CHAPTER I

INTRODUCTION
Environmental pollution has become a serious threat to plants, animals and human beings. Deterioration of the environment started early in the stage when man first collected in villages and utilized fire\(^1\). With the increase in civilization, an industrial revolution started up. Industrialization has provided humanity with many material and social problems. One of these is pollution of the environment. Pollution is actually a by-product of industrialization. Most scientists recognize pollution as a serious threat to the quality of our life and possibly to its very existence.\(^2\) Pollution results only from alterations - by excess, by default, by disappearance or poisoning of an element of the milieu.\(^3\)

Human activity has polluted the air and water with biologically harmful substances. There are a number of chemicals in the environment and industrial technology introduces thousands more every day.\(^4\) These contaminants enter the air in the form of vapours, fumes and dust particles. The soluble chemicals pollute the water resources like rivers and streams. Domestic use of fuel as wood, coal, oil, etc. results in impairment of the natural quality of the air. Exposure to toxic chemicals in urban centres is mainly due to industries and motor vehicles.\(^6\) Automobile exhausts contain toxic organic chemicals like aldehydes, organo-lead compounds and gases
like carbon monoxide and carbon dioxide which are highly toxic to animals and man.

Contamination of water and soil results due to use of various kinds of fertilizers, insecticides, pesticides, etc. The major source of pollution are industries such as textile, rubber, plastic, ceramic, fertilizer, cement, steel, dye and pigment making industries, food processing plants, etc. which release a heavy load of chemicals in the environment. The chemicals released are heavy metals, their soluble and insoluble salts, organo-metallic compounds, organic compounds, dust, fumes and vapours of volatile compounds and waste gases. The load of these chemicals on the environment increases everyday and has crossed the limit of self-purification by natural processes.

The various types of pollution, i.e., air, water, radio-active pollution, noise pollution are described as -

1) Air pollution: Air pollution occurs when one or several air pollutants are present in such amounts, for such a long period in the outside air that they are harmful to human, plants or property, contribute to damage or may impair the well-being or use of property to a measurable degree.

2) Water pollution: Water pollution is defined as 'a state of deviation from pure condition whereby its normal function and properties are affected or the impairment
of quality of natural water interfering with its proper and beneficial uses. 9

3) **Radioactive pollution**: The splitting of the atom has been one of the major technological development of the last few decades. There are numerous beneficial effects of nuclear energy and radioactive materials but along with this, the exposure to these substances results in ill-health. Ionizing radiations damage and destroy human, plant and animal tissues. Excessive exposure may lead to permanent disability or death. 10, 11

4) **Noise pollution**: With the increase in industrialization, noise producing equipments have increased. Any sound which is not required is termed noise. Noise is any sound which causes a significant hearing impairment. Noise pollution results in both temporary as well as permanent damage to hearing. Stress causing noise may contribute to ulcers and heart disease. 12

**Hazards and need for analysis** — A number of toxic substances enter the environment due to various human activities. These contaminants enter the human, plant and animal systems through air, water and food. Heavy metals are the most important toxicants to plants, 13, 14 animals 15 and man. 5, 16 Their toxicity is due to their strong attraction towards biological tissues and slow elimination of those from the biological systems. Chemical persistence of heavy metals produces undesirable
effects. These metals are environmentally stable and as long as the chemicals are present, they may induce their toxic effect.\textsuperscript{17} The metals are harmful as they are capable of reacting with binding sites of the biological tissues and their action results in "protein precipitation".\textsuperscript{17} The reaction with binding sites results in the formation of metal complexes with sulfhydryl groups, amino, phosphate, carboxylate, hydroxyl radicals of enzymes and biological proteins.\textsuperscript{17}

Many trace metals like mercury, lead, selenium, chromium, cadmium, etc. when present in water, greatly affect the aquatic life.\textsuperscript{5} Algae play a critical role in the structure and functioning of the aquatic environment and heavy metals often inhibit the growth of algae,\textsuperscript{13} thus causing an imbalance in the aquatic environment.

Organic chemicals like pesticides, insecticides,\textsuperscript{18} amines, hydrozine, aldehydes, ketones, benzene, naphthalene, phenol, organo-mercury and organo-lead compounds, etc. are also toxic.\textsuperscript{19} These chemicals bear carcinogenic properties. Pesticides cause acute toxicity to prawns, fishes and other aquatic animals as well as to human beings.

The toxic effects and accumulation of chemicals in plant, animal and human body shows the increased need for sophisticated methods for evaluation of the quality and quantity of toxicants, in various environmental parameters. The analysis of pollutants is highly essential
in order to characterize them for clinical diagnosis, treatment of their effects and to point towards a permanent solution. Pollutants are present in air, water, soil, food, plant and animal tissues and thus the study of environmental chemistry is incomplete without accurate, sensitive and specific methods for the detection and determination of toxic substances in these samples. Impurities can be detected by simple tests but chemical analysis is needed in order to allow rapid, reliable and specific identification and determination of impurities, even in extremely low concentrations.

Techniques used for pollution studies -

With increasing problem of environmental pollution, various instrumental techniques have been developed for the determination of toxic substances in different samples. Colorimeter and pH-meter are being used since a very long time. Recently, various other instrumental techniques like UV, 24-26 IR, 24-26 flame photometry, 27,28 atomic absorption spectrophotometry, 29-34 gas chromatography, 35,36 HPLC, 37,38 TLC,39,40 polarography, 41,42 etc. have been developed for the detection and determination of pollutants in air, water, soil and biological tissues.

The optical methods, i.e., UV, IR, AAS, flame photometry, emission spectrophotometry are based on any of the three principles - 1) ability of a material or solution to absorb radiation energy, 2) to emit radiation
when excited by an energy source or 3) to disperse or to scatter radiation.\textsuperscript{43}

Electrical methods are also used for the determination of various pollutants. The techniques frequently used are potentiometry, polarography, conductometry and coulometry.\textsuperscript{43} These methods make use of the relationship between electrical and chemical phenomena. Other techniques include gas chromatography, high pressure liquid chromatography, thin layer chromatography, mass spectrometry, ICP, etc.

Colorimetric technique has been used in the present investigation. The technique is simple and economic. The results obtained by colorimetric technique are sensitive and highly reproducible. The time required for analysis is also less.

Present investigation -

In the present investigation 26 hydroxyamidines and 10 amidines have been used for the preconcentration and spectrophotometric determination of bismuth, antimony, chromium and phenylhydrazine. Amidines and hydroxyamidines have been recently introduced as analytical reagents for gravimetric and colorimetric determination of various metal ions, e.g., nickel,\textsuperscript{44} copper,\textsuperscript{45} iron,\textsuperscript{46,47} vanadium,\textsuperscript{48,49} molybdenum,\textsuperscript{50} niobium,\textsuperscript{51} manganese,\textsuperscript{52} gold,\textsuperscript{53} etc. Metal ions form coloured products with these
reagents at different experimental conditions thus giving a high, selective method for their determination.

The advantage of the reagents is that they have reactive groups - C = N - in amidine and - C = N - in hydroxyamidine which is capable of forming a five-membered ring by chelation with metal ions. The reagents form binary as well as ternary complexes with metal ions. The advantages of ternary complexes are that the degree of extraction of the metal, the specificity and the sensitivity of the reaction is enhanced. In some cases the analysis of the metal is also prevented.

The other advantages of these reagents are - they are stable towards light and heat. They are soluble in various organic solvents and their solutions are stable for a long time. The synthesis of the reagents is simple and economic. The synthesis is carried out in the laboratory by condensation of N-arylbenzimidoyl chloride with N-arylamine for amidine and N-arylhydroxyamidine for hydroxyamidine in absolute ether medium, as described in the literature. The preparation can be shown as -

I. Imidoyl chloride - Chlorination of amide is carried out as given by which except that PCl₅ is replaced by thionyl chloride as the yield obtained is higher and excess thionyl chloride gets converted into products which are easily removable by distillation.
The metals and organic compounds taken for analytical study in the present investigation are - bismuth(III), antimony(III), chromium(VI), aniline and phenylhydrazine. The toxic effects of these substances are described below:

**Bismuth** - Bismuth occurs in the earth's crust in very low concentrations. It is obtained as a by-product during the extraction of tin, lead and copper from their ores. Also,
The metal enters the environment through weathering processes and combustion of fossil fuels.\textsuperscript{63} The metal and its compounds are moderately toxic to plants.\textsuperscript{64} Both the trivalent and pentavalent forms of the metal are toxic to animals and man.\textsuperscript{65,66} Systemic toxicity is not observed by dermal application of the metal compounds but it gets absorbed in the skin by combining with the fatty acid radical of the sebum.\textsuperscript{67} The exposure results in exodermatitis and ulcerative stomatitis. Ingestion of the metal and its compounds results in kidney damage, diarrhoea, albuminuria\textsuperscript{65,66}, etc. Ingestion in large quantities is fatal. Symptoms of chronic bismuth toxicity in man are weakness, rheumatic pain, fever, diarrhoea, metal line on gums, foul breath, gingivitis,\textsuperscript{65,66} etc.

The metal enters the environment through its use in various industries. It is used in the manufacture of alloy, heat sensitive devices, low melting solders, silvering mirrors, etc. Salts of bismuth, e.g. bismuth telluride is used as a semiconductor\textsuperscript{69,69,73}. The source of direct entry of the metal into the human system is its use in drugs.\textsuperscript{71} Organic bismuth compounds like bismuth glucolarsenilate, bismuth sodium thiglycollate, etc. are used for treatment of intestinal amoebiasis, schilulis and skin diseases.\textsuperscript{72-74} In ointment bismuth salts like bismuth subcarbonate and bismuth subnitrate are used for treatment of gastric disturbances.\textsuperscript{77}
Antimony - Antimony along with its compounds is a serious health hazard. The metal is found as a contaminant in air and water. It is found in the earth's crust at very low levels. The metal enters the environment through its use in various industries. It is used in the preparation of metallic products like lead alloys, storage battery grids, type alloys, bearing alloys pewter and armaments. Other sources of entry of the metal in waste water are its use in preparing flameproof textiles, paints, lacquers, rubber compounds, ceramics, enamels, glass, pottery, phosphors and matches.

The metal enters the air in the form of dust and fumes due to mining operations like crushing and roasting of ores. Direct entry of the metal in the human system is through food contamination due to use of rubber, solders and tin foils for packaging. Also, antimony leaches into the food from cheap enamelled vessels.

Antimony and its organic compounds have wide therapeutic use. Pentavalent antimony compounds like urra stibamine, sodium antimonyl gluconate and ethyl stibamine, are used as drugs for treatment of visceral leishmaniasis. Trivalent compounds are used as expectorants, for emetic activity. Antimonyl potassium tartrate is given intravenously for treatment of resistant cases of yersiosis fungoides.
both the trivalent and pentavalent forms of the metal are toxic to plants, animals and man but trivalent compounds are considered more toxic. Direct contact of antimony with the skin results in dermatitis and popular skin eruptions. Antimony is said to penetrate the skin by combining with the fatty acid radical of the sebum.

Acute poisoning results by ingestion of antimonics and the poisoning is fatal in few hours. Chronic poisoning results in headache, sleeplessness, vertigo loss of appetite and muscular pain. Other symptoms of poisoning are vomiting, diarrhoea, lowered temperature, irregular respiration, pulmonary edema, jaundice, fatty degeneration, etc. Antimony poisoning has direct cardiac effect resulting in auricular fibrillation.

CHROMIUM — Chromium exists in two stable oxidation states, Cr(III) and Cr(VI). Trivalent chromium is considered to be non-toxic whereas hexavalent chromium is toxic to plants, animals and human beings. It is frequently found as a contaminant in air, water and soil. The sources of discharge of the metal into the environment are — through weathering of natural rocks, etc. and from various industries. Industrial wastes are the major source of chromium pollution. Chromium and its compounds are used in the manufacture of paints, pigments,
dyes, etc. for use in rubber, plastic, ceramic and other industries. Chromium is also used as a mordant in textile industries.

A large amount of the metal goes into the environment through waste water from industries preparing steels and alloys with nickel, molybdenum, vanadium, cobalt, niobium, etc. The metal also finds its way into the environment through chrome-plating plants, tannery operations, leather industries, welding process and smelter works. Welding operations release the metal in the air in the form of dust and minute particles. Cooling waters are another important source of chromium pollution. Trivalent chromium is believed to be non-toxic though some authors have mentioned that it causes eczematous dermatitis. It has been also reported that Cr(III) is an essential element for the body as it is involved in carbohydrate and fat metabolism and is necessary for the maintenance of a normal glucose tolerance factor.

Exposure to chromium(VI) and its compounds results in irritation of skin, which results in dermatitis and ulcer formation. Hexavalent chromium and its salts are carcinogenic causing cancer of lungs, nasal cavity, paranasal sinus, stomach and larynx. Chromates also cause severe kidney damage and intestinal inflammation. Chromium(VI) compounds have an ability to enter the cells and reach the genetic target. All
chromates except lead chromate therefore, act as cytotoxic and genotoxic substances\textsuperscript{82, 95}. Hexavalent chromium is also said to interfere in the enzymatic sulphur uptake of the cells. Traces of chromium in sea-water has an influence on the aquatic animal and plant life.

**ANILINE** - Aniline and its homologs have wide use in a number of chemical industries. The chemical has two most important uses (i) in preparation of aniline dyes\textsuperscript{66, 67, 84} and (ii) in manufacture of rubber chemicals like vulcanization accelerators and antioxidants\textsuperscript{84}.

Aniline gets distributed into the environment as a contaminant through other industries like textile, paper and metallurgical industry. Preparation of surfactants and photographic chemicals also need aniline\textsuperscript{84}. These industries liberate aniline and its derivatives in the vapour phase as well as liquid through waste water. It is also used in pharmaceutical industries for the preparation of sulphur drugs. Animal feed industries use aniline in the production of arsanilic acid\textsuperscript{84}.

Aniline and its homologs are highly toxic chemicals\textsuperscript{19, 77, 97}. Both the vapours and liquid are toxic to algae, bacteria\textsuperscript{19}, man and animals. Cell multiplication is inhibited in algae and bacteria. In case of animals and man, direct skin contact results in irritation and burns\textsuperscript{66, 77}. Aniline gets absorbed in the skin very easily\textsuperscript{67}. Volatile amines affect the mucous membrane
and eyes, causing eye irritation, conjunctivitis, lacrimation, corneal edema, etc.\textsuperscript{66,77,98}

Exposure to high concentrations of aniline causes respiratory tract sensitization, tracheitis, bronchitis, pneumonitis, lung irritation, pulmonary edema, cough and asthmatic symptoms\textsuperscript{77,99}.

An important action of aniline is the formation of methemoglobin, resulting in aboxemia, methemoglobinemia, and depression in C\&E\textsuperscript{66,75}. Acute exposure results in jaundice, urinary bladder infection\textsuperscript{100}, papillomatous growth of bladder which becomes malignant, carcinoma of bladder, fall in B.P. and cardiac arrhythmia\textsuperscript{66,67}. Aniline is an important carcinogen.

\textbf{PHENYLHYDRAZINE} – Phenylhydrazine is an important toxic chemical\textsuperscript{67}. It enters the environment through waste products of industries preparing drugs like isonicotinic acid hydrazide, herbicides and rubber additives. It is used as an intermediate in various drug and dye industries\textsuperscript{69}.

The chemical is toxic to man and animals\textsuperscript{101}. Toxicity is observed at low concentrations of 5 ppm\textsuperscript{67}. Direct contact with the skin results in skin sensitization and contact dermatitis\textsuperscript{19,77}. Phenylhydrazine is a carcinogen causing lung cancer\textsuperscript{69}. The symptoms of toxicity are kidney injury, alteration in liver function,
cellular damage and jaundice\textsuperscript{102,103}. Oral administration causes central nervous system effects in children\textsuperscript{66}.

Acute poisoning effects of these toxic substances show the need of methods for their detection and determination in various environmental samples. Review of earlier work shows that a number of methods have been reported for the detection and determination of bismuth(III), antimony(III), chromium(VI), aniline and phenylhydrazine.

In the present investigation Chapter II describes the extraction and spectrophotometric determination of bismuth(III) with iodide and hydroxyamidine. The effect of acid, solvents, reagent, temperature, standing time, dilution, diverse ions, etc. is studied. The method has been applied for the determination of the metal content in geological and environmental samples.

Chapter III describes the extraction-spectrophotometric determination of antimony(III) with iodide and amidine. The metal is extracted from sulphuric acid medium. The effect of variables such as solvent, acid, temperature, dilution, etc. on the extraction of the complex has been studied. The tolerance limit of various diverse ions has been also determined. The method is simple, sensitive and reproducible. It has been applied for the determination of the metal in industrial waste water and coal-ash.
Chapter IV. describes the extraction and spectrophotometric determination of Chromium(VI) with hydroxyamidine. The effect of variables on the extraction of the metal has been carried out. The effect of experimental conditions e.g., temperature, dilution, standing time, extraction period, etc. has also been carried out. The method is applied for the determination of chromium content in industrial waste water.

A new method for the determination of aniline with 1,2-naphthaquinone-4-sulphonic acid is described in Chapter IV. The method is applied for the determination of aniline content in water. The method is simple, sensitive and reproducible.

Chapter V describes a new method for detection of traces of phenylhydrazine in industrial waste water. The detection is carried out using molybdenum-thiocyanate complex in hydrochloric acid medium. The method is simple, sensitive and highly selective.
REFERENCES


58. O. Wallach; Ber., 9, 1212 (1876).
59. O. Wallach and R. Hoffmann; Ann., 184, 75 (1877).
60. O. Wallach; Ann., 184, 1 (1877).
61. O. Wallach; Ann., 214, 193, 226 (1882).
64. Ref. 17, p. 32, 41.
67. Ref. 1, p. 162, 468, 144-146.

77. Frank A. Patty, "Industrial Hygiene and Toxicology", Vol. II, Interscience Publ., p. 993, 144, 2043, 2050, 2099 and references therein.


81. Environmental Pollutants - Selected Analytical Methods (Scope 6), Butterworth London, p. 112.


95. R. Schoental; Br. J. Cancer, 32, 403 (1975).


