CHAPTER I

INTRODUCTION

Air pollution is defined as any atmospheric condition in which substances are present at concentrations high enough to produce a undesirable effect on man, animals, vegetation, and materials. These substances may exist in the atmosphere as gases, liquid drops, or solid particles and are so called air pollutants.

Substances which are usually considered as air pollutants can be classified as follows :

1. sulfur-containing compounds
2. nitrogen-containing compounds
3. carbon-containing compounds (excluding carbon monoxide and carbon dioxide)
4. carbon monoxide and carbon dioxide
5. halogen compounds
6. particulate matter
7. radioactive compounds

These classifications are on both a chemical and physical basis, since particulate matter refers to the physical state whereas the other categories refer to the chemical state. The categories 1 to 5 are assumed to gaseous compounds.

Particulate matter is any substance, except pure water, that exists as liquid or solid in the atmosphere under normal conditions and is of microscopic or submicroscopic size but larger than molecular dimensions (about $2A^{o}$)[1]

Particulates are produced along with gaseous air pollutants by the various activities of industrial society. The burning of fossil fuels (especially coal in electric power plants) accounts for a large portion of particulates. Transportation, iron and steel manufacturing, cement production, rock and sand mining, and pulp and paper manufacturing contribute a small amount of particulates

Particulates are found to contain a variety of substances including inorganic compounds of aluminium, calcium, iron, lead, magnesium, copper, zinc, cadmium, sodium, and mercury ; organic compounds such as hydrocarbons ; and some acids such as sulfuric acid and nitric acid.

Particulates are great health hazards to human. Breathing particulates from polluted air can result in particulates deposited in the lungs, which affect the respiratory process. Particulates may produce directly injury due to their sizes or/and the injury may extend by a large variety of chemicals which particulates consisted. Synergistic effects of particulates with other pollutants are of considerable importance. These were the reasons why the author interested in studying some pollutants in airborne particulates.

The Environmental Protection Agency of the United States (EPA) had set the national air quality standards for aerosol suspended particulates as annual geometric mean of 75.0 $\mu g/m^3$, in conjugation with a 24-hr. maximum as 260 $\mu g/m^3$ shall not be exceeded more than once a year[2].

1.1 Particulate sources

Sources of particulates can be either anthropogenic or natural. Over 90% of the particulate matter in the atmosphere result from natural sources[3]. Many of these elements, such as sodium, chlorine, silicon, and aluminum are associated with the natural background, but certain species can be attributed to particular anthropogenic sources. Examples include lead from automobile exhaust, vanadium and nickel from fuel-oil fly ash, and barium from diesel-fuel exhaust.

1.2 Types of particulates

Particulate matter can be classified not only on the basis of chemical compositions but also with respect to sizes. Both of these properties are important in determining the effects of aerosals on atmospheric properties and human health .

In air pollution study, particulate matter is usually divided into two categories : " suspended particulates " and " dust fall or settable dust " . The first includes the particle

smaller than 10 μm , which is most numerous and comes from mechanical and industrial dust, combustion ash, and meteors. The second, which is larger than 10 μm, comes from mechanical process, erosion, grinding, spraying, and meteors. Because of the ability of small particles to penetrate into the aveoli, the suspended particulate is more health hazards to humans than settable dust.

Some chemical forms of airborne particulates are given in Table 1 .

1.3 Heavy metals in airborne particulates.

Airborne particulates, especially in the urban area, are found to contain some heavy metals. Many heavy metals or their compound are particularly toxic to human beings, animals, and plants. Not much is known about their distributions in nature and their roles in air pollution. Heavy metals such as mercury, zinc, cadmium, lead, and copper are currently concerned in this study.

1.3.1 Mercury

Mercury is a very useful element, since it is the only metal which is a liquid at room temperature and has a high electrical conductivity. Unfortunately, mercury and its compounds are poisons to all living systems. Mercury enters the environment in elemental forms as loss from industrial processes and scrapped equipments, and

Table 1 Probable chemical forms of some airborne pollutants[4]

As	G, P	element, trioxide, arsine, organic derivatives
Ba	P	sulfate
Cd	P	element, salts
Cu	P	oxides
Hg	G, P	element, oxides, organic derivatives
Pb	P	element, oxides, carbonates, organic derivatives
Zn	P	oxides

G gas and P particulate

in the form of mercury compounds from industrial and agricultural endeavors.

It is thought that most mercury compounds are degraded into elemental mercury or oxidized rapidly to mercuric oxide under the action of sunlight. In either case, these airborne particulates can be inhaled by man directly or can be ingested through water or food.

Mercury and its compounds can produce abdominal pain, vomiting, diarrhea, pneumonia , renal damage and circulatory and respiratory failure in acute severe exposures. Chronic exposures can lead to conditions manifested by signs of gingiritis, tumor, emotional instability and nerve damage[3]. These symptoms were known as " Minamata " disease because it was occurred at Minamata bay in Japan.

1.3.2 Lead

Lead is a rare element in the lithosphere. The percentage of lead in the crust of the earth is about 0.00002 %[5]. Lead deposits consisting of the ore galena, PbS, are used as source of lead.

Lead is a quite soft metal. This malleability allows it to be casted easily. Lead is used in a variety of products including alloys, storage batteries, gasoline antiknock chemicals, paint pigments, and ceramic glazes. It is easily vaporized during melting[5], and thus is an industrial hazard. Lead becomes widely distributed in the environment by automobile exhaust as gaseous

substances or particulates. It was estimated that the chief lead products exhausted from automobile are lead halides and ammonium lead halides. Lead chlorobromide is the principle component[6].

The signs and symptoms of lead poisoning can include abdominal pain and tenderness, constipation, headache, weakness, muscular aches and vomiting[3]. There is frequently a characteristic lead line on the gum margin. Chronic feeding of tolerable levels of lead induces tumors of the kidney subsequent to the renal degenerative changes[7].

The total body burden of lead is divided from food, water and inspired air. Lead intakes from food and water were estimated to range between 0.1 and 0.4 mg per day , and from inspired air ranges from about 0.01 to about 0.10 mg per day. Only 5 % to 10 % of the lead taken in by consumption of food and water may be absorbed in the body but between 30 % and 50 % of inspired lead is absorbed by lungs[8].

1.3.3 Cadmium

Cadmium is a toxic metal, and it is also widely distributed in the environment by man's activity. All of the cadmium is produced as a by-product in the refining of zinc from zinc ore, since cadmium is geologically associated with lead and zinc. Electroplating, iron alloys, pigments, alloys, batteries and plastic additives also utilize cadmium in their processes. Cadmium pollution exists as fumes, and vapors in air pollution. Airborne cadmium comes about as a by-product in the processing of scrap steel, the reclaiming of copper

and the refining of lead, copper and zinc. There are only small amounts of cadmium in air, water, and food. However, cadmium can be absorbed by the body and can remain in the system for long periods of time. Schoeder, et al[9] reported that the hypertension was observed in man with a high Cd/Zn ratio in the kidneys. Further evidence for the link between cadmium and hypertension had been furnished by Caroll[10] and Hickey et al[11].

A disease specifically associated with cadmium poisoning has been recognized in Japan as "itai-itai ". This disease was related to pollution from a mining complex and resulted in multiple fractures arising from osteomalacia.[12] The amount of cadmium in the body that can cause problems are not known. Thus, it is important to be aware that the increase of cadmium level in the environment could present a significant health hazard.

1.3.4 Zinc

A bluish-white metallic element occuring as the sulfide, oxide, carbonate, silicate etc, is zinc. It resembles magnesium in its chemical reactions. It is used very extensively throughout industry, mainly in galvanizing and in manufacture of brass, roofing material, gutters and other alloys.

In agriculture, zinc dimethyl-dithio-carbamate and zinc ethylenebis-dithio-carbamate are used as fungicides[13]. Among minor uses, zinc pentamethylene-dithio-carbamate, zinc benzyl - dithio - carbamates find application as additives to lubricating oils[14].

Zinc is an essential element for both plant and animal lives[15-17]. It was found to act as a cofactor in a variety of enzyme systems, including arginase, enolase, several peptidases, and oxalacetic decarboxylase[18].

Zinc is not inherently a toxic element, however, its fume (zinc oxide) when inhales fresh, can cause a disease known as " brass founder's ague or brass chills" . It was the opinion of some who worked with zinc chloride that it was carcinogenic[19].

1.3.5 Copper

Copper is another chaleophile element which is found in sulfide deposits along with lead, cadmium, and zinc. it is usually present in zinc concentrates and in smelters as small quantities[20].

Copper is often found as common air contaminants in forms of copper fume and copper salts. These compounds come from smelting, grinding and alloying of copper mixtures. Since copper is recognized as an essential element in the diets of animals and plants, its toxicity will be lower than lead.

Although copper is extensively used in industries, it does not appear to have had its toxicity studied as much as many other elements. There was certainly a high incidence of lung cancer among coppersmiths[21], but there was no direct evidence that this element is carcinogenic. Absorption of excess copper by man results in " Wilson's Disease ", in which excess copper is deposited in the brain, skin, liver and pancreas.

1.4 Air Pollution in Thailand

In Thailand, expert in air pollution is meager, high-price in the instrument and insufficiency finance are the problems. Therefore, the data concerned the determination of heavy metals in airborne particulates in Thailand are rare.

The committee for Investigating the Hazards from Motor Vehicle Exhaust Gases (1962-1971) had reported that concentrations of lead in air in Bangkok Metropolis were found in the range of 4.50 to 30.60 $\mu g/m^3$ [22]. In 1973-1974, Pescod, et al[23] found that the maximum concentration of lead in air at two heavy traffic roads, Yawaraj and Rama IV, and other three additional roads was 2.19 $\mu g/m^3$. During the period of May 1976 to April 1977, Kanatharana, et al[24-27] investigated respirable air particulates in Bangkok Metropolistan area from Samyan, Patumwan, Ratchaprasong, Phloenchit, Sukhumvit to Samrong and reported that there were 0-600 $\mu g/m^3$ of lead, 0-135.4 $\mu g/m^3$ of cadmium, 0-88.7 $\mu g/m^3$ of copper, and 0-114.0 $\mu g/m^3$ of zinc in these respirable air samples. The Bangkok Metropolistan Authority collected the suspended particulates in Bangkok Metropolistan area from 19 September 1977 to 12 October 1977, and informed that the range of 24-hr. average of particulate concentrations for twelve stations was 162.0-1171.0 $\mu g/m^3$ and the average concentration was 533 $\mu g/m^3$[28].

Heavy metals in air particulates in working environment had also been investigated. The Occupation Health Division, Department of Health reported that the maximum concentration of

lead as 2.5184 mg/m^3 was found at plating and cutting plant processes in battery manufacturing. In 1977, Kanatharana, et al also investigated the respirable air particulates in various factories and found the high level of lead, nickel, and cobalt in the working room air of the battery manufactering as 860.2 µg/m^3, 247.1 µg/m^3, and 97.1 µg/m^3, respectively. High chromium level (103.2 µg/m^3) was also found in the chromium plating and polishing plant and high level of zinc vapors (284.4 µg/m^3) was found in the welding plant[29].

The problems that caused an air pollution in Bangkok Metropolistan area are myriad of different mobile and stationary source. Mobile sources such as diesel and gasoline vehicles played an important role. Consequently, identification of the numerous constituents released into the atmosphere becomes very difficult.

Methods for trace analysis in airborne particulate matter mostly included physical techniques. Usually physical techniques such as microscopy, atomic absorption spectrophotometry, neutron activation, x-ray fluorometry, mass-spectroscopy, and stripping voltammetry have been used for elemental analysis. Among several techniques atomic absorption spectrophotometry (AAS) and anodic stripping voltammetry (ASV) were the most widely used methods for trace analyses of metals . Therefore, the analytical techniques utilized herein for analyses of some trace elements in air particulates in Bangkok Metropolistan area are anodic stripping voltammetry (ASV) and atomic absorption spectroscopy (AAS). These two techniques were selected since they offered the required sensitivity, availability,

simplicity, and capability of multielement analysis.

Heavy metals such as zinc, cadmium, lead, copper and mercury are interested for three reasons.

Firstly, these metals are common air pollutants in the urbanized and industrialized area.

Secondly, these metals or their compounds are toxic to human beings, animals and plants and may be the most harmful pollutants since they are not biodegradable and often have a long systemic effects.

Thirdly, the concentrations of these metals in ambient air trend to increase every year because of an inadequate control. In order to assess the pollutant effects on man and the environment the determination of these air pollutants is necessary.