL REAGENTS

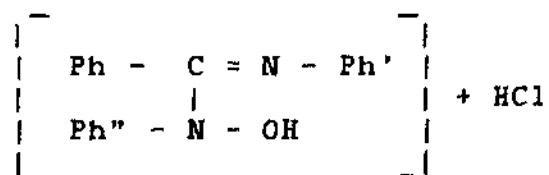
Hydroxyamidine is a new synthesized reagents, which is explored in this laboratory, created a new interest in organo-analytical chemistry. These reagents have an excellent properties of chelation with metal ion in the presence or absence of secondary ligands. It is a monobasic bidentate chelating agent having a reacting group - [I]



which is capable of forming a five or six membered ring with metal ion. These compounds have been several noteworthy features. They can be synthesized easily, stable towards heat and light, and appreciably soluble in various organic solvents. The solution of these compounds can be stored for a long time without deterioration.

The N-hydroxy-N,N'-diarylbenzamidines(hydroxyamidines) can be prepared by the condensation of N-arylbenzamidoyl chloride, [II] with N-arylhydroxylamine [III] in dry ether medium at low temperature and thus corresponding hydroxyamidine hydrochloride [IV] is obtained, which are treated with dilute ammonium hydroxide solution gives hydroxyamidines [V]





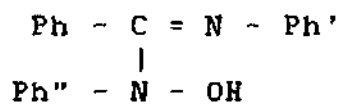
[V]

Where Ph is phenyl group.

Thus, the synthesis of organic reagents with specified properties stimulates the development of a new spectrophotometric method for the determination of nickel(II), cobalt(II), palladium(II) and manganese(II) in the presence of other complexing agents.

REVIEW OF THE EARLIER WORK

Ley and Holzweissig^{61,62} reported a synthesis of aromatic hydroxyamidines of the general formula [V] and their studies were,



[V]

mainly concerned with the isomerism and reduction of hydroxyamidines.

A number of hydroxyamide derivatives have been synthesized by Mishra et al.⁶³⁻⁷³ The analytical potentialities of various hydroxyamidines have been tested towards a number of metals and they have been found as an excellent reagent for gravimetric and spectrophotometric determinations of various transition metals.⁷⁴⁻⁹³

SPECIAL FEATURES OF THESE REAGENTS

When hydroxyamidine is introduced as chelating agent in the field of analytical chemistry, a promising field is open. As compared with a commercially employed reagents such as oxine,⁹⁴ cupferron,⁹⁵ oximes,⁹⁶ hydroxamic acids⁹⁷ hydroxytriazines⁹⁸ and dithizones⁹⁹ the present compound have wider scope as analytical reagents. The special features of these reagents are summarised as follow-

- (1) These compounds consist three phenyl rings, therefore, substitution reaction takes place at three sites of the compounds.
- (2) The compound has a high molecular weight therefore it is widely used in gravimetric and spectrophotometric determination of several metal ions.
- (3) The reaction of hydroxyamidines towards metal ions are highly selective.

PRESENT INVESTIGATION

In the present investigation effort has been made to increase the sensitivity as well as the selectivity of the spectrophotometric methods for the determination of metals viz. Ni(II), Co(II), Pd(II) and Mn(II) using PAN and hydroxyamidines (HOAs). 1-(2-Pyridylazo)-2-naphthol (PAN) is a versatile reagent containing chromophore azo group which participate in the formation of complexes with a large number of metal ions under different experimental conditions.¹⁰⁰⁻¹⁰⁵ However the colour intensity and the selectivity of the complexes of these metal ions using PAN have been found to increase when used alongwith hydroxyamidines (HOAs). Whereas in case of Co(II) and Mn(II), PAN forms binary complexes because it replaces the hydroxyamidines (HOAs) molecules from Co(II)/Mn(II)-HOA complexes after the reaction of PAN with Co(II)/Mn(II)-HOA complexes.

The review of the earlier work reveals that the complexes of hydroxyamidines (HOAs) have wide scope in the field of analytical chemistry. They have been found to be useful for extraction and spectrophotometric determination of trace amount of metals.

In the present investigation, seven different hydroxyamidines (HOAs) have been used for the extraction and spectrophotometric determination of trace amounts of metal ions in the presence of other complexing agents from the various types of complex materials and environmental samples. In the

present investigation, extraction-spectrophotometric determination of Ni(II), Co(II), Pd(II) and Mn(II) with hydroxyamidines in the presence of 1-(2-pyridylazo)-2-naphthol(PAN) have been studied.

The thesis has been divided into five chapters.

Chapter I contains the introductory part of the thesis.

Chapter II deals with extraction-spectrophotometric determination of nickel(II) in the form of ternary complex with N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) and 1-(2-pyridylazo)-2-naphthol(PAN). The complex is extractable into various organic solvents. Various analytical parameters such as effect of pH, reagent concentration, solvent effect, dilution effect, etc. have been examined. The reliability of the method has been checked by applying it to the determination of metal content in standard steel sample and brass metal, and it has been applied successfully for the determination of nickel(II) in coal ash at trace levels.

Chapter III deals with the extraction-spectrophotometric determination of cobalt(II) with N-hydroxy-N,N'-diphenylbenzamidine (HDPBA) and 1-(2-pyridylazo)-2-naphthol(PAN). The effect of various analytical parameters such as volume of the aqueous phase, temperature effect, diverse ions, composition of the complex, etc, have been studied. The method is free from the rigid control of experimental conditions. The method has been applied successfully for the determination of cobalt(II) in vitamin B12 samples at trace levels.

Chapter IV deals with spectrophotometric determination of palladium(II) with N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) and 1-(2-pyridylazo)-2-naphthol(PAN) in favourable experimental conditions. The analytical variables like pH range, reagent concentration, optimum concentration range, volume ratio of the organic to aqueous phase, temperature effect, etc. have been studied. The method has been applied for the recovery of palladium from synthetic mixtures.

Chapter V describes sensitive method for the extraction-spectrophotometric determination of manganese(II). The extraction and colour reaction of manganese with N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) and 1-(2-pyridylazo)-2-naphthol (PAN) have been discussed. The effect of experimental variables on the determination of metal at trace levels have been investigated. The method has been applied satisfactorily for the determination of manganese(II) in environmental samples.

REFERENCES

1. V.I. Poypaiko and N.A. Vasina, "Analytical Chemistry in Metallurgy", Mir Publishers, Moscow 1984.
2. M. Iliniskii and G. Knorre; Ber. 18, 699, 1885.
3. L.A. Tachugaeff; Ber. 38, 2520, 1905.
4. H. Fischer; Wiss Veroffentl Siemens-Konzern; 4, 158, 1925; Angew. Chem. 47, 685, 1934; 50, 919, 1937.
5. D.D. Perrin, "Organic complexing Reagents", Interscience Publishers, New York 1964.
6. A.A. Schitt, "Analytical Applications of 1,10-Phenanthroline and Related-Compounds", Pergamon Press, Oxford 1969.
7. F. Feigl, "Spot Test in Inorganic Analysis", 5th Ed., Elsevier Publishing Company, Amsterdam 1958.
8. F.J. Welcher, "Organic Analytical Reagents", Vol. 1-4, D. Van Nostrand Company, New York 1947-48.
9. O. Baudish et al; Ber. 45, 1164, 1912; 48, 1665, 1915; 49, 180, 191, 203, 1916.
10. G. Deniger, "Precis de Cheme Analytique", 4th Ed., Paris, Maloine, et fils p. 42, 1913.
11. F.W. Altach; J. Soc. Chem. Ind. 34, 936, 1915.
12. F. Feigl; Ber. B 56, 2083, 1923.
13. A.C. Rice, H.C. Fogg and C. James; J. Amer. Chem. Soc. 48, 895, 1926.
14. R. Berg; Z. Anal. Chem. 70, 341; 71, 23, 1927.
15. H.B. Knowles; J. Research Natl. Bur. Standards 9, 1, 1932.
16. R. Berg and H. Kustenmecher; Z. Anorg. Allegen. Chem. 204, 215, 1932.
17. H. Fischer; Angew. Chem. 47, 685, 1934.
18. P. Ray and M.K. Bose; Z. Anal. Chem. 95, 400, 1934.
19. F. Feigl, Ind. Eng. Chem., Anal. Ed. 8, 404, 1936.
20. G.F. Smith, "Cupferron and Neo-cupferron", G.F. Smith Chemical Company, Columbus-Ohio 1938.

21. H. Diehl, "The Applications of the Dioximes to Analytical Chemistry", G.F. Smith Chemical Company, Columbus-Ohio 1940.
22. W. Prodinger, "Organic Reagents Used in Quantitative Inorganic Analysis", Translated by S. Holmes, Elsevier Publishing company, New York 1940.
23. I. Mellon, "Organic Reagents in Inorganic Analysis", P.P. Blakinstonia Son and Compnay, Philadelphia 1941.
24. J.H. Yoe and L.A. Server, "Organic Analytical Reagents", John Wiley and Sons, New York 1941.
25. G.F. Smith and F.P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators", G.F. Smith Chemical Company, Columbus-Ohio 1944.
26. J.F. Flagg, "Organic Reagents used in Gravimetric and Volumetric Analysis". Interscience Publishers, INC., New York 1949.
27. F.D. Snell and C.T. Snell, "Colorimetric Methods of Analysis", Vol. II, D. Van Nostrand Company, INC., New York 1949.
28. F. Feigl; Ind. Eng. Chem., Anal. Ed. 21, 1296, 1949.
29. R.E. Treybal, "Liquid Extraction", McGraw Hill Book Company, INC., New York 1951.
30. D. Dryssen; Anal. Chim. Scand. 10, 353, 1956.
31. F.W. Welcher, "The Analytical uses of Ethylene-Diamine tetra acetic acid", D. Van Nostrand Company, INC. New York 1957.
32. O.H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley and Sons, INC., New York 1957.
33. I.M. Kolthoff, P.J. Elving and E.B. Snell, "Treatise on Analytical Chemistry", Part I, Vol. II, Interscience Publishers INC., New York 1961.
34. J. Stray, "The Solvent Extraction of Metal Chelates", Pergamon Press, London 1964.
35. P. Sanyal and S.P. Mushran; Anal. Chim. Acta 35, 400, 1966.
36. H.R. Littel and T.M. Florence; Anal. Chem. 39, 320, 1957.
37. A.I. Busev and Z.P. Reryakina; Zh. Anal. Khim. 22, 1350, 1968.

38. W. Rekeo; Chem. Anal. 14, 795, 1969.
39. M. Katyal, D.P. Goel and R.P. Singh; Talanta 15, 711, 1968.
40. B.K. Afghan and J. Israeli; Talanta 16, 1601, 1969.
41. A.T. Pilipenko and V.V. Lukeehina; Zh. Anal. Khim. 25, 2125, 1970.
42. A. I. Busev and N.G. Soloreva; Zh. Anal. Khim. 27, 1529, 1972.
43. Y.P. Rick and N. Vesely; Anal. Chim. Acta 73, 377, 1973.
44. B.S. Crag and R.P. Singh; Microchem. J. 18, 509, 1973.
45. W.I. Stephen; Analyst 102, 793, 1977.
46. L.M. Kulberg, "Organic Reagents in Analytical Chemistry", Goskhimizdat, Moscow 1950.
47. G.T. Morgan and H.D.V. Drew; J. Chem. Soc. 117, 1456, 1920.
48. J. Stary; Anal. Chim. Acta 28, 132, 1963.
49. C.H.R. Gentry and L.G. Sherrington; Analyst 75, 17, 1950.
50. S.K. Menon, Y.K. Agrawal and M.N. Desai; Talanta 36, 675, 1989.
51. A. Izquierdo and J. Carrasco; Analyst 109, 605, 1984.
52. A. Dejena and B.S. Chandravanshi; Anal. Lett. 23, 1729, 1990.
53. K. Motijima and N. Tamura; Anal. Chim. Acta 45, 327, 1969.
54. R.E. Stanton, A.J. McDonald and I. Carmichel; Analyst 87, 134, 1962.
55. V.I. Kuznetsov, Yu.A. Bankovskii and A.F. Levin'sh; Zh. Analit. Khim. 13, 267, 1958.
56. K.S. Math, K.S. Bhatki and H. Freiser; Talanta 16, 412, 1969.
57. B.S. Freiser and H. Freiser; Talanta 17, 540, 1970.
58. G. Iwantscheff "Das Dithizone und Seine Anwendung in der Mikro und Spurenanalyse", Springer Verlag, Weinheim 1958.
59. Z. Marczenko and M. Krasiejko; Chem. Anal. 9, 291, 1964.
60. M. Kawahata, H. Mochizuki and T. Misaki; Jpn. Analyst 11, 819, 1962.

61. H. Ley; Ber. 34, 2620, 1901.
62. H. Ley and E. Holzwissig; *ibid.* 36, 18, 1903.
63. K. Satyanarayana and R.K. Mishra; Anal. Chem. 46, 1609, 1974.
64. K.K. Deb and R.K. Mishra; J. Indian Chem. Soc. 53, 178, 1976.
65. R.S. Kharsan and R.K. Mishra; Polish J. Chem. 53, 2597, 1979.
66. K.S. Patel; Ph.D. Thesis, Ravishankar University, Raipur, 1979.
67. H. Mohabey; Ph.D. Thesis, Ravishankar University, Raipur, 1980.
68. A.R. Jha; Ph.D. Thesis, Ravishankar University, Raipur, 1982.
69. K.B. Bumerkar; Ph.D. Thesis, Ravishankar University, Raipur, 1976.
70. R.M. Verma and R.K. Mishra; Current Z. Anal. Chem. 307, 128, 1981.
71. L.P. Chandrakar; Ph.D. Thesis, Ravishankar University, Raipur, 1987.
72. R.S. Kharsan; Ph.D. Thesis, Ravishankar University, Raipur, 1979.
73. S.K. Sinha; Ph.D. Thesis, Ravishankar University, Raipur, 1987.
74. K. Satyanarayana and R.K. Mishra; Indian J. Chem. 13, 295, 1975.
75. K. Satyanarayana and R.K. Mishra; J. Indian Chem. Soc. 53, 469, 1976; 63, 928, 1976; 55, 787, 1978.
76. K.K. Deb and R.K. Mishra; *curr. sci.* 45, 134, 1976; 47, 341, 1978.
77. K.K. Deb and R.K. Mishra; J. Indian Chem. Soc. 55, 289, 733, 1978.
78. K.K. Deb and R.K. Mishra; Indian J. Chem. 16A, 727, 1978.
79. K.S. Patel and R.K. Mishra; J. Indian Chem. Soc. 55, 462, 773, 1978.
80. K.K. Deb and R.K. Mishra; Talanta 25, 698, 1978.

81. R.S. Kharsan, K.S. Patel and R.K. Mishra; *J. Less Common Metals* 64, 155, 1979.
82. K.K. Deb, K.S. Patel and R.K. Mishra; *J. Less common Metals* 68, 67, 1979.
83. K.S. Patel and R.K. Mishra; *Bull. Chem. Soc. Jpn.* 52, 592, 1979.
84. K.S. Patel, K.K. Deb and R.K. Mishra; *Bull. Chem. Soc. Jpn.* 52, 595, 1979.
85. K.S. Patel, K.K. Deb and R.K. Mishra; *Sep. Sci.* 14, 333, 1979.
86. R.S. Kharsan, K.S. Patel and R.K. Mishra; *Talanta* 26, 50, 254, 1979.
87. R.S. Kharsan, K.S. Patel, K.K. Deb and R.K. Mishra; *Z. Anal. Chem.* 295, 415, 1979.
88. K.S. Patel, K.K. Deb and R.K. Mishra; *Sep. Sci.* 14, 815, 1979.
89. K.S. Patel, K.K. Deb and R.K. Mishra; *Chinese Chem. Soc.* 26, 79, 1979.
90. H. Mohabey and R.K. Mishra; *J. Indian Chem. Soc.* 57, 562, 1980.
91. P.K. Sharma and R.K. Mishra; *Croat. Chem. Acta* 53, 87, 1980.
92. R.S. Kharsan and R.K. Mishra; *Bull. Chem. Soc. Jpn.* 53, 1256, 1980.
93. R.S. Kharsan and R.K. Mishra; *Croat. Chem. Acta* 54, 121, 1981.
94. E. Sudo and H. Goto; *Trans. Natl. Res. Inst. Metals* 5, 166, 1963.
95. J.F. Flagg, "Organic Reagents used in Gravimetric and Volumetric Analysis", INC., New York 1949.
96. G.F. Smith and F.P. Richter, "Phenanthroline and Substituted Phenanthroline Indicator", G.F. Smith Chemical Company, Columbus-Ohio 1977.
97. W.I. Stephen; *Analyst* 102, 793, 1977.
98. B.S. Garg and R.P. Singh; *Microchem. J.* 18, 509, 1973.
99. Y.P. Dick and N. Vesely; *Anal. Chim. Acta* 73, 377, 1973.

100. R.G. Anderson and G. Nickless; *Analyst* 92, 207, 1967.
101. D. Betteridge, P.K. Todd, Q. Fernando and H. Freiser; *Anal. Chem.* 35, 729, 1963.
102. D. Betteridge, Q. Fernando and H. Freiser; *Anal. Chem.* 35, 294, 1963.
103. K.L. Cheng and R.H. Bray; *Anal. Chem.* 27, 782, 1955.
104. K. Ohshita, H. Wada and G. Nakagawa; *Anal. Chim. Acta* 124, 193, 1983.
105. G. Goldstein, D.L. Manning and O. Menis; *Anal. Chem.* 31, 192, 1959.