CHAPTER I

INTRODUCTION

The trace metals occur as natural components of the earth's crust and are ever present as constituents of soils, natural waters and living matter. In the past three decades there has been a rapid growth of industries. Hence with the increase in industrialisation, the problem of disposal of waste has also been increasing. There is always a possibility in all the effluents/waste water that several trace elements may be present. The trace elements like Se, Te, As, Sn, Bi, Cd, Hg, Ti, Pb, Zn, Ni, V, Mn etc. have been increasing attention in the present times as toxic pollutants in aquatic ecosystems (1,2). Hence environmental pollution which includes water, air and soil pollution, mainly caused by industrial effluents, has emerged as a major threat to the human beings, animals, marine life, plants, crops etc.. With the rapid industrialisation (pharmaceuticals, pesticides, chemicals and textile industries), obviously, more efficient and economical methods for removal of pollutants from industrial effluents are being devised.

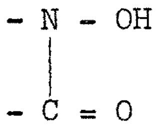
The poisonous trace elements which are having the vital impact on environment (including flora and fauna) caused serious concern to public health authorities. They do not respond to conventional treatment of ultratrace levels. There are no such simple rapid, sensitive, selective methods for detection and determination of these metals except atomic absorption, voltametry, plasma emission technique that have a limited use and many of the laboratories and industries can not afford to have it.

Solvent extraction process, is widely used for separation of metals, nonmetals, organics etc.. This method enjoys a favoured position among separation techniques, because of its speed, simplicity and convenience of operation. The process can be carried out by using a separatory funnel and merely shaking the sample for a few minutes. This method is having advantage that it does not involve co-precipitation which is undesirable feature of separations based on precipitation. This technique finds application in preparation, purification and enrichment on all scales from micro analysis to production processes. The inherent use and simplicity of spectrophotometric methods coupled with the availability of more suitable extraction systems are undoubtedly important for its popularity among many other competative analytical techniques. The work carried out about this subject of extraction and photometric analysis is excellently covered by a number of specialised monographs, review articles and textbooks (3-21).

ORGANIC REAGENTS AS EXTRACTANTS

The use of organic reagents in analysis has made possible many new analytical methods by titrimetric, gravimetric and colorimetric measurements. New type of organic reagents are constantly under investigation for possible analytical and industrial applications. A large number of coordination compounds have been synthesised especially by reacting metal ions with organic ligands. The most considerable applicability of many organic reagents of an analytical importance is mainly based on its ability to form a complex with the metal ions.

Hydroxamic acids with bidentate functional grouping (I), are the versatile reagents for organic and inorganic analysis (22-50).



$$\begin{array}{l} -\mathrm{N}-\mathrm{OH} \\ \;\;\, | \\ -\mathrm{C}=\mathrm{O} \end{array}$$

(I)

These reagents satisfy the basic requirements of complex formation with metal ions, and therefore, form an important family of complexing agents. Hydroxamic acids are the N-aryl derivatives of hydroxylamine (51-53). Structurally the hydroxamic acids can be represented in their two tautometric forms as (II) and (III).

The metal chelate thus produced have formed the basis of diverse analytical application from early times. Due to their non-ionic nature, these metal chelates (or inner complexes) can be often extracted from aqueous solutions or suspensions with water immiscible solvents such as toluene, benzene, chloroform, carbon tetrachloride, higher alcohols or o-dichlorobenzene to form the basis of separation processes involving solvent extraction. If the aqueous solution and their extracts are coloured and stable, these can be used for developing colorimetric methods for the determination of metal ions. Further, the inner complexes are highly insoluble in water, sufficiently stable and have constant composition. They can be used in gravimetric methods. A detailed survey of literature on hydroxamic acids is deliberately avoided because various aspects of their chemistry namely their methods of preparation, properties, molecular arrangements, structures and applications in diverse field have been reviewed (57-61).

Similarly the proton ligand and metal ligand stability constants of hydroxamic acids have recently been reviewed by Agrawal and his coworkers and summarised in well documented review articles (62-63). The physico-chemical properties and analytical aspects of the hydroxamic acids have also been reviewed by Agrawal et al. (64-148) and others (149-179).

TRACE METALS OF THIS STUDY

Trace elements have been classified by Underwood as dietary essential, possible essential and non-essential (180). Some of these non-essential elements enter into the body and produce undesirable effects, therefore, referred as 'Toxic Elements', e.g. Se, Te, As, Sb, Bi, V, Pb, Mn, Cd, Zn, Ti etc. regarding trace element requirements of plants and animal have been performed in large number by withdrawing or adding some of the elements from the diet in an otherwise controlled environment. The effect of growth, survival and level of trace elements in tissues have been studied for such elements (181).

A BRIEF REVIEW ON SPECTROPHOTOMETRIC DETERMINATION OF TRACE METALS

Selenium, tellurium, arsenic, antimony, bismuth, vanadium and titanium are receiving attention for their detection because of their increasing levels in the environment and their impact on human health. A large amount of information is available on the various reagents used in solvent extraction of various metal ions. The work on the solvent extraction and spectrophotometric method of analysis of these metal ions is enormous and still in progress. The spectrophotometric characteristics are the most important and the recent rapid developments in spectrophotometric and separation methods for the elements have become feasible especially for a new organic reagents and their reactions with inorganic ions. However, a survey of progress on the spectrophotometric determination of selenium and tellurium in the past ten years has been carried out and these data are summarised in the Table 1. A detailed review on the spectrophotometric determination of arsenic, antimony, bismuth, vanadium and titanium with hydroxamic acids and other reagents is deliberately avoided since it has already been recently published by Agrawal et al. (182).

THE PRESENT INVESTIGATION

A thorough investigation of literature on hydroxamic acids and their application led to the following considerations.

(1) A new series of the hydroxamic acids could be synthesised having long chain and high molecular weight.

(2) The hydroxamic acids are capable to form very stable complexes.

(3) Development of spectrophotometric methods for the determination of toxic metal ions using hydroxamic acids.

TABLE 1

Spectrophotometric Determination of Trace Metals (Selenium & Tellurium)

Sr. No. 1	Reagents 2	pH/ acidity 3	Solvent 4	λmax nm 5	Beer's Law (ppm) 6	1 $mol^{-1} cm^{-1}$ 7	Interferences/ applications 8	Ref. 9
			Selenium					
1.	(2-Acetyl) Thioacetanilide	0.3-0.7	$CHCl_3$	400	8-30	-	Ag,Pd,Pt,Ce	183
2.	Alizarine maroon + Eosin	6.5-7.2	H_2O	560	0.16-2.0	-	Cyanide	184
3.	Chrompyrazol I	0.5 M (HCl)	-	645	-	63,000	High purity sulphur.	185
4.	4,5-Diaminopyrimidine-2, 6-dithiol	5 M(HCl)	C_2H_5OH + Diethylene Glycol + H_2O	495	0 - 4.5	-	Semiconductors and animal feeds	186
5.	Diethyldithiocarbamate	3.0	$CHCl_3$	760	-	-	Water	187
6.	1,1-Diphenyl hydrazine	10 M(HCl)	$CHCl_3$	530	0.2-12.0	-	Cosmetic dyes	188
7.	Dithizone	6 M(HCl)	CCl_4	620	0.2-1.0	-	-	190
8.	Dithizone	5.5 M (H_2SO_4)	CCl_4	620	0.03-1.0	-	Lead,copper, rocks, ores etc.	189
9.	N-(2-Hydroxypropyl)-O-phenylene diamine	0.1-1 M (HCl)	-	348	-	1,993	-	191
10.	2-Hydroxy thiobenzo-hydrazide	0.5 M (HCl)	$CHCl_3$+ C_2H_5OH (9:1)	360	1.8-6.3	-	-	192

Contd..

Table 1. Contd.

1	2	3	4	5	6	7	8	9
11.	2-Mercaptobenzothiazole	6.5-7.7 M (HCl)	$CHCl_3$	-	-	-	-	193
12.	Methiomeprazine hydrochloride	1.3 M (H_3PO_4)	H_2O	644	0.4-2.0	-	Iodide	194
13.	N-Methyl-O-Phenylene-diamine	3.0	-	346	-	-	-	195
14.	4-Nitro-O-Phenylene diamine	-	Toluene	350	1-10	-	Biological materials	196
				Tellurium				
1.	Ammonium pyrrolidine-1-carbodithioate	8.0	$CHCl_3$	257	-	81,200	-	197
2.	1-Benzyl-2-mercapto-8-methoxy benzimidazole	7-8,1 M (H_2SO_4) in NaB	C_6H_6	440	1-5	29,450	Se	198
3.	Bismuthiol II	-	CCl_4	330	-	-	Sulphur	199
4.	Bismuthiol II	3 M (HCl)	$CHCl_3$	330	-	-	-	200
5.	Bromopyrogallol Red	4.0	Isobutyl alcohol	545	0.1-2.0	57,000	IV,V,VI group elements	201
6.	Butylrhodamine	9.2 M (H_2SO_4)	C_6H_6	557	1.0-2.0	-	Cu,Zn,Ores	202

Contd..

Table 1. Contd.

1	2	3	4	5	6	7	8	9
7.	Tanus green	1.4 N (HBr)	C_6H_6 + Acetone (1:2)	-	-	12,100	-	203
8.	2-Mercaptobenzimidazole	9 M (H_2SO_4)	H_2O	320	-	32,300	Ag,Hg,Ca,Se	204
9.	Naphthyl-bismuthiol	5.4	$CHCl_3$	360	0.02-0.2	-	Rocks and ores	205
10.	Pyrrolidine-1-carbodithioic acid	0.95	H_2O	310	-	-	Fe,Co,Ni, Cd,Cu	206
11.	Rhodamine 6 G	5 M (H_2SO_4)	C_2H_5OH	535	0.02-0.5	1,70,000	Hg,Sb,Pt, Pd,Sn,steels, effluents.	207
12.	Thiourea	($HClO_4$)	Isobutyl methyl ketone	322	0-60	-	-	208
13.	Trioctylamine	2 M (HBr)	C_6H_6	452	-	4,300	-	209
14.	Victoria blue UR (C.I.Basic Blue 8)	9-10 N	C_6H_6	602	0-9	80,000	Hg,semiconductors, alloys	210

The present thesis describes mainly in following three parts :

Part I	Synthesis and physico-chemical properties of N-arylhydroxamic acids
Part II	Extraction and spectrophotometric determination of trace elements
Part III	Trace determination of metals in high purity grade metals, alloys, pharmaceuticals and in the environment.

The synthesis and properties of nine new N-arylhydroxamic acids derived from substituted α-phenylcinnamic acids are described. The syntheses are made by reacting N-arylhydroxylamine with acid chlorides at low temperature in diethyl ether containing aqueous suspensions of sodium bicarbonate.

These acids are characterized by elemental analysis, melting point, ultraviolet, infrared, nuclear magnetic resonance and mass spectra.

The thermal analysis (DTA, TG) and non-aqueous titrations are also performed.

The thermodynamic ionization constants of hydroxamic acids have been determined in different mole fractions of dioxan (0.174-0.33) at 25 and 35±0.1°C. The pK_a varies linearly with the mole fraction of dioxan and the linear relationship have been obtained using the method of least square. The relevant correlation coefficients have also been calculated. The thermodynamic parameters, $\Delta G°$, $\Delta H°$ and $\Delta S°$ are calculated. The effect of substituent on ionization of hydroxamic acids is discussed.

Solvent extraction spectrophotometric and atomic absorption spectrophotometric methods for the determination of selenium(IV) in microgram quantities are described. The selenium(IV) forms yellow coloured complex with N-phenylbenzohydroxamic acid (PBHA) extractable into chloroform from 7 M $HClO_4$. Se-PBHA complex has maximum absorbance at 345 nm with a molar absorptivity 1.5×10^5 l mol^{-1} cm^{-1} and Sandell's sensitivity 0.000526 $\mu g/cm^2$. Effect of molarity, reagent concentration, diverse ions on the extraction of selenium complex were studied. The selenium is determined in presence of tellurium.

Solvent extraction, spectrophotometric and atomic absorption spectrophotometric determination of tellurium(IV) in nanogram levels are described. The tellurium(IV) forms yellow coloured complex with N-phenylbenzohydroxamic acid (PBHA) which is extractable into chloroform from 7 M $HClO_4$.

Te-PBHA complex has a maximum absorbance at 345 nm with the molar absorptivity 3.5×10^4 l $mol^{-1}cm^{-1}$ and Sandell's sensitivity 0.00365 µg/cm^2. The tellurium(IV) is also determined in the range of 0.01-0.08 ppm by flameless atomic absorption spectrophotometry using GBC HG 900 vapor generation accessary. Effect of molarity, reagent concentrations, diverse ions on the extraction of tellurium complex were studied. The tellurium was determined in presence of selenium and also in standard sample.

The solvent extraction and spectrophotometric method for the determination of arsenic(III) is described. Arsenic forms a yellow coloured complex with N-p-tolyl-α-phenyl-p-methoxy-cinnamohydroxamic acid (PTPMCHA) at pH 4.5 - 5.2 which can be extracted into chloroform. The molar absorptivity of As-PTPMCHA is 1.3×10^4 l $mol^{-1}cm^{-1}$ at 410 nm. Many common ions associated with arsenic do not interfere. The effect of pH, reagent concentration and solvent is described. The arsenic is determined in standard samples.

The solvent extraction and spectrophotometric determination of antimony(III) in the sub-ppm quantities with N-p-tolyl-α-phenyl-p-methoxy-cinnamohydroxamic acid (PTPMCHA) is described. The antimony forms a colourless complex with PTPMCHA at 1.0 M HCl extractable into chloroform. Phenyl fluorone is added into the Sb-PTPMCHA extract which forms a reddish yellow coloured mixed-ligand complex having a maximum absorbance at 505 nm and molar absorptivity 1.0×10^4 l $mol^{-1} cm^{-1}$. The photometric sensitivity of the colour reaction is 0.0122 µg of antimony per cm^2. The effect of diverse ions and several experimental parameters have been studied. The composition of the antimony : PTPMCHA : phenylfluorone is 1:1:2. The antimony is also estimated by atomic absorption spectrophotometry.

A sensitive and selective method for extraction spectrophotometric and atomic absorption spectrophotometric determination of bismuth(III) utilising N-p-tolyl-α-phenyl-p-methoxy cinnamohydroxamic acid (PTPMCHA) as an extractant is reported. It forms a colourless complex, extractable at pH 5.0 into chloroform. The sensitivity of the method is enhanced by the addition of phenyl fluorone in the Bi-PTPMCHA extract, which gives the red colour complex having maximum absorbance at 550 nm and molar absorptivity 3.1×10^4 l $mol^{-1} cm^{-1}$. Beer's law obeyed in the range of 0.33-10.00 ppm of Bi(III).

The present method has been applied for the determination of bismuth in standard metals and alloys. These results were compared with atomic absorption spectrophotometric data.

Extraction and spectrophotometric method for the determination of titanium(IV) is described. The titanium(IV) is extracted with α-phenyl-substituted hydroxamic acid into chloroform from strongly acidic solutions. The α-phenyl-p-methoxy cinnamohydroxamic acid (PTPMCHA) is the most sensitive reagent amongst the synthesised hydroxamic acids which forms the yellow Ti-PTPMCHA complex having maximum absorbance at 375 nm with molar absorptivity 1.9 x 10^4 l $mol^{-1}cm^{-1}$. Various parameters for the optimum extraction conditions and the effect of thiocyanate to increase the sensitivity have been discussed.

Nine newly synthesised substituted α-phenyl cinnamohydroxamic acids have been reported for the extraction and spectrophotometric determination of vanadium(V) in trace amount. The N-p-tolyl-α-phenyl-p-methoxycinnamohydroxamic acid (PTPMCHA) is found the most sensitive reagent amongst the substituted hydroxamic acids. The vanadium(V) is extracted with PTPMCHA from 2-5 M HCl. The bluish violet extract has a maximum absorbance at 550 nm and molar absorptivity 6.4 x 10^3 l $mol^{-1}cm^{-1}$. The various parameters viz. effect of acidity, reagent concentration, diverse ions and stoichiometry of the complex have been discussed. A comparison has been made with atomic absorption spectrophotometric method.

The solvent extraction and spectrophotometric methods, developed in PART II are applied for the trace determination of selenium, tellurium, arsenic, antimony, bismuth, titanium and vanadium in high purity grade metals, alloys, pharmaceuticals and in the environment samples viz. standard samples, blood serum, urine, soil, plant, water, industrial effluents and waste water samples collected from different areas of Baroda district. These results are also compared with those determined by atomic absorption spectrophotometry.

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