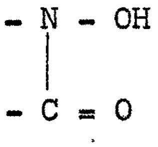
CHAPTER I

INTRODUCTION

Organic reagents have become an important tool in the field of analytical chemistry. The thousands of reagents are synthesised and their analytical behaviour is evaluated. Eventhough in recent years they are in great demand and play a vital role. The N-arylhydroxamic acids are a mile stone in the analytical chemistry of organic reagents.

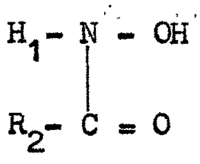
Hydroxamic acids having the bidentate functional grouping (I), fulfill the basic requirement of complex formation with metal ions and therefore form an important family of chelating agents.



$$\begin{array}{c} -\mathrm{N}-\mathrm{OH} \\ | \\ -\mathrm{C}=\mathrm{O} \end{array}$$

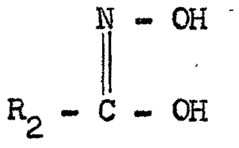
(I)

Chemically, hydroxamic acids are regarded as the N-aryl derivatives of hydroxylamine (1-3). Structurally, the hydroxamic acids can be represented in their two tautomeric forms (II) and (III)



$$\begin{array}{ccccc} H_1 & - & N & - & OH \\ & & | & & \\ R_2 & - & C & = & O \end{array}$$

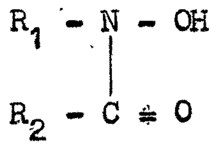
(II)



$$\begin{array}{ccccc} & & N & - & OH \\ & & \| & & \\ R_2 & - & C & - & OH \end{array}$$

(III)

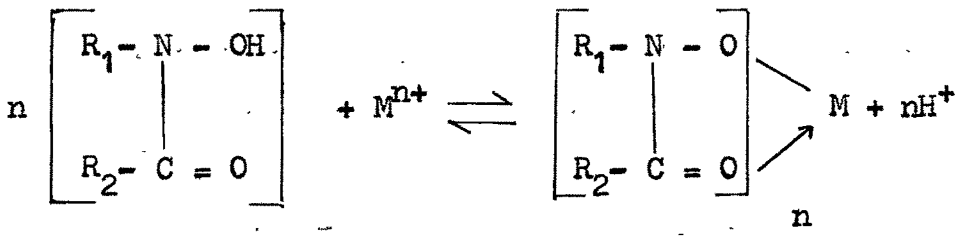
Alternatively, the hydroxamic acids are regarded as N-hydroxy derivatives of acid amides or as oximes of carboxylic acids (4). By substituting the hydrogen atom attached to the nitrogen atom in (II) by alkyl or amyl groups, numerous N-substituted hydroxamic acids of the type (IV) can be obtained.



$$\begin{array}{ccccc} R_1 & - & N & - & OH \\ & & | & & \\ R_2 & - & C & = & O \end{array}$$

(IV)

The complex formation of hydroxamic acids of the type (IV) usually takes place with the replacement of hydroxylamine hydrogen by the metal ion and ring closure through the carbonyl oxygen.

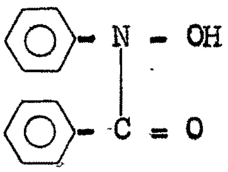


$$n\left[\begin{array}{c} R_1-N-OH \\ | \\ R_2-C=O \end{array}\right] + M^{n+} \rightleftharpoons \left[\begin{array}{c} R_1-N-O \\ | \\ R_2-C=O \end{array}\right]_n M + nH^+$$

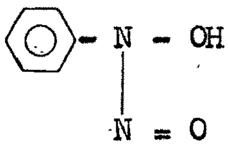
The metal chelates of hydroxamic acids are non-ionic in nature. Therefore, it is possible to extract their uncharged metal chelates or inner complexes with different water immiscible solvents. The coloured and stable solutions of these complexes often provide photometric methods for the quantitative determination of several metal ions. At the same time the water insoluble and thermally stable metal complexes of hydroxamic acids have provided excellent gravimetric methods for the quantitative determinations of various metal ions. However, the stability of metal complexes, depending on the type of metal ion and the donor atoms rests much on the base strength and the number of coordination sites of the ligand, the chelate ring size, and steric and the resonance effects.

REVIEW OF THE PREVIOUS WORK

In recent years N-phenylbenzohydroxamic acid (V) (PBHA) also popularly known as N-benzoylphenylhydroxylamine (BPHA) has received a great deal of attention as a versatile reagent for determining metal ions (4-10). This reagent was first synthesised by Bamberger (11) in 1919 but its analytical potentialities were recognized only after 30 years by Shome (12), who regarded PBHA (V) as an analogue of cupferon (VI),



(V)



(VI)

the ammonium salt of N-nitroso-N-phenylhydroxylamine (VI). Further PBHA and other N-substituted hydroxamic acids gained wide popularity due to their most selective colour reactions with vanadium and other metal ions (3-100). These methods afford direct determination of metals in presence of large number of foreign ions and have been applied for the vide varieties of samples.

The general survey of literature on N-arylhydroxamic acids is deliberately avoided here because the various aspects of their chemistry, structure and analytical applications has been recently reviewed exhaustively by Agrawal et.al. (13-19) and others and well documented in several research papers (5,6,10,20-100). However a brief account on their analytical application of recent five years is summarised in Table 1.

TABLE 1

ANALYTICAL APPLICATIONS OF N-ARYLHYDROXAMIC ACIDS

(Solvent Extraction and Spectrophotometric Determination)

S.No. 1	Hydroxamic acid 2	pH/ acidity 3	Solvent 4	λ max 5	Beer's Law (μg/ml) 6	Molar absorptivity (l mol^{-1} cm^{-1}) 7	Remarks 8	Ref. 9
	VANADIUM							
1.	N-Phenylbenzo-	5 M HCl	Chloroform	510	0.7 - 12.0	4,300	V in biological samples.	101
2.	N-m-Tolyl-(o-carboxy)-benzo-	3.6-8.4	Ethanol	530	0 - 2.5	28,300	Fe,Ti,Mo and U interfere.	102
3.	N-m-Chlorophenyl-cinnamo-	4-7 M HCl	Chloroform	540	0.88-7.1	5,750	V,Zr,W,Mo interfere.	103
4.	N-Phenylbenzo-	2.2-3.3	Benzene	510	-	3,267	-	104
5.	N-3-Diphenyl-propiolo-	4-8 M HCl	Chloroform	560	1.75-6.05	5,900	Mo,W interfere.	105
6.	N-p-Chlorophenyl-2-theno-	3-9 M HCl	"	530	-	5,500	-	106

1	2	3	4	5	6	7	8	9
7.	N-m-Tolyl-p-methoxybenzo-	4-8 M HCl	Chloroform	530	1.0 - 7.0	-	Traces of Zr and Mo can be tolerated.	107
8.	N-p-Tolylbenzo-	2-4	Molten naphthalene	445	10.0-20.0	2,350	-	108
9	N-Phenylacetyl-mandelo-	6-8 M HCl	Chloroform	640	-	-	Mo and W interfere.	109
10.	N-p-Tolyl-2,4-dimethoxybenzo-	3-6 M HCl	"	570	0.1 - 9.0	5,990	Mo, Ti and Zr interfere masked by citrate and F^-.	110
11.	N-p-Tolylacetyl-mandelo-	6-8 M HCl	"	520	-	4,050	-	111
12.	N-p-Tolylacetyl-mandelo- + O-methoxyphenol	6-8 M HCl	"	645	1.7 - 6.3	5,950	Mo and W interfere.	111
13.	N-o-Chlorophenyl-cinnamo-	4.7 M HCl	"	550	1.5 - 5.5	-	Zr, Ce, Mo and W interfere.	112
14.	Salicylo-	0.5 M H_2SO_4	Heptanol: Carbontetra chloride (3 : 2)	330	0.5 -20.0	-	-	113

1	2	3	4	5	6	7	8	9
15.	N-2,3-Xylyl-cinnamo-	3.5-9 M HCl	Chloroform	535	0.5 - 7.0	6,600	Fe and Ti interfere.	114
16.	N-p-Tolyl-p-methoxybenzo- + SCN^-	0.8-2.2	"	570	0.5 -12.0	7,260	Ti,Mo,W,Zr,Cu,Cr interfere.	115
17.	N-o-Methoxyphenyl-cinnamo-	2-5 M HCl	"	530	1.0 -14.0	6,000	Ti,Mo,W,Nb and Zr8 interfere Ti-masked with NaF and Mo. extracted with ethyl xanthate	116
18.	N-p-Tolylcinnamo-	1-5 M HCl	"	550	0.4 -14.0	5,900		116
19.	N-p-Tolyl-p-methoxybenzo-	1-4 M HCl	"	540	0.5 -14.0	5,552	Ti,Mo,W,Nb and Zr interfere.	117
20.	N-p-Tolyl-p-methoxybenzo-	2-4 M HCl	"	530	0.4 -14.0	5,094	-	117
21.	N-p-Tolyl-p-methoxybenzo- + SCN	1.0	"	560	0.4 -14.0	6,400	Fe,Ti and Pt group interfere	118
22.	N-Anthranilo- + SCN^-	0.95	MIBK	630	0.5 -12.0	6,750	-	119
23.	N-p-Methoxyphenyl-2-furo-	4-8 M HCl	Chloroform	545	0 - 12.0	7,300	-	120

1	2	3	4	5	6	7	8	9
24.	N-p-Chlorophenyl-p-methoxybenzo-	4 MHCl	Chloroform	-	1.04-10.8	-	Fe,Mo,and Zr interfere.	121
25.	N-p-Chlorophenyl-2-naphtho-	4-8 M HCl	"	535	0.09-20.0	5,600	Ti,Mo,Zr interfere; masked by the addition of NaF and ammonium oxalate before extraction.	122
26.	Sodium-N-phenyl-2-sulphobenzohydroxamate	0.01-0.5 M HCl	Water	370	0.4-4.0	2,750	Fe interfere.	123
27.	N-o-Tolyl-benzo-	4-8 M HCl	Carbon-tetra chloride	510	-	5,250	-	124
28.	N-Phenyl-p-chlorocinnamo-	2-8 M HCl	Chloroform	540	6.5-10.0	6,200	-	125
29.	N-m-Tolyl-p-chlorocinnamo-	2-8 M HCl	"	540	0.5-10.0	6,900	-	125
30.	N-p-Chlorophenyl-p-chlorocinnamo-	2-8 M HCl	"	540	0.5-10.0	6,100	-	125
31.	N-p-Tolyl-p-chlorocinnamo-	2-8 M HCl	"	540	0.4-10.5	6,900	Ti,Mo and Zr interfere	125

1	2	3	4	5	6	7	8	9
32.	N-Phenyl-p-nitrocinnamo-	2-8 M HCl	Chloroform	540	0.5-10.0	5,000	-	125
33.	N-m-Tolyl-p-nitrocinnamo-	2-8 M HCl	"	540	0.5-10.0	5,300	-	125
34.	N-p-Tolyl-p-nitrocinnamo-	2-8 M HCl	"	540	0.5-10.0	5,300	-	125
35.	N-p-Chloro-phenyl-p-nitrocinnamo-	2-8 M HCl	"	540	0.5-10.0	5,500	-	125
36.	Salicylo-	3.1	MIBK	575	0.2-8.0	5,710	Fe,Ti,Mo,W	126
		1.8 M HCl	MIBK	510	0.25-9.0	5,730	Zr,Nb and Hf interfere.	
37.	Salicylo- + SCN$^-$	0.95	MIBK	540	0.4-12.0	8,340	-	126
38.	5,5'-Methyl bis Salicylo-	2 M HCl	EtOH+H_2O	490	1.0-12.0	5,100	Ag,Hg,Se,Be,W,SCN,oxalate interfere.	127
39.	Benzo- + SCN$^-$	0.75-2.1 M HCl	MIBK	535	0.4-12.0	7,400	Mo,W,Ta and Nb interfere.	128

1	2	3	4	5	6	7	8	9
40.	N-Anthranilo-	3.2	MIBK	470	0.2-7.5	3,450	Fe,Ti,Mo,Nb,W,Zr interfere but tolerated at pH 2.5 with F^-.	129
		1.8 M HCl	"	595	0.2-6.5	3,060		
	+ SCN	0.95	"	630	0.5-12.0	6,750		
41.	N-Phenyl-cinnamo- + SCN^-	0.16 M HCl	Chloroform	580	0.4-12.0	7,000	Fe,Ti,Nb and Ta interfere.	130
42.	N-Phenyl-cinnamo-	3-7 M HAC^-	"	590	0.8-6.4	7,500	Fe and W interfere.	131
43.	N-o-Chloro-phenylcinnamo-	-	"	-	-	6,500	V in complex materials	132
44.	N-Phenylbutyro-	3.5 M HCl	"	510	-	4,450	-	133
45.	N-o-Chloro-phenyl-o-chlorobenzo-	6 M HCl	"	530	-	4,400	-	134

1	2	3	4	5	6	7	8	9
46.	N-m-Chloro-phenyl-myristo-	6 M HCl	Chloroform	515	-	4,900	-	134
47.	N-m-Chloro-phenyl-palmito-	6 M HCl	"	520	0.5-12.0	4,900	Ta,Nb and Mo interfere.	134
48.	N-m-Chloro-phenyl-stearo-	6 M HCl	"	515	-	4,700	-	134
49.	N-o-Chloro-phenylmyristo-	6 M HCl	"	510	-	4,500	-	134
50.	N-o-Chloro-phenyl-palmito-	6 M HCl	"	515	-	4,600	-	134
51.	N-o-Chloro-phenylstearo-	6 M HCl	"	515	-	4,600	-	134
52.	N-m-Chloro-phenyl-o-chloro-benzo-	6 M HCl	"	535	-	3,900	-	134
53.	N-p-Chlorophenyl-2-naphtho-	6M.HCl	"	530	1.3-8.9	5,720	Pb and W interfere.	135
	TITANIUM							
54.	N-m-Sulpho-phenylbenzo-	1.5-2.5	Water	410	4.0-14.0	1,580	Ag,V,Mo,CrO_4 PO_4,F^-, EDTA interfere.	136

1	2	3	4	5	6	7	8	9
55.	N-Phenylcinnamo-	-	Chloroform	550	-	-	-	137
	+ Phenyl fluorone							
56.	N-m-Tolyl-p-methoxybenzo-	2-8 M HCl	"	330	1.0-8.0	6,800	Mo,W,V,Sn^{2+},Fe,Nb,Cu,F^-, interfere.	138
57.	Benzo-	4 M HCl	Iso-amyl alcohol	390	1.0-14.0	1,480	-	139
		8 M HCl	"	390	1.0-11.0	2,320	-	
58.	N-Phenylfuro-	1.0-2.0	Chloroform	355	-	8,800	-	140
		Conc HCl	"	360	-	9,600	-	
	+ Catechol	2.2-4.4	"	355	-	11,300	-	
		6.9 M HCl	"	355	-	12,500	-	
	+ Pyrogallol	2.4-3.5	"	355	-	13,000	-	
		8.4-9.6 M HCl	"	355	-	11,700	-	

1	2	3	4	5	6	7	8	9
	+ Naphthalene 1,8 diol	4.4-6.4	Chloroform	455	-	8,400	-	
		4.4-6.4	"	355	-	11,500	-	
		0-4.8 M HCl	"	465	0.1-4.5	7,600	Fe,Mo,V interfere (masked by $SnCl_2$).	
		0-4.8 M HCl	"	355	-	7,900	-	
59.	N-Phenyl-o-carboxylbenzo-	3-10 M HCl	"	375	-	1,820	-	141
60.	Benzo- + tetrabromo-catechol	0.01-0.8 M HCl	"	390	-	11,000	-	142
	+ Catechol	0.01-0.8 M HCl	"	390	-	10,600	-	
61.	N-Phenylbenzo-	0.2 M HCl	"	540	0.4-8.0	-	Fe and Cr interfere (masked by ascorbic acid)	143
	+ lumogallion	0.2 M HCl	"	360	0.12-2.4	-		
62.	Benzo- + Trioctylamine	7.0-8.0 M HCl	Carbon-tetra-chloride	370	0.2-5.0	10,000	Fe and Cu interfere (masked by ascorbic acid)	144

1	2	3	4	5	6	7	8	9
63.	Benzo- + Tributyl-phosphate	7.0-10.0 M HCl	Toluene	350	0.2-5.0	10,000	-	145
	+ Tributyl-phosphate + SCN^-	0.4 M HCl	Carbon-tetra chloride	350	-	28,000	-	
64.	Sodium-N-phenyl-2-sulphobenzo-hydroxamate	0.03-0.1 M HCl	Water	330	0.8-14.0	3,500	Fe interferes (masked F^-, PO_4 or Sn^{2+}	123
65.	N-Benzoylamino-thioformyl-N-phenylhydroxylamine	8.4	Iso-amyl alcohol	415	0-1.8	38,000	Fe,Ce,V and Mo interfere.	146
66.	Castor oil based hydroxamic acid	0.02	Petroleum ether(100-120°C)	325	-	-	-	147
67.	N-p-Methoxyphenyl-2-furo- + $SnCl_2$	10-12 M	Chloroform	385	0.5-10.0	-	-	148
68.	N-Phenyllauro- + Phenylfluorone	0.1-0.5 M HCl	Iso-amyl alcohol	560	0-0.4	1,23,000	Zrinterferes (masked with F^-)	149
69.	N-Phenyl-2-sodiosulfobenzo-	1.0-1.4	Water	-	-	-	Fe interferes(masked with ascorbic acid)	150

1	2	3	4	5	6	7	8	9
70.	N-p-Chlorophenyl-pivalo-	7-11 M HCl	Chloroform	380	0.2-12.0	5,300	V,Mo,W and Nb interfere.	151
71.	N-m-Tolyl-p-chlorocinnamo-	6-10 M HCl	"	415	0.08-3.6	14,000	V,Cr interfere but masked by reduction with iron	152
	<u>ZIRCONIUM</u>							
72.	N-p-Chlorophenyl- + morin	0.2-0.5 N H_2SO_4	Iso-amyl	420	-	35,000	-	153
73.	N-Phenylbenzo- + bromothymol blue	1.0-2.2	Butanol	600	-	31,000	Fe,Hf,SO_4, oxalate and F^- interfere.	154
	<u>NIOBIUM</u>							
74.	N-Phenylbenzo- + lumogallion	5.0 M HCl	Chloroform	505	-	-	Interferences of Fe,Mo and W are removed by the addition of $SnCl_2$	155
75.	N-m-Tolyl-p-methoxybenzo-	8.0 M HCl	"	320	0.02-4.0	21,500	Ti,Mo,W,V,Sn^{2+} and F^- interfere.	156
76.	N-m-Tolyl-p-methoxybenzo- + SCN	8.0 M HCl	"	360	0.2-2.5	31,200	Ti,Mo,W,V,Sn^{2+} and F^- interfere.	157

1	2	3	4	5	6	7	8	9
77.	N-Phenylbenzo-	1.4-1.7 M HCl	Chloroform	340	4,900	4,900	Mo and W can be masked with Sn^{2+}, but Ti and Zr interfere.	158
		9.8-10.5 M HCl	"	340	0.6-8.3	11,200		
78.	N-p-Chlorophenyl-	8-10 M HCl	Toluene	365	0.3-20.0	30,000	Bi interferes but eliminated with thioglycolic acid.	159
79.	N-Phenylcinnamo- + phenylfluorone	-	Chloroform	502	-	-	-	137
	<u>TANTALUM</u>							
80.	N-m-Tolyl-p-methoxythiobenzo-	-	-	380	0.02-4.0	21,800	-	160
81.	N-p-Chlorophenyl-benzo- + Malachite green	8-9 M HCl	Benzene	635	0.05-4.0	40,000	Zr, Bi and Ag interfere.	161
	<u>CERIUM</u>							
82.	N-p-Tolyl-o-methoxybenzo-	7.9-8.2	Chloroform	460	2.4-39.4	3,250	Zr, Fe, Ti, U, Cu, citrate, tartrate and EDTA interfere.	162
83.	N-p-Chlorophenyl-2-theno-	7.8-10.0	"	460	2.0-20.0	6,000	Tartrate, oxalate and citrate interfere; but removed by treating with HNO_3.	163

1	2	3	4	5	6	7	8	9
84.	N-p-Tolyl-p-chlorobenzo-	8.5-9.0	Chloroform	460	0.5-28.0	4,500	-	164
85.	N-Phenyl-p-chlorocinnamo-	8-10	"	470	0.2-3.0	5,500	-	165

The high complexing power of the hydroxamic acids towards some ions such as uranium, plutonium, neptunium, cerium, thorium, zirconium, niobium, molybdenum, iron etc. led to considerable nuclear interest. The stability of these complexing agents is at least equal to that of the corresponding oxalates, acetyl acetone, thenoyl trifluoacetates and when the study is limited to the ions most strictly bound to the nuclear technologies, the stability of the complexes with the hydroxamic acids is without any doubt one of the highest (166-175).

AIMS AND SCOPE

A series of the hydroxamic acids are synthesised by Ryan, Tandon, Bhattacharyya, Agrawal, Exner and others and their analytical potentialities were discussed (176-190). Gasparani et.al. (191-195) have synthesised some new hydroxamic acids and discussed their complexing ability with metals. A thorough investigation of literature concerning hydroxamic acids reveals that there is not much work has been reported on the synthesis, physico-chemical properties and analytical potentialities of high molecular weight hydroxamic acids which led to the following considerations:

1. A new series of hydroxamic acids could be synthesised having the high molecular weight and tertiary carbon atom and conjugated double bond.

2. The hydroxamic acids are capable to form very stable complexes.
3. During the last 20 years the practical use of hydroxamic acids has been widely shown by a lot of analytical applications.
4. The idea of an application of hydroxamic acids in the field of solvent extraction has already been taken into consideration, by means of utilization of N-aryl-hydroxamic acids.

Starting from these considerations, it was decided to carry out a series of studies arrived at synthesising the hydroxamic acids, which, fully meeting the requirement featured could be satisfactorily used as selective chelating agents.

(a) Synthesis of new high molecular weight hydroxamic acids.
(b) Establishment of physico-chemical properties of the newly synthesised acids for their analytical behaviour.
(c) Application of the synthesised acids for the extraction and spectrophotometric determination of the heavy metals and their comparison with the existing methods.

PRESENT INVESTIGATION

The present investigation is a part of the broad project of our laboratory dealing with several aspects of the Chemistry of "Hydroxamic Acids".

This thesis describes the preparation and properties of five new high molecular weight hydroxamic acids. The preparations are made by reacting hydroxylamine with acid chloride at low temperature in benzene and diethyl ether containing aqueous suspensions of sodium carbonate.

These 5 new N-arylhydroxamic acids synthesised by above method, are characterised by elemental analysis, mp, ultraviolet, infrared, nmr and mass spectra.

The physico-chemical properties viz. thermogravimetric (TG) and differential thermal analysis (DTA), thermal stability, chemical stability, non-aqueous titration, ionization and hydrolysis constants have been described.

The thermal dissociation of hydroxamic acids are studied by differential thermal analysis (DTA). The DTA curves show exothermic peaks by melting of the compound.

The synthesised hydroxamic acids are titrated visually in non-aqueous media (methanol and dimethylformamide) using thymol blue as indicator against 0.1N potassium methoxide. Potentiometric titrations were also performed in non-aqueous media with platinum and calomel electrodes. The molecular weights of hydroxamic acids are calculated.

The chemical and thermal stability and thermodynamic ionization constants of the synthesised acids in 50 - 70 % dioxan-water media at 35°C ± 0.1°C have been determined. The hydrolysis constants are also reported.

A rapid selective and sensitive spectrophotometric method for the trace determination of cerium(IV), Niobium(V) Zirconium(IV) is described with synthesised high molecular weight N-arylhydroxamic acids. A comparative study for the sensitivity of different hydroxamic acids towards these metal ions has been made. A detailed study of various parameters for the optimum extraction of these metals have been undertaken with N-p-Chlorophenyl-3,4,5 trimethoxy-cinnamohydroxamic acid (PTCHA). The ternary complexes with suitable chromogenic reagents were also studied and applied for the enhancement of the sensitivity of the method. These metal ions have been determined in presence of several diverse ions and in standard samples.

REFERENCES

1. Sidwick, N.V., "The Organic Chemistry of Nitrogen", Clarvendon Press, Oxford (1937), p. 137.
2. Yale, H.L., Chem. Rev., 33, 209 (1943).
3. Johnson, A.W. and Walker, J., "Chemistry of Carbon Compounds", Vol.I, Rodd, E.H., Ed., Elsevier Publishing Co., Amsterdam (1951) p. 612.
4. Macdonald, A.M.G., Ind. Chemist., 36, 512 (1960).
5. Alimarin, I.P., Sudakou, F.P. and Golovkin, B.G., Russ. Chem. Rev., 31, 466 (1962).
6. Shendrikar, A.D., Talanta, 16, 51 (1969).
7. Belcher, R., Wilson, C.L., "New Methods of Analytical Chemistry", 2nd Ed., Chapman and Hall, London (1964).
8. Stary, J., "The Solvent Extraction of Metal Chelates", Pergamon Press, London (1964).
9. Morrison, G.H. and Freiser, H., "Solvent Extraction in Analytical Chemistry", John Wiley, New York (1957).
10. Majumdar, A.K., N-benzoylphenylhydroxylamine and its Analogues", Pergamon Press, London (1971).
11. Bamberger, E., Ber., 52, 1116 (1919).
12. Shome, S.C., Analyst, 75, 27 (1950).
13. Agrawal, Y.K., Russ. Chem. Rev., 48, 948 (1979); cf. Uspekhi Khim., 48, 1773 (1979).

14. Agrawal, Y.K., Revs. Anal. Chem., 5, 3 (1980).

15. Agrawal, Y.K. and Patel, S.A., Revs. Anal. Chem., 4, 237 (1980).

16. Agrawal, Y.K. and Jain, R.K., Revs. Anal. Chem., 6, 49 (1982).

17. Agrawal, Y.K. and Mehd, G.D., Revs. Anal. Chem., 6, 185 (1982).

18. Agrawal, Y.K. and Roshania, R.D., Bull. Soc. Chim., Belgs., 89, 159 (1980).

19. Agrawal, Y.K., "Hydroxamic Acids and their Analytical Applications", Freund Publishing House Ltd., Israel.

20. Ludwig, B. and Exner, O., Angew. Chem. Internat. Edu., 13, 376 (1974).

21. Mizukami, S. and Nagata, K., Coordin. Chem. Rev., 3, 267 (1967).

22. Bhura, D.C., "N-Phenylbenzohydroxamic Acid and Analogues as Analytical Reagent", Technical News Service, S.M. Chemicals, Baroda, 5(1973).

23. Tandon, S.G. and Bhattacharyya, S.C., Anal. Chem., 33, 1267 (1961).

24. Priyadarshini, U. and Tandon, S.G., Chem. & Ind. (London), 931 (1960).

25. Priyadarshini, U. and Tandon, S.G., Anal. Chem., 33, 435 (1961).

26. Ryan, D.E., Marryatt, R.G. and Afghan, B.K., Anal. Chim. Acta, 41, 131 (1968).

27. Shukla, J.P., Agrawal, Y.K. and Bhatt, K., Sep. Sci., 8, 387 (1973).

28. Agrawal, Y.K., Anal. Chem., 47, 940 (1975).

29. Agrawal, Y.K., and Kapoor, H.L., J. Indian Chem. Soc., 52, 826 (1975); 53, 174 (1976).

30. Agrawal, Y.K. and Kapoor, H.L., Ann. Chim., 66, 117 (1976).

31. Agrawal, Y.K., Mudaliar, A., Shashimohan, A.L., Chattopadhyaya, M.C. and Rao, V., J. Indian Chem. Soc., 53, 617 (1976).

32. Agrawal, Y.K., Ann. Chim., 66, 377 (1976); 67, 491 (1977).

33. Agrawal, Y.K., Montain Fur Chem., 108, 713 (1977).

34. Agrawal, Y.K., Z. Anal. Chem., 285, 256 (1977).

35. Agrawal, Y.K., Sci. Cul., 43, 265 (1977).

36. Agrawal, Y.K., Chem. Anal. Z., 22(2), 215 (1977).

37. Agrawal, Y.K., J. Indian Chem.,Soc., 54, 451 (1977).

38. Agrawal, Y.K., J. Inorg. Nucl. Chem., 39, 2011 (1977).

39. Agrawal, Y.K., Ann. Soc. Sci. Brux., 91(IV), 255 (1977).

40. Agrawal, Y.K. and Sharma, T.P., J. Indian Chem. Soc., 54, 771 (1977).

41. Verma, P.C., Khadikar, P.V. and Agrawal, Y.K., Ann. Soc. Sci. Brux., 91(IV), 264 (1977).

42. Agrawal, Y.K. Ann. Soc. Chim. Burx., 92, 287 (1978).

43. Agrawal, Y.K., Anal. Lett., 8, 257 (1975).

44. Patel, S.A. and Agrawal, Y.K., J. Inst. Chemists., 51, 84 (1979).

45. Bhatt, K. and Agrawal, Y.K., Synth. Inorg. Metal Org., Chem., 2, 175 (1972).

46. Agrawal, Y.K., Shashimohan, A.L. and Rao, V., Talanta, 21, 626 (1974).

47. Agrawal, Y.K., Patke, S., Sharma , T.P., Varma, P.C. and Maru, P.C., Z. Anal. Chem., 280, 30 (1976).

48. Agrawal, Y.K. and Khare, V.P., Z. Phys. Chem., 258, 337 (1977).

49. Agrawal, Y.K., J. Indian Chem. Soc., 54, 454 (1977); 55, 180 (1978).

50. Agrawal, Y.K., Anal. Lett., 8, 257 (1975).

51. Roshania, R.D. and Agrawal, Y.K., Microchem. J., 24, 378 (1979).

52. Agrawal, Y.K., Bull. Acad. Pol. Sci., 27, 681 (1979).

53. Raghavan, T.N.V., and Agrawal, Y.K., Bull. Soc. Chim. Belg., 89, 261 (1980).

54. Agrawal, Y.K. and Roshania, R.D., Bull. Soc. Chim. Belg., 89, 159 (1980).

55. Patel, S.A. and Agrawal, Y.K., Microchem. J., 25, 48 (1980).

56. Patke, S.K. and Agrawal, Y.K., Intern. J. Environ. Anal. Chem., 8, 67 (1980).

57. Raghavan, T.N.V. and Agrawal, Y.K., Indian J. Tech., 18(10), 422 (1980).

58. Patke, S.K. and Agrawal, Y.K., Ann. Soc. Sci. Bruxlles., 94, 153 (1980).

59. Agrawal, Y.K. and Patel, S.A., Bull. Soc. Chim. Belg., 88, 1033 (1979).

60. Agrawal, Y.K., Bull. Soc. Chim. Belg., 90, 263 (1981).

61. Agrawal, Y.K. and Roshania, R.D., Bull. Soc. Chim. Belg., 89, 175 (1980).

62. Raghavan, T.N.V. and Agrawal, Y.K., Bull. Soc. Chim. Belg., 89, 89 (1980).

63. Agrawal, Y.K. and Patel, S.A., Bull. Soc. Chim. Belg., 89, 9 (1980).

64. Patke, S.K. and Agrawal, Y.K., Intern. J. Environ. Anal. Chem., 8, 157 (1980).

65. Pilipenko, A.T., Shpak, E.A. and Bakardzhieva, D.I., Ukr. Khim. Zh., 42, 1073 (1976).

66. Bag, S.P. and Khastagir, A.K., Indian J. Chem., 15A, 233 (1977).

67. Majer, J. and Springer, V., Chem. Zvesti., 16, 633 (1962).

68. Jain, R.K. and Agrawal, Y.K., Croat, Chim. Acta, 53, 471 (1980).

69. Rowland, R. and Meloan, C.E., Anal. Chem., 42, 1261 (1970).

70. Priyadarshini, U. and Tandon, S.G., Analyst, 86, 544 (1961).

71. Agrawal, Y.K. and Patke, S.K., Anal. Chem., 8, 157 (1980).

72. Agrawal, Y.K. and Patel, S.A., Rev. Anal. Chem., 4, 237 (1980).

73. Agrawal, Y.K. and Patke, S.K., Intern. J. Environ. Anal. Chem., 10, 175 (1981).

74. Agrawal, Y.K. and Mehd, G.D., Intern. J. Environ. Anal. Chem., 10, 183 (1981).

75. Agrawal, Y.K. and Jain, R.K., Ann. Chim., 601 (1981).

76. Agrawal, Y.K. and Chudasma, S.P., Bull. Soc. Chim. Belg., 90, 1033 (1981).

77. Agrawal, Y.K. and Patel, S.A., Bull. Soc. Chem. Belg., 90, 1039 (1981).

78. Roshania, R.D. and Agrawal, Y.K., Chem. Analz., 76, 191 (1981).

79. Agrawal, Y.K. and Desai, S.J., Patel, M.P. and Merh, S.S., Sci. Cult., 48, 95 (1982).

80. Agrawal, Y.K. and Mehd, G.D., Thermochim. Acta, 55, 113 (1982).

81. Agrawal, Y.K., Dayal, U. and Singbal, K.C., Res. & Indus., 27, 255 (1982).

82. Agrawal, Y.K., J. M.S. Univ. Baroda, 29, 71 (1980).

83. Agrawal, Y.K. and Roshania, R.D., Z. Phys. Chem. (Leipzig), 263, 822 (1982).

84. Agrawal, Y.K., Indian J. Chem., 22, 80 (1983).

85. Agrawal, Y.K. and Raghavan, T.N.V., Indian J. Tech., 20, 498 (1982).

86. Mehd, G.D. and Agrawal, Y.K., J. Indian. Chem. Soc., 60, 686 (1983).

87. Agrawal, Y.K., J. Indian Chem. Soc., 60, 839 (1983).

88. Menon, K.S. and Agrawal, Y.K., Trans. Metal. Chem., 8, 292 (1983).

89. Menon, K.S. and Agrawal, Y.K., Analyst, 109, 27 (1984).

90. Agrawal, Y.K. and Rathi, B.N., Acta Cienciax India, 9, 3 (1983).

91. Agrawal, Y.K. and Kapoor, H.L., J. Indian Chem. Soc., 53, 174 (1976).

92. Agrawal, Y.K. and Kapoor, H.L., Analusis, 5, 62 (1977).

93. Verma, P.C., Khadikar, P.V. and Agrawal, Y.K., Indian J. Chem., 14A, 637 (1976).

94. Agrawal, Y.K., 14A, 1024 (1976).

95. Agrawal, Y.K., Z. Anal. Chem., 285, 258 (1977).

96. Agrawal, Y.K., Talanta, 20, 1353 (1973).

97. Agrawal, Y.K. and Shukla, J.P., J. Indian Chem. Soc., 51, 373 (1974).

98. Bhura, D.C. and Tandon, S.G., Anal. Chim. Acta, 53, 379 (1971).

99. Bhura, D.C. and Tandon, S.G., Indian J. Chem., 8, 466 (1970).

100. Das, H.R. and Shome, S.C., Anal. Chim. Acta, 35, 256 (1966).

101. Nanewar, R.R. and Tandon, U., Talanta, 25, 352 (1978).

102. Mathur, S.P., Thakur, R.S., Bhandari, C.S. and Sogani, N.C., Chem. Ana. (Warsaw), 23, 1029 (1978).

103. Agrawal, S.K. and Gupta, V.K., Indian J. Chem., 16A, 92 (1978).

104. Doadrio, L.A. and De Frutos Martinez, M.I., Anal. Quim., 74, 1470 (1978).

105. Chandravanshi, B.S. and Gupta, V.K., Croat. Chem. Acta, 51, 107 (1978).

106. Pande, R. and Tandon, S.G., Croat. Chem. Acta, 51, 353 (1978).

107. Chandravanshi, B.S. and Gupta, V.K., Fert. Technol., 15, 183 (1978).

108. Abbasi, S.A., Pol. J. Chem., 53, 1929 (1979).

109. Chandravanshi, B.S. and Gupta, V.K., Chem. Anal. (Warsaw) 24, 143 (1979).

110. Agrawal, Y.K. and Patel, S.A., Bull. Soc. Chim. Belgs., 88, 1033 (1979).

111. Chandravanshi, B.S. and Gupta, V.K., J. Indian Chem. Soc., 56, 180 (1979).

112. Agrawal, S.K. and Gupta, V.K., J. Indian Chem. Soc., 56, 419 (1979).

113. Grigoreva, M.F., Slesar, M.I. and Tserkovnitskaya, I.A., Zh. Anal. Khim., 34, 2171 (1979).

114. Yamashiga, T.O. and Shigetoni, Y., Bunseki Kagaku, 29, 537 (1980).

115. Bag, S.P. and Saha, S., J. Indian Chem. Soc., 57, 564 (1980).

116. Bag, S.P. and Saha, S., J. Indian Chem. Soc., 57, 957 (1980).

117. Bag, S.P. and Saha, S., Indian J. Chem., 19A, 355 (1980).

118. Bag, S.P. and Saha, S., Indian J. Chem., 19A, 358 (1980).

119. Bag, S.P., Chatterjee, A.B., Chakrabarti, A.K. and Chakraborti, P.R., Indian J. Chem., 19A, 1200 (1980).

120. Abbasi, S.A., Sep. Sci.Techol., 15, 1679 (1980).

121. Agrawal, D.R. and Tandon, S.G., Croat. Chem. Acta, 54, 115 (1981).

122. Roshania, R.D. and Agrawal, Y.K., Chem. Anal. (Warsaw), 26, 191 (1981).

123. Zaboeva, M.I., Proskuryakova, I.V. and Shvarev, V.S., Zh. Anal. Khim., 36, 2308 (1981).

124. Agrawal, Y.K., Bull. Soc. Chim. Belgs., 89, 261 (1980).

125. Agrawal, Y.K. and Jain, R.K., Anal. di Chim., 601 (1981).

126. Bag, S.P., Chatterjee, A.B., Chakrabarti, A.K. and Chakraborti, P.R., J. Indian Chem. Soc., 59, 1085 (1982).

127. Salinas, F., Capitan-Vallvey, L.F. and Gazquez, D., Microchem. J., 27, 188 (1982).

128. Bag, S.P., Chatterjee, A.B., Chakrabarti, A.K. and Chakraborti, P.R., Talanta, 29, 526 (1982).

129. Bag, S.P. Chatterjee, A.B., Chakrabarti, A.K. and Chakraborti, P.R., J. Indian Chem. Soc., 60, 226 (1983).

130. Bag, S.P., Chatterjee, A.B., Chakrabarti, A.K. and Chakraborti, P.R., J. Indian Chem. Soc., 59, 630 (1982).

131. Assefa, M. and Chandravanshi, B.S., Mikrochim. Acta, 1, 255 (1983).

132. Paul. K.U., Khanna, R. and Gupta, V.K., Am., Ind. Hyg., Assoc. J., 43, 529 (1982).

133. Shukla, J.P., Afinidad, 39, 47 (1982).

134. Agrawal, Y.K. and Mehd, G.D., Int. J. Environ. Anal. Chem., 10, 187 (1981).

135. Koshy, V.C. and Tandon, S.G., Croat. Chem. Acta, 54, 459 (1982).

136. Majumdar, A.K., Chakraburthy, A.K. and Panigrahi, S.K., J. Indian Chem. Soc., 55, 235 (1978).

137. Bakurdzhieva, D. and Panova, A., Metalurgiya (Sofia), 33, 24 (1978).

138. Gholse, S.B. and Kharat, R.B., J. Indian Chem. Soc., 55, 894 (1978).

139. Bag, S.P. and Khestagir, A.K., J. Indian Chem. Soc., 55, 74 (1978).

140. Eremenko, M.V. and Pilipenko, A.T., Zh. Anal. Khim., 33, 1955 (1978).

141. Takur, D.S., Mathur, S.P., Bateja, S. and Bhandari, C.S., Rev. Chim. Bucharest, 30, 191 (1979).

142. Pyatnitskii, I.V. and Nazarenko, A.Yu., Zh. Anal. Khim., 34, 398 (1979).

143. Nenova, P.P., Pilipenko, A.T. and Shpak, E.A., Dokl. Bolg. Akad. Nauk., 32, 473 (1979).

144. Zmievskaya, O.R. and Fadeeva, V.T., Zh. Anal. Khim., 34, 908 (1979).

145. Zmievskaya, O.R., Fadeeva, V.I. and Philipenko, S.V., Zh. Anal. Khim., 35, 909 (1980).

146. Calla, S., Mathur, S.P., Thakur, R.S. and Bhandari, C.S., Afinidad, 38, 53 (1981).

147. Gunawardhana, H.D. and Wikramanyake, D.N., Indian J. Chem., 21A, 88 (1982).

148. Abbasi, S.A. Int. J. Environ. Anal. Chem., 11, 1 (1982).

149. Dasaratha, G.H., Analyst, 108, 952 (1983).

150. Zaboeva, M.I. and Kirzhaikina, N.Ya., Otkrya, Izobret., Prom. Obraztsy, Tovarnya Znaki, 13, 97 (1982); C.A., 97, 103616 (1982).

151. Nivaldo, B., Fresenius, Z. Anal. Chem., 316, 796 (1983).

152. Agrawal, Y.K. and Jain, R.K., Bull. Soc. Chim. Belgs., 90, 437 (1981).

153. Patel, S.A., Ph.D. Thesis, M.S.University of Baroda (1980).

154. Shtokalo, M.I., Ostrovskaya, M.S., Ryzhenko, V.L. and Tolok, V.N., Zh. Anal. Khim., 33, 2383 (1978).

155. Patratii, Yu. V. and Pilipenko, A.T., Ukr. Khim Zh., 44, 752 (1978).

156. Gholse, S.B, and Kharat, R.B., J. Indian Chem. Soc., 55 455 (1978).

157. Gholse, S.B. and Kharat, R.B., J. Inorg. Nucl. Chem., 41, 416 (1979).

158. Pilipenko, A.T., Patratii, Yu.V. and Zulfigarov, O.S., Zh. Anal. Khim., 36, 908 (1981).

159. Agrawal, Y.K. and Patel, S.A., Bull. Soc. Chim. Belgs., 89, 9 (1980).

160. Narkhede, M.R., Sharma, Y. and Shivahare, G.C., Bangladesh J.Sci. Ind. Res., 16, 28 (1981).

161. Agrawal, Y.K. and Patel, S.A., Bull. Soc. Chim. Belgs., 90, 17 (1981).

162. Murti, M.V.R. and Khopkar, S.M., Sci. Cult., 44, 366 (1978).

163. Abbasi, S.A., Sep. Sci. Technol., 15, 1789 (1980).

164. Agrawal, Y.K. and Patel, S.A., Microchem. J., 25, 48 (1980).

165. Jain, R.K. and Agrawal, Y.K., Croat. Chim. Acta, 54, 249 (1981).

166. Abubacker, K.M. and Krishna Prasad, N.S., J. Inorg. Nucl. Chem., 16, 296 (1961).

167. Baroncelli, F. and Grossi, G., 27, 1085 (1965).

168. Barocas, A., Baroncelli, A., Biondi, G.B. and Grossi, G., J. Inorg. Nucl. Chem., 28, 2961 (1966).

169. Halla, J., J. Inorg. Nucl. Chem., 29 187 (1967).

170. Hala, J., J. Inorg. Nucl. Chem., 29, 1777 (1967).

171. Fouche, K.F., Roux Le, H.J. and Philips, F., J. Inorg. Nucl. Chem., 32, 1949 (1970).

172. Gasparini, G.M., Giannini, M. and EL Haggan, A., CNEN-RT/CHI (79) 2 (1979).

173. Agrawal, Y.K. and Tandon, S.G., J. Inorg. Nucl. Chem., 34, 1291 (1972).

174. Agrawal, Y.K. and Tandon, S.G., 36, 869 (1974).

175. Agrawal, Y.K., Khare, V.P., J. Inorg. Nucl. Chem., 38, 1663 (1976).

176. Ryan, D.E. and Lutwick, G.D., Can. J. Chem., 31, (1953).

177. Tandon, S.G. and Bhattacharyya, S.C., J. Chem. Eng. Data, 7, 553 (1962).

178. Bhura, D.C. and Tandon, S.G., J. Chem. Eng. Data, 16, 106 (1971).

179. Priyadarshini, U. and Tandon, S.G., J. Chem. Eng. Data, 12, 143 (1967).

180. Gupta, V.K. and Tandon, S.G., J. Indian, Chem. Soc., 48, 753 (1971).

181. Gupta, V.K. and Tandon, S.G., 17, 248 (1972).

182. Gupta, V.K. and Tandon, S.G., J. Indian Chem. Soc., 46, 831 (1969).

183. Agrawal, Y.K. and Tandon, S.G., J. Chem. Eng. Data, 16, 371 (1971).

184. Agrawal, Y.K. and Tandon, S.G., J. Chem. Eng. Data, 16, 495 (1971).

185. Agrawal, Y.K. and Tandon, S.G., J. Indian Chem. Soc., 48, 397 (1971).

186. Agrawal, Y.K., J. Chem. Eng. Data, 22, 70 (1977).

187. Agrawal, Y.K. and Roshania, R.D., J. Chem. Eng. Data, 23, 258 (1978).

188. Mudaliar, A. and Agrawal, Y.K., J. Chem. Eng. Data, 24, 246 (1979).

189. Jain, R.K. and Agrawal, Y.K., J. Chem. Eng. Data, 24, 250 (1979).

190. Shukla, J.P., Agrawal, Y.K. and Kuchya, K.P., J. Indian Chem. Soc., 51, 437 (1974).

191. Gasparini, G.M. and Polidori, E., J. Chem. Eng. Data, 21, 504 (1976).

192. Gasparini, G.M., Gazz. Chim. Acta, 109, 357 (1979).

193. Gasparini, G.M., Nuclear Processes, CIM Special Volume 21, p. 77.

194. Gasparini, G.M. and Brignocchi, A., CNEN, RT/CHI (78) 4, (1978).

195. Gasparini, G. and Polidori, E., CNEN RT/CHI (73) 5 (1973).