CHAPTER I

INTRODUCTION

Environmental pollution and chemical process control are vitally concerned with impurities at trace and ultratrace levels in aquatic environment. The increase concern over the last decade with heavy metal pollution of natural waters and sediments is interesting phenomenon (1-4). Most of the heavy metals fraction carried to the ocean by river discharge is retained in the estuarics/costal zone. A wealth of information is available on the distribution of heavy metals in the terrestrial environment (5-10). Many industrialized areas are characterized by a high degree of metal pollution and increase in recent decades of deposition rate has been demonstrated on a regional scale. Thus there is a continuous demand for the development of the selective, sensitive and rapid methods for the detection, determination and control of heavy metals.
HEAVY METALS

The term heavy metal has found its way into standard texts (11-13) although no definition is rendered. Even no explanation is provided by the editors of the 'Symposium Proceedings of the First International Conference of Heavy Metals in the Environment'. (14).

'Heavy metals' are more rigorously defined in a few dictionaries of technical terms. Lapedes (15) includes those metals where specific gravity is approximately 5 or higher, while Anon (16) adopted the view of metals of Burrell (17) who designated the rectangular block of elements in the periodic table flanked by Ti, Hf, As and Bi and its corners as the 'heavy metals'. According to this interpretation, the 'heavy metals' characteristically have specific gravities ranging from 4.5 (Ti) to 22.5 (Os).

Recently Nieboer et al (18) proposed that the term 'heavy metals' be abandoned in favour of a classification which separates metal ions into class A (oxygen-seeking), class B (nitrogen/sulphur seeking) and borderline (or intermediate). This classification is related to atomic properties and solution chemistry of metal ions. A survey of the numerous papers on the analytical, biological,
ecological and health aspects of heavy metal pollution adds that the Pb, Cd, As, Bi, Sb, Ti and Mo are in the list (1-24).

TRACE HEAVY METALS

The term 'Trace Heavy Metals' arise from the limitation of early analytical methods. They were the elements that were present in tissues in such small amounts that they could not be measured accurately, and hence their levels were reported as "Trace". The term includes all these elements required by animals in amounts no greater than the amount of iron required. Thus 'Trace Heavy Metals' are those inorganic nutrients that are required in 'small' or 'trace' amounts, a few microgram to a few milligrams per day for man or per kilogram of diet for an experimental animal. However, metals viz. lead, cadmium, arsenic etc. regarded as toxic trace metals (17-27).

TRACE HEAVY METAL IN THE ENVIRONMENT

Metallic elements are an intrinsic component of the environment, their presence is considered unique in the sense that it is difficult to rid completely the environment of a metal with which it has been contaminated.
Erosion of surface deposits of minerals, forest fires and volcanic activity are some of the natural causes of environmental pollution with the toxic metals. The processes involved in the extraction of metals from tin ores and their extensive use resulting from improved technology are also responsible for their dispersion in the biosphere. With the increasing use of a wide variety of metals in industry and in our daily life, problems arising from toxic metal pollution of the environment have assumed serious dimensions.

A distinction between environmental contamination and pollution has been shown by Bowern (28), contamination is the release of the metal into the environment at measurable concentrations, while pollution implies the manifestations of measurable effects produced by metals on the living systems. Toxic metals, to a large extent, are dispersed in the biosphere through industrial effluents, organic wastes, refuse burning, transport and power generation. Industrial smoke containing arsenic, antimony, copper, nickel etc. is a potential source of contamination of air. The exhausts of motor vehicles using petrol to which tetraethyl lead has been added is a potential source of atmospheric pollution. Metal
containing industrial effluents constitute a major source of metallic pollution of the hydrosphere.

The event of contamination is conditional upon the amount or concentration of a substance. The mere presence of a certain amount of a metal species does not constitute a threat. Iron and copper are required in various respiratory pigments and in oxidative enzyme systems required in metabolism. Cobalt requirement for vitamin B\textsubscript{12} synthesis and zinc requirement for carbonic anhydrase and dehydrogenases may vary with the organism. Higher plants which may ultimately be consumed by both animals and humans require aluminium, boron and vanadium. Molybdenum is necessary in all organisms which derive nitrogen from inorganic sources. Many other metals are commonly found in small quantities, but no known biological function has been established for them. Other metals viz. antimony, arsenic, barium, beryllium, bismuth, cadmium, mercury, lead, silver, tellurium and thorium have no known nutritive value and are commonly considered as toxicants (28, 29).

**LEAD**

For years lead has been recognized as a health hazard to man and animals. Lead occurs naturally and is distributed
widely at varying levels in soils, plants and animal tissues (30-34). The common sources of lead in the environment are lead-base pigments in paints, lead-containing pesticides, discarded wet cell batteries, shooting ranges or waterfowl hunting sites, putty, plumbing installations or repair sites, manufacturing fillers, untaxed whiskey, liniments and lotions, water pipes, auto exhausts, used motor oil (24). Other sources of lead have been vegetation contamination resulting from highway traffic or close proximity to a smelter (24,35-38). Lead recycling plants are also a constant source of environmental lead.

The environmental contamination from lead to date is not known to have caused any teratogenic effects. However, the treatment of chick embryos with lead salt has shown to produce a toxic effect on the morphogenesis of the lead primordium, hydrocephalus and anterior meningoceles (39-41). The addition of 25 ppm of lead to the drinking water of breeding can cause early deaths of the offspring (42). Lead levels in the fetal blood and amniotic fluid were found to be 55% of that of the maternal blood in a goat infused for 2 hr with lead chloride (43). Monitoring for excessive levels of lead in edible animal tissue remains essential since low levels in the diet of
children and animals are thought to produce neurological changes (31). It is interesting to note that lead is found in all tissues of cattle at ranges from 0.01 to 2.96 ppm in the muscle, 0.01 to 3.74 ppm in liver and 0.01 to 4.90 ppm in the kidney (44).

Cadmium

Cadmium concentrations in ambient air and water are generally low (1 ng/m$^3$-50 ng/m$^3$) (45) but play a role for the daily intake of the cadmium under special circumstances. Cadmium occurs naturally in all food-stuffs but polluted soil or water may cause increased concentrations. Concentrations are generally low, on the order of a few /μg/kg, in some basic food stuffs like milk, potatoes, fruits, and meat, whereas in rice and wheat and some other grains, they may be 50 to 100 /μg/g, even in polluted areas (45-55). Cadmium concentrations in tobacco are relatively high, varying between 1 and 2 /μg/g tobacco (45). Data on cadmium in soils near the sources of emission, such as smelters and metallurgical plants, indicate high concentrations of cadmium fallout. Sewage sludge and phosphate fertilizers also contain notable amounts of cadmium (56).
Several recent publications have reviewed extensively the toxic manifestations induced by cadmium in man (45, 57, 58). In human being the main target organs are the gastrointestinal tract and the lung after acute exposure by the oral or the pulmonary route and the kidney, the lungs, the bones, the hematopoietic system after chronic exposure.

Arsenic

Inorganic arsenical compounds are used widely as rat poisons and in insecticides, paints, and dyes (31, 59). Organic arsenical compounds are used in poultry and swine feeds as growth promotants and are also employed therapeutically in swine (30).

Poisonings from various arsenical compounds are frequent and, when detected, cause considerable regulatory difficulty. However, excessive use of organic arsenicals in animal feeds and improper observation of the approved withdrawal period consistently create great regulatory problems in poultry and swine (60).

The approved regulatory method of analysis for both the organic and inorganic forms in the dry ash atomic absorption method, which detects the elemental arsenic. A
tolerance has been established by both the FDA and the EPA for poultry and swine (61,62). The tolerance for arsenic in chickens and turkeys is 0.5 ppm in uncooked muscle and 2.0 ppm in cooked edible by-products. The tolerance for edible tissue in swine is 2.0 ppm in liver and kidney and 0.5 ppm in uncooked muscle tissue and by-products other than liver and kidney.

Antimony

Antimony occurs in the earth's crust at less than 1 ppm. The important uses of this metal are with lead alloys, in storage of battery grids and in type alloys, pewter, bearing alloys, rubber, matches, ceramics, enamels, paints, lacquers and textiles.

Antimony is a common pollutant in urban air, occurring at an average concentration of 0.001 μg/m³ and maximum 0.160 μg/m³ (63). Antimony may be present in food, resulting from the use of rubber, solders and tinfoil for packaging. Leaching of antimony from cheap enameled vessels has caused some food contamination. Tarter emetic (antimony potassium tartrate) has been used as an insecticide.
Acute poisoning has resulted from accidental or suicidal ingestion of antimonials. The symptoms are similar to those of arsenical poisoning and consist of vomiting, watery diarrhea, collapse, irregular respiration and lowered temperature. In fatal cases death occurs only a few hours after ingestion (64,65). Toxicity data have also been derived in connection with therapeutic use of antimonials. Cardiac effects, in a few cases auricular fibrillation due to the direct effect on the heart, liver toxicity, characterised by jaundice and fatty degeneration, pulmonary congestion and edema; papular skin eruptions and deaths have been reported (66).

Bismuth

Bismuth is obtained as a by-product of tin, lead, and copper ores. The concentration in the earth's crust is less than 1 ppm. It is used in the manufacture of type alloys, silvering of mirrors, low-melting solders (sometimes in canning), and heat-sensitive devices such as automatic fire extinguishers. Bismuth telluride is used in the electronics industry as a semiconductor.

Trivalent insoluble bismuth salts are used medicinally to control diarrhea and other gastrointestinal
distress. Some of these preparations are available without prescription. Various bismuth salts have been used externally for their astringent and slight antiseptic properties. Further self-exposure comes from the use of insoluble bismuth salts in cosmetics. Bismuth salts have also been used as radio-contrast agents. Injections of soluble and insoluble salts, suspended in oil to maintain adequate blood levels, were used to treat syphilis. Bismuth sodium thioglycollate, a water-soluble salt, was injected intramuscularly for malaria (Plasmodium vivax). Bismuth glycoly arsonilate is one of the few pentavalent salts that have been used medicinally. This material was formerly used for treatment of amebiasis. Exposure to various bismuth salts for medicinal use has decreased with the advent of newer therapeutic agents.

Bismuth is one of the contaminants measured in U.S. urban air. The average concentration was 0.0005 μg/m³, while the maximum concentration reported was 0.064 μg/m³ (63).

Most bismuth compounds that one is exposed to are insoluble and poorly absorbed whether taken orally or applied to the skin, even if the skin is abraded or burned. Thus, most of the information on their distribution in the body is related to therapeutic use. Once the bismuth is absorbed
from the site, tissue binding appears minimal. A diffusible equilibrium between tissues, blood, and urine is established. Tissue distribution, omitting injection depots, reveals the kidney as the site of the highest concentration. The liver concentration is considerably lower at therapeutic levels, but with massive doses in experimental animals (dogs) the kidney/liver ratio is decreased. Passage of bismuth into the amniotic fluid and into the fetus has been demonstrated. The urine is the major route of excretion. Traces of bismuth can be found in the milk and saliva. The total elimination of bismuth after injection is slow, depending on mobilization from the injection site (67).

Titanium

Rutile (TiO₂) and ilmenite (FeTiO₃) are the primary ores of titanium. It is abundant in the earth's crust, at a level of 4400ppm. Titanium is used as a deoxidizer, in permanent magnets, in corrosion-resistant alloys, in pigments, in welding rods, in electrodes and lamp filaments, and in surgical appliances. Titanium dioxide salve has been used in the treatment of burns. It is also used in some cosmetics.

Titanium is a contaminant of U.S. urban air. The average concentration was 0.04 μg/m³ with values as high
Titanium is found in North American rivers at levels of 2-107 μg/l. The mean concentration in municipal U.S. drinking water is 2.1 μg/l. Titanium has been detected in some foods: butter, corn oil, shrimp, lettuce, pepper, and other condiments. The daily intake is about 0.3 mg. Part of the food content may be done to contamination during processing. Oral absorption of titanium is limited; only about 3% of that ingested is absorbed. The majority of that absorbed is excreted in the urine.

The estimated body burden of titanium is about 15 mg. Most of it is in the lungs, probably as a result of inhalation exposure. Inhaled titanium tends to remain in the lungs for long periods. It has been estimated that about one-third of the inhaled titanium is retained in the lungs. There is some geographic variation in lung burden, dependent on air concentration. For example, concentrations of 430, 1300, and 91 in ppm of ash have been reported for the United States, Delhi, and Hong Kong, respectively. Titanium is not constantly present in newborns (68).

Incorporation of titanium at 5 ppm into the drinking water of mice for their lifetime produced no effects on growth, survival, longevity, or tumor incidence (69).
However, 5 ppm of titanium as titanate in the drinking water for three generations resulted in reduction of rats surviving to the third generation, reduction of the male/female ratio, and an increase in runts in all generations (70). Intramuscular injection of titanocene caused a variety of neoplasms at the site of injection and in other organs of mice and rats. However, similar results were not obtained with titanium dioxide (71).

Molybdenum

Molybdenosis has appeared in many parts of the world due to industrial molybdenum (Mo) contamination of nearby pastures. In addition, it has been used as a growth promotant in pastures, and excesses have been found in the plants. Molybdenum is not considered to be very toxic nor teratogenic in the golden hamster. Ferm (72) found that Mo produced no embryocidal or teratogenic effects up to 100 mg/kg. However, Schroeder (42) demonstrated that 10 ppm in the drinking water of breeding mice caused a significant increase in young deaths in F₁ and F₃ generations and in dead litters in the F₃ generation.

Colmano (73) postulated that Mo may be an inhibitor of cellular fission, evoking nuclear and
chromosomal polyploidy and abnormal mitosis. He further hypothesized that Mo may activate the uncontrolled patterns observed in some neoplastic growths.

Jeter and Davis (74) found no effect on the fertility nor gestation of female rats given high doses of Mo. Mills and Fell (75) found severe demyelinization of the CNS in newborn lambs from dams who, during pregnancy, were maintained on diets high in Mo. However, affected lambs were also found to have a low content of copper in their livers.

The studies on mercury have not been taken in the present investigation deliberately since it is widely discussed by earlier workers.

DETERMINATION OF TRACE HEAVY METALS

A detailed survey of literature on the methods of estimation on lead, cadmium, arsenic, antimony, bismuth, titanium and molybdenum is deliberately avoided because it is excellently covered by a number specialised monographs, review articles and text books (26, 77-88). As the present investigation is essentially concerned with the selective and sensitive spectrophotometric methods for Pb, Cd, As, Bi, Sb, Ti and Mo a brief review and merits and demerits of
the methods described in Chapter III individually.

THE PRESENT INVESTIGATION

The poisonous metals Hg, Pb, Cd, As, Sb, Ti, Bi, Mo etc. which are invariably discharged by the industries and having the vital impact on the environment (including flora and fauna). Hg, Cd, As, Bi and Pb present in trace amounts in industrial effluents have caused serious concern to public health authorities. They do not respond to conventional treatment of ultratrace levels. There are no such simple, sensitive, selective methods for the detection and determination of these metals except the atomic absorption technique that too have a limited use and very expensive. Many of the laboratories and industries can not afford to have it. With this object in the present investigation the suitable specific colorimetric methods are developed.

A survey of the literature reveals that various analytical methods are available for the determination of heavy metal viz. spectrography, polarography, spectrometry, chromatography and colorimetry (89-94). Although these methods have a limited use and are expensive. Colorimetry is still in practice. Organic reagents viz. dithizone, B-diketons, diethyl ammoniumdiethyl-dithiocarbomate, hydroxyquinoline and cupferron are most common reagents used for extraction of heavy metals (79,95). Although
some of these reagents are sensitive but no systematic study has been made and several diverse ions are interfering in their determination.

Hydroxamic acids are versatile reagents for organic and inorganic analysis (96-105) which possess bidentate grouping responsible for forming metal complexes. So far these hydroxamic acids are not applied for the extraction and spectrophotometric determination of As, Sb, Bi, Hg, Pb etc. except gravimetry. With these consideration the broad outline of the present investigation is as under:

(1) Synthesis of the suitable specific chelating agents which have the greater affinity to form the complexes with the heavy metals and be easily detected and determined in trace and ultratrace levels.
(2) Solvent extraction methods for the separation of hazard metals.
(3) The use of FeS column for the decontamination of industrial effluents.

The present thesis describes that the hydroxamic acids have been used as a chelating agents for the trace determination of heavy metals. These acids were synthesised by reacting hydroxylamine and acid chloride at lower temperature in the suspension of sodium bicarbonate in the
ethereal media. These acids were characterised by elemental
analysis, mp, ir and uv spectra.

A detail procedure for the environmental sample is
described.

Benzohydroxamic acid (BHA) and phenylbenzohydroxamic
acid (PBHA) are used as the chelating agents for the extract-
ion and spectrophotometric determination of lead, cadmium,
arsenic, antimony, bismuth, titanium and molybdenum in trace
quantities. The optimum conditions are stabilised.

The methods are applied for the trace determination
of Pb, Cd, As, Sb, Bi, Ti and Mo in industrial effluents, soil
and plant samples.

In the present investigation the lead, cadmium, arsenic,
antimony or bismuth was removed from the effluents by
precipitation as an insoluble sulphide by passing through the
bed of commercial iron sulphide in a glass column at acidic pH.
The acidic effluents react with FeS and are precipitated as
insoluble respective sulphides. The effluents were tested for
presence of Pb, Cd, As, Sb and Bi by spectrophotometric methods
(Chapter III) and atomic absorption spectrophotometer.
REFERENCES

34. ibid, January (1975), p. 47.


52. Schutz, A., Personal Communication.


62. idem, ibid., Title 21, Section 135.


