CHAPTER 1

INTRODUCTION

Particulate matter has been used as a convenient parameter of air quality at least since 1976(Archer and Barratt, 1976). Particulate matter generically comprises solid particles, liquid droplets, aerosols and respirable particles. Particulate matter in the air are of varying sizes and shapes. They range from 0.1-1µm for photochemical aerosols to 1-100µm for aerosol spray products. Tobacco smoke particle diameter is about 0.25µm whilst zinc oxide fumes is about 0.05µm (Reist,1993). Most industrial dust is between 0.1µm to 10µm. Dust is one of the principal contributing substances to ambient solid particulate matter besides fumes, smoke and spray. Dust is indeed a common geological material throughout the environment. The degree of accumulation and composition of dust, however, depend on many variables including sources of emission (building construction materials, traffic density and industrial activity), weather conditions and its behaviour. Nevertheless, dust analysis is scarce and continues to be a significant subject for environmental research due to its ubiquity and hence apparent nuisance. There is also a need to enhance the incomplete knowledge on the nature, sources of emissions and dust types, analytical techniques and data/inventory collection and interpretations.

1.1 NATURE OF DUST

1.1.1 Definitions of Dust

According to the Concise Oxford Dictionary, dust: are "finely powdered earth or other matter lying on ground or on surfaces or carried about by wind."

A two-pronged description of dust has been proposed (Green and Lane,1964). In the colloidal sense, dust: consist of solid particles dispersed in a gaseous medium as the result of the mechanical disintegration of matter. Examples of these are clouds formed by disintegrating rocks or minerals during processes involving crushing, grinding, drilling and blasting or by subjecting powders to strong aerodynamic forces (Ng et al.,1995a). In the popular sense, dust: usually refer to solid particles which have settled on a surface and which can readily be redispersed in the atmosphere. It has been proposed that dust is particulate matter smaller than 76μm but with a lower limit of 1μm (Barratt,1990).

1.1.2 Some Physical Properties of Dust

Three physical properties of dust may be readily identified: namely, settling velocities, optical properties and absorption tendency.

The settling velocity of a dust particle in the atmosphere depends on its size (and density). Particles of size 0.1μm have a settling velocity of 4×10^{-5} cm/s while that of size 10μm have a settling velocity of 0.3 cm/s. Particles with diameters greater than 20μm display a significant settling velocity. For instance, particles of size 100 μm settle at a velocity of 25 cm/s. Generally, larger particles settle more rapidly than smaller ones (Baron and Willeke, 1993).

The optical properties relate to the scattering, reflection and absorption of solar radiation by suspended dust particles in the atmosphere. The extent and degree of these depend largely on the size, shape, nature and the wavelength of the incident radiation (Stoker and Seager, 1972).

The absorption tendency of a suspended dust particle refers to its ability to absorb molecules which may collide with it. This could account for the toxity or corrositivity of certain dust particles when the molecules are of toxic or corrosive in nature (Stoker and Seager,1972).

1.1.3 Significance of Particle Size

1.1.3.1 Impact on Efficiency of Dust-Removal Devices

The removal of dust particles from the gaseous medium is essentially the sole function of most particulate control equipment. These particles are suspended in the medium due to air flow forces. The particles must therefore be displaced to regions where the forces no longer prevail and thereby removed. This displacement of the dust particles to the removal regions is mainly governed by the particle size (Batel,1976).

The efficiency of a dust-removal device is therefore dependent on the effective displacement of dust particles from the mainstream of gaseous medium. These particles must be withdrawn either continuously or intermittently from the removal region for the dust -removal device to perform efficiently.

1.1.3.2 Impact on Human Respiratory System and General Health

Particulate matter enters the human body almost exclusively by way of the respiratory system. The extent of penetration and deposition in the human respiratory system is determined by the particle size. Particles larger than 10 μm are removed in the nasal cavity filtered by the nostril hair . Particles in the size range of 5 μm to 10 μm are mostly removed in the trachea and bronchii. Particles ranging in size from 0.5 μm to 5 μm can be deposited in the lungs as far as the bronchioles. Particles less than 0.5 μm may reach and settle in the alveoli. Particles retained in the alveoli are absorbed into the bloodstream (Walton,1974).

Calculated depositions of aerosol particles in the human respiratory system has increased the understanding on the relationship between particle size and the specific health problems of concern. Dust is not only a nuisance but also a health hazard. This is especially so when particulate dust matter contain some toxic trace elements such as arsenic, cadmium or lead. Smaller particles in the range of 0.1 μm to 12.5 μm are known to be more toxic than larger particles since the concentrations of toxic substances increase with decreasing particle size (Godish,1991).

In one related study (Natusch and Wallace, 1974), concentrations of certain metallic elements in airborne flyash was determined according to particle size. It was found that the concentrations of lead amongst other trace elements like arsenic, chromium, nickel and zinc, was 1,100 μg/g for particle diameter of 11.3μm and 1,600 μg/g for particle diameter 1.1-2.1 μm. The other elements showed similar trends in that their

concentrations increased with decreasing particle diameter. This observation revealed that smaller particles may be more toxic than larger ones.

Inhalation of high concentration of cadmium dust in industry may lead to kidney and lung damage (Stern,1977).

Prolonged exposure and inhalation of coal dust may eventually lead to anthracosilicosis and anthracosis. Silica and asbestos dust may trigger the formation of pulmonary fibrosis such as silicosis and asbestosis when deposited in the lungs. Lead dust may cause mental impairment in children and also damage the gastrointestinal tract and the nervous system (Green and Lane,1964).

1.2 SOURCES OF DUST EMISSIONS FROM SELECTED INDUSTRIES

Like any other developing and developed countries, industries are one of the major contributing sources of dust pollution in Malaysia (Ng et al.,1995b). They emit dust at various stages of the manufacturing and production processes. Typical examples of dust-emitting industries are presented below (Forte et al.,1992).

1.2.1 Paint and Varnish

The manufacture of paint involves the dispersion of a coloured oil or pigment in a vehicle followed by the addition of an organic solvent for viscosity adjustment. The emissions of particulate matter amount to 0.5% to 1% of the pigment handled.

1.2.2 Printing Ink

Printing ink is produced by adding dyes to water and then flushing it with an ink vehicle. The particulate matter emissions result from the addition of pigments to the vehicle during the preliminary stages of ink production.

1.2.3 Coffee Roasting

Coffee must be cleaned, blended, roasted and packaged before being sold. Dust, chaff, coffee oils, smoke and odours are the principal air pollutants emitted from coffee processing.

1.2.4 Starch Manufacturing

Starch is obtained through the separation of coarse starch in corn to a fine dry powder form ready for marketing. Dust emissions result from cleaning, grinding and screening operations.

1.2.5 Copper Smelters

Copper is produced primarily from low-grade sulphide ores which are concentrated by gravity and subjected to melting and purifying procedures. Significant amounts of dust and sulphur oxides are contained in the waste gases from the process.

1.2.6 Ferro Alloy Production

The major method used to produce ferro alloy for steel making is the electric furnace process. The furnace uses carbon as the reducing agent. Carbon monoxide and dust are emitted during the process from the furnace.

1.2.7 Gray Iron Foundry

The major type of furnace used to produce gray iron castings is the cupola which uses an extremely hot bed of coke to melt the iron. Emissions from cupola furnaces include carbon monoxide, dust, fumes, smoke and all vapours.

1.2.8 Iron and Steel Mills

Iron ore is reduced to pig iron and some of its impurities are removed in a blast furnace. The pig iron is further purified in other processes. Particulate matter and carbon monoxide are the major pollutant emissions resulting from the various furnace reactions.

1.2.9 Steel Foundries

Steel foundries produce steel castings by melting steel metal and pouring it into moulds. The basic melting process operations are furnace charging, melting, tapping the furnace into a ladle and pouring the steel into moulds. Particulate matter emissions from steel foundry operations include iron oxide fumes, sand fires, graphite and metal dust.

1.2.10 Asphalt Batch Plants

Hot-mix asphalt paving consists of a combination of aggregates, coarse or fine, uniformly mixed and coated with asphalt cement. The coarse aggregates are usually crushed stone, crushed slag or crushed gravel while the fine aggregates are usually

natural sand and finely crushed stones. The largest pollutant type is dust, emanating from the rotary dryers and filtering systems normally used in producing asphalt.

1.2.11 Portland Cement Manufacturing

Lime, silica, alumina and iron are the four major components used to manufacture cement. The various substances are crushed in exact proportions, fired in a kiln and then ground in gypsum to be bagged for shipment as cement. Particulate matter is the primary emission and is emitted primarily from crushing operations and rotary kilns.

1.2.12 Clay and Fly Ash Sintering

Both the sintering clay and flyash involve the firing and burning off of residual matter to the desirable product. Dust is the major pollutant emitted from the sintering and screening process.

1.2.13 Concrete Batching

This involves the proportioning of sand, gravel, cement and water by means of weight hoppers and conveyors into a mixing receiver. Particulate matter emissions consist primarily of cement dust but some sand and aggregate dust emissions do occur during batching operations.

1.2.14 Glass Manufacturing

Soda lime glass is produced in large, direct fired, continuous melting furnaces in which the blended raw materials are melted at 2,700 degrees Celsius to form glass. Emissions from the glass melting operations consist primarily of particulate matter.

1.2.15 Stone Quarrying and Processing

Rock and gravel products are loosened by drilling and blasting from their deposit beds and removed with the use of heavy equipment. Further processing includes crushing,

regrinding and removal of fines. Dust emissions occur from many operations in stone quarrying and processing.

1.2.16 Thermal Power Plant

Coal-fired power plant is also a major source of dust emission. Coal contains many non-combustibles called ash. The major constituents of ash are minerals and mineral oxides such as silica and alumina. During combustion, minerals and oxides partition into either the bottom ash or the flyash. In a pulverized-coal furnace, the coal is pulverized in a mill into very fine particles before being fed through the burners to the combustion chamber where it is fired in suspension. Dry bottom pulverized-coal furnace fires coals with high ash fusion temperature. Dry ash removal techniques are usually employed such as electrostatic precipitator or fabric filter. Wet bottom pulverized-coal furnace fires coal with low ash fusion temperature and the molten ash is drained from the bottom of the furnace.

1.3 CONVENTIONAL DUST-REMOVAL DEVICES

The principal means for control of particulate matter emissions from industrial sources are cyclones, fabric filters, scrubbers and electrostatic precipitators. The following are brief description of the devices (Sittig,1977).

1.3.1 Cyclones

Cyclonic collectors are round, conically shaped vessels in which the gas stream enters tangentially and follows a spiral path to the outlet. Figure 1 shows the operation of a typical cyclone separator .The spiral motion produces the centrifugal forces that cause
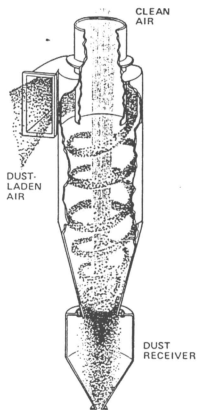
Figure 1 Operation of Cylone

Source: Buonicore,A.J. and Davies,W.T.(1992)

the particulate matter to move toward the periphery of the vessel and collect on the walls and fall to the bottom of the vessel. The centrifugal force is the major force causing separation of the particulate matter in a cyclone separator. A cyclone is meant for coarse particles(>5μm) removal and is usually installed/placed upstream of an electrostatic precipitator . It is slightly cheaper for pretreatment work where there is no necessity for complete removal of fine particulate matter.

1.3.2 Fabric Filters

Fabric filter systems or baghouse, usually consist of tubular bags made of woven synthetic fabric or fibreglass in which the dirty gases pass through the fabric while the particles are collected in the upstream side by the filtering action of the fabric. The dust retained on the bags is periodically shaken off or is removed by a brief burst of compressed air injected into the tube jet at the top through a venturi and falls into a collecting hopper for removal. A fabric filter is capable of capturing particles in the size range of 0.1-0.5 μm. Figure 2 shows a pulse-air-jet type of bagfilter.

1.3.3 Wet Scrubbers

Wet scrubbers are collectors using water "spray" to collect and remove particulate matter. They are capable of removing particulate matter of size 5 μm or less in diameter. The low energy scrubbers may consist of simple spray towers, packed towers or impingement plate towers. The high energy scrubber or Venturi, imparts high velocity to the gas stream by means of converging-diverging duct section and contacts the
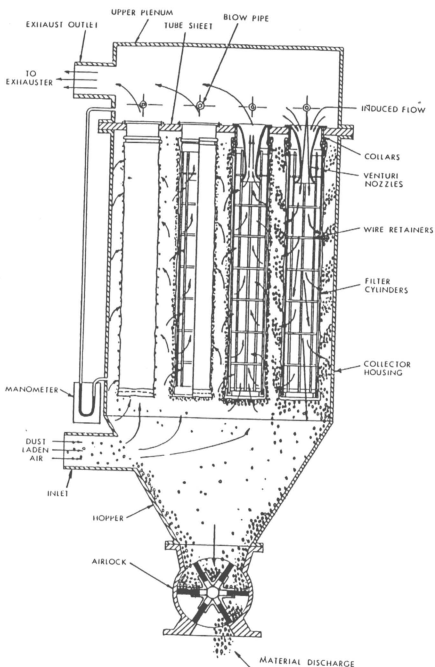
Figure 2 Pulse-Air-Jet Bag Filter

Source: Orr,C.(1987)

stream with injected water. The principal mechanisms involved in wet scrubber are (i) increasing the size of the particles by combination with liquid droplets thereby increasing their size so that they may be collected more easily and/or (ii) trapping them in a liquid film and washing them away. Figure 3 shows (a) an impingement plate scrubber and (b) a Venturi scrubber.

1.3.4 Electrostatic Precipitators

The principle involved in electrostatic precipitators consists of passing the particle-laden gas through an electric field produced by a high-voltage electrode and a grounded collection surface. The gas is ionized by the high voltage discharge and the particulate matter is charged by the interaction of the gas ions. The particles migrate to the collecting surface which has an opposite polarity and are neutralized. The particles are removed by rappers or by other mechanical devices that vibrate the collector surface and dislodge the particulate matter which drops by gravity to the hoppers below. The electrostatic precipitator is meant for finer particle(< 5 μm) and is usually installed downstream of a cyclone separator. Figure 4 shows the construction of a typical electrostatic precipitator.

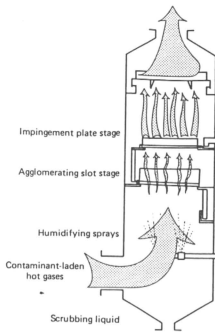**Figure 3 (a) Impingement-Plate Scrubber**
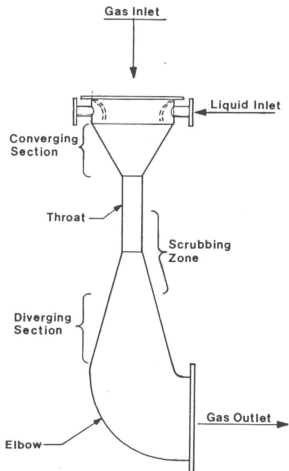
Source: Buonicore,A.J.(1982)

Figure 3 (b) Venturi Scrubber

Source: Schifftner,K and Hesketh,H.(1992)

DISCHARGE ELECTRODE RAPPER

COVER PLATE

INSULATOR COMPARTMENT

COLLECTING PLATE RAPPER

TOP END PANEL

SIDE PANEL

PERFORATED GAS DISTRIBUTION PLATE

COLLECTING PLATE

GAS FLOW

HOPPER BAFFLE

BOTTOM END PANEL

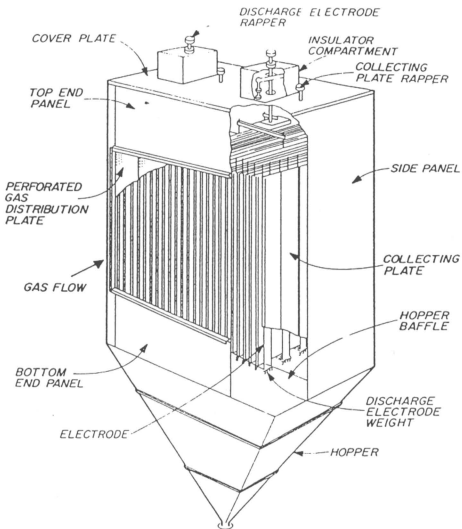DISCHARGE ELECTRODE WEIGHT

ELECTRODE

HOPPER

Figure 4 Internal Arrangement of a Standard Electrostatic Precipitator

Source: Cheremisinoff,P.N.(1993)

1.4 ANALYTICAL TECHNIQUES FOR TRACE ELEMENT ANALYSIS IN DUST SAMPLES

Trace element contamination can result primarily through atmospheric particles. Most trace elements are released through industrial emissions. For instance, coal and fuel power generation release traces of arsenic, chromium, copper, mercury, selenium and zinc into the atmosphere. In addition to these elements, metal processing and smelting plants also release cadmium, cobalt and nickel.

The analytical techniques for measuring trace elements should have the following ideal characteristics: (a) very low detection limits (b) a wide linear dynamic range (c) simple interference-free data (d) qualitative, semi-quantitative and quantitative analysis (e) possible simultaneous multi-element capability (f) simple sample preparation (g) high throughput and low cost per determination (Ward, 1995).

The analytical techniques that are most frequently used at present for the determination of trace elements in dust samples include atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry(ICP-AES), neutron activation analysis (NAA), X-ray fluorescence analysis (XRF) and proton-induced X-ray emission (PIXE). A brief review of these techniques are presented below.

1.4.1 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry is based on the process that occurs when free atoms in the ground-state of the analyte element produced by specific atomization, absorb radiation of characteristic wavelength given off by a special source made from that element. The light absorption is proportional to the concentration of the selected element being atomized in the light path, following Beer's law.

In Flame AAS, air-acetylene or nitrous oxide-acetylene flame is most commonly used as atomization source. The sample solution is introduced through a pneumatic nebulizer as a fine aerosol into the flame in a burner mixing chamber. Here, fuel and the oxidant gases are mixed with the sample aerosol and carried to the burner head where combustion and sample atomization occur. The flame burner head is aligned so that the light beam passes through the flame where light is absorbed.

The spectral light source include the hollow cathode lamp and electrodeless discharge lamp of specific elements. An individual radiation source is needed for every element to be determined which makes it difficult for simultaneous multi-element determination.

With the use of different flame types, many elements can be determined satisfactorily in the low μg/L to high mg/L range except for elements like aluminium and titanium which form refractory compounds and would not dissociate in the combustion flame where the temperature varies from 2,000K to 3,000K. Due to the high stability of the flame system, excellent precision(0.2-2%) can be achieved. The interferences are few and well documented.

However, the detectability of Flame AAS is limited by the inefficiency of the conventional nebulizer-burner system. No more than 10% of the sample reaches the

flame and the high velocity of the flame gases allows the analyte atoms very short residence time of a millisecond or less in the beam path of the spectrometer. The large dilution of the sample in the flame gases results in further loss of sensitivity. The detection limits are in the range of subparts per million. It is inadequate for aluminium, arsenic, lead, mercury and titanium.

The Graphite Furnace AAS provides a 50-500 fold improvement in sensitivity relative to Flame AAS. This higher sensitivity is achieved by atomizing samples in a small, electrically heated graphite tube furnace. A small sample aliquot of 10-100µL is pipetted into the graphite tube and the temperature of the tube is then increased in a controlled manner to dry, ash and atomize the sample. The residence time of sample atoms in the graphite tube is several orders of magnitude longer than the atom rsidence time in Flame AAS applications. This longer atom residence time in the optical path accounts for the dramatically improved sensitivity achieved with the graphite furnace. The graphite furnace technique is however noticeably slower than the flame technique and also requires automatic correction for non-specific background absorption generated by the sample matrix.

It is highly sensitive with detection limits as low as subparts per billion. It demands high operator skill and knowledge. It involves higher costs. It is good for heavy metals and metalloids such as arsenic, cadmium, copper and lead which require high sensitivities. It is of single element capability and the technique involved is very difficult. The relative precision is 2-5%. It requires smaller sample size.

The Hydride Generation AAS involves the generation of volatile hydride of the analyte by means of a reducing agent added to a reaction vessel containing an acidic solution of the sample. The liberated hydride is transported to a heated quartz cell atomizer by an inert carrier gas. Sodium borohydride is most commonly used as the reducing agent. Since the hydride is separated from the matrix, advantages include high sensitivity and reduced interference. However, this technique is only applicable to a limited number of elements. Those elements that form volatile hydrides include arsenic, antimony, bismuth, selenium and tellerium.

The Cold Vapour AAS is specific for the determination of mercury which can exist in an atomic state at ambient temperature due to its high vapour pressure. A reducing agent is added to a reaction vessel containing a sample with trace levels of ionic mercury. Stannous chloride or sodium borohydride are the most commonly used reducing agents. The atomic mercury vapour is then transported to a photometer. While extremely sensitive, this technique is only applicable for the determination of mercury. The detection limit is 0.01-0.001 µg/L.

The AAS techniques are highly selective and spectral interference caused by overlapping atomic lines of other elements is very rare. They are excellent quantitative techniques but are not suitable for qualitative analysis. The quantitative determination is in the range of 0.1-100ppm and the relative precision is 0.2-5% (Strobel and Heineman, 1989).

The disadvantages are that samples must be in solution or at least volatile, individual source lamps are required for each element, it is time-consuming, it requires sample

destruction and it needs a relatively large sample sizes for analysis. AAS techniques can only determine one element at any one time. The techniques become slow and tedious for multi-element analysis. Also, variations in concentrations of samples can be problematic as the linear range of AAS techniques is very limited.

1.4.2 Inductively Coupled Plasma-Atomic Emission Spectrometry(ICP-AES)

The plasma of inductively coupled plasma spectrometry(ICP) is basically an electrically induced gas(argon) discharge caused by the application of an oscillating radio frquency power (700 to 1500W) on an induction coil around the top of three concentric quartz tubes or torch through which three argon gas flows along the three tubes are maintained (Metcalfe,1991; Strasheim and Montaser, 1992). An ionised argon plasma is formed accompanied by high heating to about 10,000K inside the coil. The sample solution is aspirated as an aerosol by means of a commonly used concentric pneumatic nebulizer. Other forms of nebulizers such as the cross flow nebulizer and the Babington nebulizer have also been used. The sample aerosol is carried into the center of the plasma by the nebulizer argon flow. As the sample mist passes through the plasma, it undergoes desolvation, vaporization, atomization, ionization and excitation. The chief analytical advantages of the ICP over other emission sources are derived from the ICP's ability to perform these processes efficiently and reproducibly for a wide range of elements present in many different sample types. The decomposition products of the sample enter the normal viewing zone (15 to 20mm above load coil) and stay for 2 minutes in the plasma at 5,500-8,000K. The residence time and the temperature which the sample particles experience in the ICP are about twice those of the hottest flame. Moreover, the

free atoms and ions are present in a chemically inert atmosphere in the ICP, thus ensuring their longer lifetime in the plasma than in the flame. Besides improving excitation and ionization efficiencies, the high temperature of the ICP also reduces or eliminates many of the chemical interferences found in flames and furnaces.

In an ICP-AES spectrometer using a polychromatic dispersion system, the light emitted by the excited atoms and ions is directed onto the entrance slit of a Paschen-Runge mount spectrometer in which a high resolution diffraction grating disperses the emitted radiation into its component wavelengths and focuses them onto a number of exit slits mounted on the periphery of a "Rowland" circle. Each of the exit slits are precisely aligned to an atomic line for a specific element. The radiations are detected simultaneously by using photomultiplier tubes placed behind each exit slit. The electronic conversion of the photocurrent to digital form allows the use of microcomputer for concentration readout and data manipulation. Another common form of ICP-AES spectrometer, equipped with a high resolution wavelength scanning system and appropriate computer control can be programmed to rapidly scan through specific wavelength regions.

The major advantage of the ICP-AES technique is that multiple elements per sample can be determined simultaneously under a single set of compromised operating conditions. Their detection limits in solutions are at the 0.1-100 µg/L level. Generally, the detection limits for ICP-AES with pneumatic nebulization are between those for the Flame AAS and the Graphite Furnace AAS. The ability of the plasma source to

reproduce atomization conditions ensures long term stability and precision of 1 to 3% can be achieved.

The upper limit of linear calibration for ICP-AES is usually 10^4 to 10^6 times the detection limit for a particular emission line. The advantage of a wide linear dynamic range is that it makes calibration of the instrument simpler because only a few standard solutions typically need to be analysed to produce a calibration curve. The other advantage of large working range is that it allows trace, minor and even major elements to be determined simultaneously at a single dilution level.

The common forms of nebulization systems for ICP-AES are pneumatic nebulization and ultrasonic nebulization. Pneumatic nebulizers such as the concentric or "Meinhard" nebulizer are standard devices that can give good sensitivity but the small orifice in the nebulizer can be plagued by clogging problems, often by solution containing as little as 0.1% dissolved solids. Aspiration of concentrated solutions of mineral acids and organic liquids with large changes in density and viscosity could affect the droplet size and the rate of sample injection and hence the sensitivity of measurements. The nebulization efficiency of the pneumatic nebulizer is only 1 to 2%. The use of ultrasonic nebulization can improve the transport efficiency and can increase the sensitivity by about 10 times (Brenner and Taylor, 1992).

The ICP-AES technique is used widely for qualitative and quantitative analysis of metals and some non-metals particularly at trace levels over the concentration range 0.01-100mg/L. The relative precision is 0.5-2%. It is a sensitive and precise qualitative and quantitative technique with a wide linear response with operating range in the

region of parts per billion. However, the instrument is complex and expensive to purchase and operate. Capital cost and operating costs are higher for analysis of small number of samples. It is cost effective for analysis of large numbers of samples with large numbers of elements. It is nevertheless of much higher analytical throughput than the single element AAS techniques. It requires sample destruction and dissolution before analysis(see later:Chapter 2) and sample size requirement ranges from 100mg to 1g.

1.4.3 Neutron Activation Analysis (NAA)

In neutron activation analysis, a sample is subject to neutron bombardment in a nuclear reactor. Radioactivity will be induced in each of the element present that is capable of being so activated. The radioactive species can be identified by such specific nuclear properties as gamma-ray energies and intensities, beta-ray energies or half-lives. Quantitative analyses are carried out by simultaneous irradiation of standard samples with the unknown and the analysis results are obtained by simple comparison.

The technique is one of the most sensitive, versatile and precise analytical methods. It has a wide application in the determination of metal pollutants in aerosols and in air particulate matter (Ward et al., 1987; Adepetu et al., 1988; Fardy et al., 1989).

This technique is also non-destructive and multi-elemental in nature and the precision and accuracy of the method has been well-established (Ondov et al., 1975). It is claimed to have surpassed all other chemical and instrumental methods of analysis (Winchester and Desaedeleer, 1981).

Detection limits for elements in airborne particulate matters can be as low as 2×10^{-5} µg/m^3. There is no necessity for chemical pre-treatment. The only physical treatment is grinding and homogenization of large samples. The operating range is 10-10^{-4} ppm with relative precision 1-5%. It requires as little as 0.1 µg of samples. It is useful for qualitative and quantitative determination at ultra-trace level. It affords high specificity and few sources of systematic errors, thus high accuracy is attainable (Salbu and Steines, 1992).

The disadvantages in NAA analysis are that it is time-consuming, expensive and unable to provide data on certain elements such as lead (the product of radionuclides decay) and light elements (e.g. sulphur and silicon) with acceptable accuracy and precision. It requires a source of neutrons, usually a nuclear reactor.

1.4.4 X-Ray Fluorescence Analysis (XRF)

The principle of X-ray fluorescence spectrometry involves the irradiation of a sample with a beam of X-rays which are absorbed by its constituent atoms. The atoms so excited then emit fluorescent X-rays at wavelengths or energies characteristic of the elements present. These rays are then being separated according to wavelength (wavelength dispersion) or energy (energy dispersion) and their intensities measured and compared with those of appropriate standards.

Wavelength dispersive instruments include an X-ray tube to irradiate the sample, a crystal to disperse the emitted X-rays according to Bragg's law and a detector to determine the intensity of the characteristic X-rays. The detector is placed at an appropriate angle to measure the intensity at a particular wavelength.

Energy-dispersive instruments often induce sample fluorescence with X-rays from a secondary target (eg., nickel, molybdenum, titanium). A solid state detector (a silicon diode containing a small amount of lithium) and a multichannel analyzer are used to disperse, detect and record the emitted X-rays.

X-rays incident on the sample interact either by the photoelectric effect (leading to X-ray fluorescence) or by scattering, mainly from the atoms in the low atomic number constituents of the collection medium. These scattered X-rays constitute an unwanted background that defines the detection limit for the fluorescence measurement.

The precision of XRF depends on statistical counting error, drift in instrumental signal, homogeneity of the sample and miscellaneous operational errors (Appel, 1993).

Like plasma emission spectrometry, XRF technique is capable of simultaneous determination of a large number of elements. XRF is advantageous for the direct analysis of solids although matrix effects may pose significant challenges. Suspended solids or sediments can be prepared on suitable matrix for direct measurement of metal contents.

XRF technique can be used for non-destructive elemental analysis of solid or liquid samples for major and minor constituents. It is most suitable for the determination of heavy elements in light matrices (eg. bromine or lead in petroleum). It is suited for qualitative and quantitative applications and very simple to operate.

Detection limits are generally in the range of 10-100mg/L but for airborne particulate matters, the detection limit is of the order of 10^{-2} µg/m^3 (Reeve,1994). The relative

precision is 5-10% and operating range is 20mg/L-0.1%. The analysis cost and time are relatively low and it requires minimal sample preparation (Adams et al., 1983).

The major disadvantages are that matrix absorption, secondary fluorescence and scattering phenomena may limit its sensitivity and precision in many cases especially with dense matrices. The sensitivity falls off with atomic number; elements with atomic number less than 15 are particularly difficult to analyse. The instruments are often bulky, complicated and costly.

1.4.5 Proton-Induced X-Ray Emission (PIXE)

PIXE technique can provide data for up to 20 elements. An analysis normally requires about 100 second per sample of the accelerator time and about 25 second of computer time to run concurrently for data reduction. It requires no sample preparation and is non-destructive in nature. However, it cannot analyze large masses of material and the sample needs to be placed on a Mylar or similar thin film. Also, the emitted X-rays are absorbed to some extent by the sample deposit which require a size-dependent correction to the data.

This technique involves a collimated 18 MeV beam of α-particles from a cyclotron impinging on the thin samples which is mounted at an angle of 45 degrees to the incoming beam. The energy on the sample is made uniform by the use of an aluminium diffusion foil. The beam is collected by the Faraday cup and integrated to a precision of about 2% to give the total charge that passes through the samples. X-rays are passed into a detector and a 25 μm beryllium window and then converted into electrical pulses by a liquid nitrogen-cooled silicon(lithium) detector and associated pulsed-optical

feedback circuitry. Data are accumulated and analysed in a computer, giving a spectrum of characteristic X-ray and a smooth background (Shendrikor and Ensor, 1986).

1.5 OBJECTIVES AND SCOPE OF THE PRESENT STUDY

Various studies on dust pollution have been reported worldwide. Most of these studies however focussed on ambient airborne particulate matter in urban areas and in the vicinity of industrial areas. Work on dust analysis from bulk dust samples collected from and within industrial and manufacturing operations has been rather meagre and scanty. The present short-term study has been initiated to provide input to this knowledge gap.

1.5.1 Objectives

The main objectives of the present study are two-fold:

(a) To determine the mean particle size and particle size distribution in the dust samples

(b) To determine the presence or absence of selected toxic elements and their relative concentrations in bulk dust samples

1.5.2 Selection of Dust-type and Toxic Elements

The dust type chosen for this study is a composite of paint pigment and other raw materials used for the manufacture of solvent-based and water-based paint. The dust were sampled from two dust-collecting hoppers from a paint manufacturing plant in Shah Alam, Selangor Darul Ehsan, Malaysia.

A group of heavy metal elements were selected for the study on the basis of their potential toxicity to human health and their potential for inhalation deposition. These elements include arsenic, copper, lead and zinc. Non-digestible fractions of the dust samples would not be potentially toxic to human health (see page 59 on sample digestion).

1.5.3 Significance of Analysis on Bulk Dust Samples from Dust-Collecting Hopper

The significance and utility of bulk sampling from an industrial hopper cannot be underestimated for the following reasons.

(i) It allows useful comparison with information generated from ambient air sampling. This usually throws sufficient light as to the effectiveness of the dust-removal device.

(ii) Bulk sample analysis can provide information useful for improved dust-removal equipment design. An equipment can only perform efficiently if it is designed to remove dust of certain particle size.

(iii) Dust collected from the hopper can be used to fingerprint those that have escaped to the ambient environment. A more thorough and precise study can therefore be easily made from the bulk sample collected (source of emissions) as opposed to ambient air samples which are usually available only in small quantities and which involve longer sampling time.