CHAPTER 3

MATERIALS AND METHODS

3.1 SOURCE AND SAMPLING METHODOLOGY OF DUST SAMPLES FOR THE PRESENT STUDY

The industrial dust collected for the present study is a composite mixture of paint pigment obtained from a paint manufacturing plant in Shah Alam. The plant manufactures two types of paint, namely solvent-based paint and water-based paint. Dust is generated as a result of the production process steps which involve mixing of the various raw materials together in a high-speed mechanical mixing tank. The raw materials comprise primarily paint pigments which are the major particulate matter and other essential ingredients. Vacuum pumps are installed in the vicinity of the tanks to suck up the fugitive dust generated as the result of the mixing process. The dust is transported along overhead ducts and eventually collected in the dust hopper situated outside the factory. Plate 1 shows the overhead duct wherein the dust are transported from the factory to the dust-collection equipment. Plate 2 shows the plastic bag placed under the hopper for collecting the solvent-based pigment dust and Plate 3 shows the barrel under the hopper for collecting the water-based pigment dust. The plant has installed at its premises two dust-collection equipment of the pulse-air-jet type of bagfilter, one for collecting solvent-based pigment dust and the other for collecting water-based pigment dust. The dust is subsequently recycled and re-used. Plate 4 shows

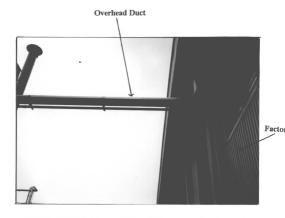


Plate 1 Overhead Duct for Transport of Dust from Factory to Dust-Collection Equipment

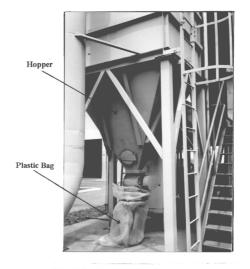


Plate 2 Plastic Bag collecting Solvent-Based Paint Dust from Hopper

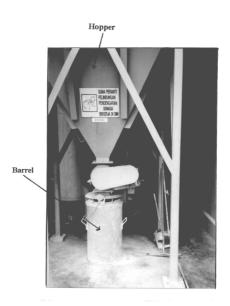


Plate 3 Barrel collecting Water-Based Paint Dust from Hopper

the dust-collection equipment for the solvent-based pigment dust and Plate 5 shows the dust-collection equipment for the water-based pigment dust.

There are two dust-collection equipment in the factory which cater for dust samples generated from the manufacture of solvent-based paint and water-based paint. Dust samples from the barrel placed under the dust-collecting hoppers were scooped up using plastic spoons. The dust samples were then placed in self-sealing polyethylene bags (7" by 7"). The date, time and dust-type from each dust-collecting hopper were labelled on the bags for ease of reference. The sampling was done at regular intervals on a weekly basis over a period of twelve weeks. This sampling frequency and durations, conditions and safety measures at the plant's premises as well as logistics arrangement agreed upon were strictly adhered to in order to keep confidentiality desired by the management board of the paint manufacturing plant.

3.2 PARTICLE SIZE ANALYSES

3.2.1 Instrumentation

A COULTER LS 230 particle size analyzer available at the Institute of Postgraduate Studies and Research, University of Malaya was used for measuring the particle size distribution of the dust particles. This light-scattering particle size analyzer uses the diffraction of laser light by particles to establish the particle size. The particle analyzer consists of four components: namely, the optical module, the fluid module, the computer, and the plotter. The computer belongs to the AccuComp Computer System. The LS Series Software programme is an integrated set of Microsoft Windows-based application programmes which control the LS Series instrument, process the data, analyse, plot graph and test results and print test reports. The COULTER LS 230

Factory Factory

Hopper

Plate 4 Dust-collection Equipment for Solvent-Based
Paint Dust

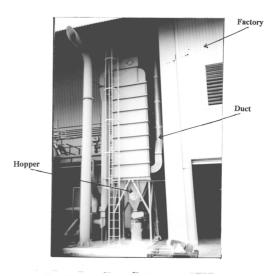


Plate 5 Dust-collection Equipment for Water-Based Paint Dust

Particle Size Analyzer has the advantages of speed, accuracy and ease of operation with minimum operator interference thereby reducing any risk of random error.

The physical specifications are listed in Table 1

Table 1 Physical Specifications for COULTER LS 230 Particle Size Analyzer

AmW operating power Wavelength 750 nm Type Tungsten-Halogen Ratings 6.0 V, 1.7A, 10W Output 150 Lumens at 2900K Particle sizing Range 0.04μm-2000μm Size channel 116 Run time 1-999 s Sample required 0.1-20g Fluid Module Ratings 240±20 V, 50/60 Hz, < 6A Capacity 1.7 L Pump flow rate variable speed 4-16 L/min Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample	Laser	T .	
Wavelength 750 nm	Laser	Laser power	5mW
PIDS lamp Type Tungsten-Halogen Ratings 6.0 V, 1.7A, 10W			4mW operating power
Ratings 6.0 V, 1.7A, 10W		Wavelength	750 nm
Particle sizing Range 0.04μm-2000μm Size channel 116 Run time 1-999 s Sample required 0.1-20g Fluid Module Ratings 240±20 V, 50/60 Hz, < 6A	PIDS lamp	Туре	Tungsten-Halogen
Particle sizing Range 0.04μm-2000μm Size channel 116 Run time 1-999 s Sample required 0.1-20g Fluid Module Ratings 240±20 V, 50/60 Hz, < 6A Capacity 1.7 L Pump flow rate variable speed 4-16 L/min Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample		Ratings	6.0 V, 1.7A, 10W
Size channel 116 Run time 1-999 s Sample required 0.1-20g Fluid Module Ratings 240±20 V, 50/60 Hz, < 6A Capacity 1.7 L Pump flow rate variable speed 4-16 L/min Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample		Output	150 Lumens at 2900K
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Sample required 0.1-20g Fluid Module Ratings 240±20 V, 50/60 Hz, < 6A Capacity 1.7 L Pump flow rate variable speed 4-16 L/min Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample		Size channel	116
Fluid Module Ratings 240±20 V, 50/60 Hz, < 6A Capacity 1.7 L Pump flow rate variable speed 4-16 L/min Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample		Run time	1-999 s
Capacity 1.7 L Pump flow rate variable speed 4-16 L/min Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample		Sample required	0.1-20g
Pump flow rate variable speed 4-16 L/min Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample	Fluid Module	Ratings	240±20 V, 50/60 Hz, < 6A
4-16 L/min Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample		Capacity	1.7 L
Suspension fluid water supply Tap water 19L/min, flowrate 38L/sample		Pump flow rate	variable speed
Tap water 19L/min, flowrate 38L/sample			4-16 L/min
38L/sample		Suspension fluid	water supply
		Tap water	19L/min, flowrate
6.8 bar(100psig) max pressure			38L/sample
			6.8 bar(100psig) max pressure
2 bar(30psig) min pressure			2 bar(30psig) min pressure

The COULTER LS 230 analyzer uses laser light with a wavelength of 750 nm to determine the size of particles with diameter range from 0.4 μ m to 2000 μ m by light diffraction. The laser radiation passes through a spatial filter and projection lens to form a beam of light. The beam passes through a sample cell where particles suspended in a liquid scatter the incident light in characteristic patterns which depend on their sizes.

This diffraction pattern is the scattered light intensity as a function of scattering angle.

A Fourier lens focuses any light striking any part of the lens at a given angle onto a single annular area on its plane of focus. As a result, the Fourier lens forms an image of the entire diffraction pattern of each particle.

The individual diffraction patterns from the many moving particles in the sample cell are therefore superimposed, creating a single composite diffraction pattern that reflects the contributions from all the particles in the sample cell. This composite diffraction pattern is then accurately measured by a stationary set of 126 detector arrays. A running average is computed of the flux patterns at every instant. An analysis of the resulting pattern yields the true particle size distribution of the sample.

Particles smaller than 0.4 µm cannot be effectively and accurately distinguished and measured by means of diffraction patterns described above. The COULTER LS 230 analyzer however, comes with an additional measurement assembly called the Polarization Intensity Differential Scattering (PIDS) assembly.

The PIDS assembly provides the primary size information for particles in the 0.04 μm to 0.4 μm grain size range and enhances the resolution of the particle size distribution up to 0.8 μm .

It is known that light can be decomposed into its vertically and horizontally polarized components. The difference in scattering of the two components depends on the ratio of particle size to the wavelength of the incident light. The PIDS assembly uses an incandescent tungsten-halogen lamp of three sets of vertically and horizontally polarized filters to provide polarized monochromatic light at three different wavelengths: 450 nm (blue), 600 nm (orange) and 900 nm (near infra-red). The light is focussed through a slit and is formed into a narrow, slightly-diverging beam that is projected through the PIDS sample cell. The PIDS assembly measures the pattern of the difference in scattering of the vertically and horizontally polarized light. It illuminates the particles sequentially with vertically and horizontally polarized light of the three different wavelengths. The three wavelengths of light permit three independent measurements of the PIDS effect at different ratios of particle size to light wavelength.

3.2.2 Methodology

The operating procedures of the COULTER LS 230 particle size analyzer are as described in the manufacturer's manual. The optical model is based on Fraunhofer law or principle for operation. For this study, the operations related to diameters (internationally agreed method of defining the mean and other moments of particle) and distribution statistics (particularly the relative distribution of volume of particles) are of great interest.

Prior to introducing the liquid samples of dust into the sample vessel, the contents of the liquid samples of dust in the beaker were stirred uniformly each time. A drop was first introduced into the vessel by means of a dropper: Approximately 1.7 ml of dispersant agent (sodium hexametaphosphate) was then added to aid in the uniform

dispersion of the dust particles as well as to prevent agglomeration of the particles. Subsequent addition of the dust samples were continued until an appropriate concentration level was attained as detected by the particle size analyzer. The instrument was then set to measure the particle size distribution of the dust samples. The run length was set at 60 seconds and pump speed at 48 for all measurements.

Figure 5 illustrates the analytical procedure in the particle size analysis described above.

3.2.3 Calibration

Prior to an analysis, the particle size analyzer was calibrated by measuring the COULTER LS Control GB 500 Nominal 500 μm glassbeads 5x19g(clean spherical glass particles) having a shape factor of 1.0. The calibration was necessary to ensure that the instrument was operating properly.

3.2.4 Sample Preparation

Approximately 50 g of dust samples were weighed and put in a 100 ml beaker. Deionized distilled water was added up to the 50 ml mark. The contents were stirred gently but thoroughly.

For the solvent-based dust-type, a layer of scum was observed floating on the surface after thorough stirring. About half an hour after stirring, this floating layer was gently skimmed off with a plastic spoon, taking care not to disturb the particles that have settled to the bottom of the beaker. This problem of agglomeration and scum formation was not observed for the water-based dust-type (see Appendix E: Addenda).

A dispersant agent, sodium hexametaphosphate (Calgon; 10 % w/v) was also prepared.

Approximately 10 g of sodium hexametaphosphate was weighed and dissoved in 100

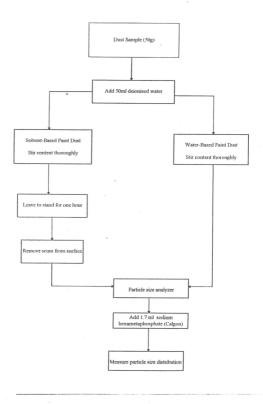


Figure 5 Flow Diagrams for Particle Size Analysis

ml of deionized distilled water. This dispersant agent helps to disperse the dust particles in the suspension fluid (water) of the sample vessel of the particle size analyzer.

3.2.5 Mathematical Formula for Particle Diameter

The COULTER LS 230 programme computes a number of statistical calculations such as particle size diameter, mode and median to characterize the particle size distribution. The statistics are calculated as they would be for a frequency distribution with the volume percent in a certain size channel being analogous to the frequency of occurrence of a certain value. Size channels in the COULTER LS 230 are spaced logarithmically and are therefore progressively wider in span towards larger sizes. Statistical calculations are based on the logarithmic center of each channel. The COULTER LS 230 series resolve particle size distributions into a number of channels. The channel center or diameter of a particle in that channel $d_{lc}(\mu m)$, is given as follows:

$$d_{lc} = \frac{antilog \; (log_{lower\; edge} + log_{upper\; edge})}{2} \; Equation \; 1$$

The derived diameter D(p,q) of particle size analyses can be based on the volume weighted mean diameter D(4,3), the surface weighted mean diameter D(3,2) or the arithmetic mean diameter D(1,0). As this study is partly concerned with the health effects of the pigment dust and therefore its potential inhalation deposition in the lungs, the volume weighted mean particle diameter was selected as the basis for particle size. This was calculated by the following general derived formula:

$$D(p,q) = \begin{bmatrix} \sum n_c \, d_e^{\ p} \\ \sum n_c \, d_e^{\ q} \end{bmatrix}^{\ l/p \cdot q} \quad Equation \ 2$$

where p,q = integer values

d_{lc} = the channel center

 n_c = the percentage of particles in the c'th channel

3.3 MULTI-ELEMENTAL DETERMINATIONS

3.3.1 Instrumentation

A BAIRD 2000 ICP-AES available at the Institute of Postgraduate Studies and Research, University of Malaya was used for the determination of heavy metals in the dust samples after sample pre-treatment by wet digestion technique. The BAIRD 2000 ICP spectrometer is equipped with a polychromator system for simultaneous multielemental analysis using photomultiplier tubes (PMT) as detectors. Forty element lines (mostly representing the most sensitive lines) are installed.

The physical specifications of the BAIRD 2000 ICP are listed in Table 2.

Table 2 Physical Specifications for the BAIRD 2000 ICP Spectrometer

Component/Parameter	Specification		
	•		
RF generator frequency	40.68 MHz		
Rated power output	1.5 kW		
ICP torch	Fused quartz(Fassel torch)		
Nebulizer	Glass pneumatic nebulizer in concentric		
	spray chamber		
Polychromator	1m Paschen runge		
Grating	1440 grooves/mm		
	400 nm/blaze angle		
Wavelength range	160-800 nm(vacuum)		
Dispersion	0.664 nm/mm 1st order		
	0.332 nm/mm 2nd order		
Detectors	Photomultipliers		
Argon gas	99.996% assay		
Inlet pressure	50 psi		
Readout/controller	BAIRD Minicamp MC 20S		
Computer workstation	BAIRD Plasmacomp Software V 5.0		
	IBM PS/2 compatible		

The spectrometer operates under vacuum and covers the analytical wavelengths from 160 nm up to 800 nm. The 40.68 MHz RF generator of the spectrometer is capable of delivering up to 1.5 kW of power output via a three-turn water-cooled copper coil through which a three-tube concentric torch (Fassel type) is placed. The sample solution is transported by a peristaltic pump to a Meinhard pneumatic nebulizer coupled with a concentric glass spray chamber.

The sample solution is nebulized into the centre of a gaseous argon plasma, sustained inside an induction coil energized with a high-frequency alternating current. The analytes dissociated into their atomic form and are excited to higher energy levels.

Relaxation of the excited species back to their ground states causes emission of radiation characteristic of the elements in the sample. The emitted light intensities at characteristic wavelengths, isolated with a diffraction grating, are measured with a photomultiplier tube (PMT).

An IBM PC-11 microcomputer is used for the control and operation of the spectrometer with the aid of the software (BAIRD Plasmacomp) provided. The pre-set slits of the selected element lines are sensitive to room temperature fluctuations. Regular alignment of the elemental spectral lines is performed automatically with the use of a reference spectral line from the built-in mercury light source and the mercury analytical channel installed in the spectrometer (see Appendix B:optimisation by mercury alignment).

The computer software allows the adjustment of a number of parameters such as the integration time, number of integrations, number of scan steps and the PMT high voltage which can be used to improve on the precision of the measurements. The software program is also capable of performing various other functions such as

computing the standard calibration curve coefficients, the inter-elemental correction factors, the analyte concentrations, the percentage relative standard deviation of the measurements and determining detection limits and performing analysis using autosamplers.

The detection limits for the BAIRD 2000 ICP-AES for some metals are listed in Table 3.

Table 3 Detection limits for ICP-AES for selected metals

Element	Detection limit (mg/L)	
Ag	0.003	
Al	0.020	
As	0.035	
Cd	0.002	
Со	0.003	
Cr	0.005	
Cu	0.002	
Na	0.020	
Ni	0.007	
Pb	0.025	
Sn	0.015	
Zn	0.002	

3.3.2 Sample Preparation and Treatment Apparatus

Teflon acid digestion bombs were used for dust sample digestion. The bombs are made up of a Teflon cup with lid enclosed in an outer steel casing.

Polycarbonate pipette of 10 ml capacity was used for measuring 10 ml of concentrated nitric acid (65% MERCK)

Precision micropipette with capacity $1000\mu L$ (GIBSON, France) was used to transfer specific aliquots of solution.

The water filtration set-up comprises a Millipore suction pump and a borosilicate glass filtration unit (SCHLEICHER & SCHNELL, Germany). The membrane filters(type HA and 45 mm in diameter) have 0.45 µm pore size (Milipore Corporation, USA).

Polypropylene bottles with screwed cap for storage of filtrate for subsequent ICP-AES analysis are of 250 ml capacity.

3.3.3 Standard Solutions and Reagents

A mixed standard solution of concentration 50 mg/L comprising elements arsenic, cadmium, cobolt, chromium, copper, nickel, lead and zinc was prepared from SPECTROSOL BDH Chemical Standard Solutions (1000 mg/L). Using a precision micropipette, 5ml of each standard stock solution of the above trace elements was taken and carefully transferred to a volumetric flask and 1 ml of concentrated nitric acid (65%, MERCK) was added to the mixed standards. The contents were then diluted up to the 100ml mark with ultra-pure deionized distilled water.

Standard solutions for calibration were prepared by suitable dilution with ultra-pure deionized distilled water from the mixed standard solution (50 mg/L) to obtain standard concentrations of the following range: 0.1 mg/L, 0.5 mg/L, 2 mg/L, 5 mg/L and 10 mg/L. The standard solutions prepared were each acidified with 1 ml of concentrated nitric acid (65%, MERCK)

A standard blank (acidified deionized distilled water) was also prepared .

3.3.4 Digestion Methodology

Two methods of digestion of dust samples using 10ml of concentrated acids of various types and mixtures were attempted: namely, the conventional oven and the microwave oven. The conventional oven used was of ULM 5001 MEMMERT model made in West Germany with ratings: 2000W, 230V, 8.70A, 50-60 Hz and temperature range between 30° C to 220° C. The range employed was between 120 °C to 130 °C.

The use of a microwave oven for sample dissolution was first reported by Abu-Samra et al., in 1975(Abu-Samra et al., 1975). Blust et al. (1985) reported on the use of a microwave oven in the sample preparation for AAS analysis.

The use of microwave oven for acid digestion of many solid samples is commonly regarded as a possible alternative for the classical open air hot plate digestion procedures and even the conventional oven. The reasons could possibly due to the many advantages that a microwave oven have that the conventional methods do not have. For instance, no acid is lost during the digestion so that less acid is needed, airborne contamination is eliminated and higher pressures can be achieved. This is because the vessels are closely tightened by means of caps. The vessels are usually made of Teflon which is very resistant to most acids. A considerably short time (e.g. 20 minutes) is

needed for the digestion process. Various acids have been attempted in this study. The microwave oven used for the above digestion trials is of the model QWave 3000 with oven specifications 220-240V, 10Amps, 50Hz and microwave power 1000W and microwave frequency 2450 MHz. The QWave 3000 Microwave digestion system includes a 486 computer along with the QWave 3000 DOS Software.

The results of using both digestion methods are summarised in Table 4.

Table 4 Summary of Dust Sample Digestion Results Using Microwave and Conventional Oven

Trial	Type of oven	Acids		Digestion	Remarks		
					conditions		
1	conventional	conc.	nitric	acid	sample 0.5g	no	complete
		10ml.			120 ° C, 2 hours	dissolu	tion
2	conventional	conc.	nitric	acid	sample 0.5g	no	complete
		10ml.			120 °C, 3 hours	dissolu	tion
3	microwave	conc. n	itric aci	d	sample 0.5g	no	complete
		10ml.			temp. control	dissolu	tion
		,			180 ° C, 30 min.		
4	microwave	conc. n	itric acid	i	sample 0.2 g	no	complete
		10 ml.			time to temp.	dissolu	tion
					140 ° C		
					ramp time 10min		
					dwell time 20min		
5	microwave	aqua re	gia		sample 0.2g	no	complete
		10ml.			time to pressure	dissolut	ion
					190psi		
					ramp time 7.5min		
					dwell time 20min		

6	microwave	conc. nitric acid	sample 0.2g	no complete	
		10 ml.	time to temp.	dissolution	
			150 °C		
			ramp time 3min		
			dwell time 17min	* •	
7	conventional	HNO ₃ +HCl+HF	sample 0.2g	appreciable	
		(2+6+2 v/v)	130 °C, 2 hours	dissolution	
		HNO ₃ +HF+HClO ₄	as above	substantial	
		(5+3+2 v/v)		dissolution	
		HNO ₃ +HCl	as above	appreciable	
		(2.5+7.5v/v)		dissolution	

However, the microwave oven and computer softwares developed technical problems (e.g. non-functional computer software, faulty artefacts) during several trials which made it impractical and inaccurate to adopt this mode of digestion any further for this study. Based on these comparative attempts, it was judged that there was no necessity for complete dissolution of the samples for metal extraction in concentrated acids insofar as the paint pigment and the defined objectives of this short-term study were concerned (see Appendix E: Addenda).

The conventional oven was then adopted for subsequent digestion purposes. Although this mode could achieve similar objective, it was certainly more time-consuming. The following dust sample digestion methodology was adopted. Dust samples of 0.2 g was carefully weighed using an analytical balance capable of reading up to four decimal places. The sample was then transferred into a Teflon digestion bomb in a stainless steel casing.

A total of 10 ml of concentrated nitric acid (65%, MERCK) was measured using a pipette and was introduced into the dust sample. The bomb was heated in a conventional oven at 120 degrees Celsius for 2 hours.

After cooling, the contents was diluted with deionized distilled water and filtered through a 0.45 μ m membrane filter (45mm diameter) using a Milipore filtration set.

The filtrate was collected and made up to 100 ml with deionized distilled water and kept in a polypropylene bottle for subsequent analysis by ICP-AES.

Sample blanks were subjected to the same treatment as the dust samples. Certified reference material NBS SRM 1633a coal flyash was also digested concurrently for method evaluation.

The overall analytical procedures for the analysis of arsenic, cadmium, cobolt, chromium, copper, nickel, lead and zinc in the dust samples are given in Figure 6.

3.4 ANALYTICAL QUALITY CONTROL PROCEDURES

In an environmental analysis involving field sampling and laboratory analyses, serious errors may be introduced during sample collection and storage and at every stage of the analytical procedures. Appropriate quality control was therefore necessary to ensure the reliability and accuracy of the analytical results obtained for this present study.

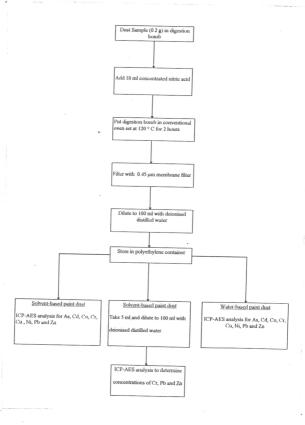


Figure 6 Flow Diagrams of the Analysis Schemes for Selected Elements

3.4.1 Quality Control in Field Samplings

3.4.1.1 Sampling Protocol

The quality and utility of analytical data depend critically on the validity of the sample and the adequacy of the sampling program (Keith et al., 1983). All aspects of a sampling program were planned and documented in detail. The sampling program considered criteria for the choice of sampling sites, the number of samples, the timing and the frequency of sample acquisition. A detailed description of the sampling procedure included the sampling methodology, labelling, container preparation, proper use of essential instruments for field measurements, storage and pre-treatment procedures.

3.4.1.2 Dust Sample Collection

Great care was exercised in this initial step to avoid introducing contaminated metals from sampling equipment and devices, sampling containers and other potential sources. Self-sealing transparent polyethylene bags (7" by 7") and separate plastic spoons for different dust-types were used for this study to avoid cross-contamination.

The dust samples were collected from the bulk to ensure representative samples were obtained. Dust along the upper rim of the barrel and on the hoppers were avoided during sampling as these dust are likely to be contaminated by airborne sources. The samples were quickly sealed to prevent possible contamination and clearly labelled.

3.4.2 Quality Control in Laboratory Analysis

3.4.2.1 General Precautions

To avoid the possibility of metal contamination in laboratory, all sample containers, pipette tips and sample storage vials were specially cleaned. New polypropylene containers and volumetric flasks were cleaned with concentrated nitric acid and thoroughly rinsed with distilled water and followed by deionized distilled water rinsing.

3.4.2.2 Analysis of Particle Size

Errors would inevitably result when the individual particles agglomerate to form a bigger cluster. To prevent particle agglomeration and to help in particle dispersion, sodium hexametaphosphate (Calgon; 0.1% w/v) was added to the sample vessel.

3.4.2.3 Analysis of Standard Reference Material

Certified reference material Standard Reference Materials (NBS SRM) from a reliable source such as the National Bureau of Standards (NBS) was used to test the accuracy of the analytical method employed. In this study, NBS SRM 1633a coal flyash was appropriately used since it is a species of industrial dust. The standard reference material was also used as a laboratory control standard for the verification of calibration of the analytical instrument (ICP-AES).

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3.4.2.4 Analysis of Reagents/Sample Blanks

For trace metal analysis, it is essential to verify the purity of the reagents used. The metal contents in a new batch of reagents was therefore individually tested before being used.

Sample blanks (10 ml concentrated nitric acid) were analyzed through the entire procedure of digestions and instrumental measurements.

Standard blanks (acidified deionized distilled water) were analyzed throughout the entire procedure of instrumental measurements.

3.4.2.5 Calibration with Standards

Prior to an analysis, the ICP-AES instrument was optimised. This was done by adjusting the mercury lamp until an almost centralised mercury curve was obtained (see Appendix B for the mercury alignment curve). The sensitivities of the ICP-AES instrument were determined and compared with historical values. A calibration curve was established by measuring a calibration blank (deionized distilled water) and five different dilutions of the standards were prepared in 0.1% ultra pure nitric acid.

The calibration was checked after every 10 determinations using the blank and a midrange standard. Re-calibration was done when the instrument drift exceeded the limits of \pm 10%. A standard reference material (e.g. NBS SRM 1633a) at appropriate dilution was used as an additional calibration check standard. Only results lying within the linear calibration range were accepted for further data computations, analyses and interpretations. For results lying outside the range, appropriate dilution of the sample solution was carried out and samples were re-analyzed following the standardized procedures as described above. It was observed during the ICP analysis that chromium, lead and zinc showed concentration values well beyond the range for the solvent-based sample solutions. The sample solutions were therefore diluted 20 times and the concentration values of the three elements were re-determined. No such excessive values were noted for water-based sample solutions.

3.4.2.6 Analysis of Replicates

The analysis of subsamples made from a single sample was done to assess the precision of the analytical methodology.

3.4.2.7 Accessories

Glasswares and accessories such as micro-pipettes and volumetric flasks were calibrated regularly.

3.5 DATA COMPUTATIONS AND STATISTICAL ANALYSES

3.5.1 Particle Size Diameter and Distribution Statistics

The solvent-based and the water-based pigment dust were described based on particle size and the relative distribitions. The computed values were: volume (% of the sample analyzed), diameters (μm) in terms of mean and standard deviation of the mean diameters and modal (peak) distributions of the particles.

In this study, the volume weighted mean diameter calculated by the COULTER LS 230 Particle Size Analyzer is defined by the following simplified equation:

$$D(4,3) = \frac{\sum n_c d_{lc}^4}{\sum n_c d_{lc}^3}$$
....Equation 3

where D(4,3) = the derived diameter D(p,q) when p=4 and q=3 (see earlier Equation 2 describing the volume weighted mean diameter) $d_{lc} = the\ channel\ center$

 n_c = the percentage of particles in the c'th channel

The statistics of the distribution were then calculated from the raw results (see Appendix A: Raw data for particle size analyses by COULTER LS 230 Particle Size Analyzer) using the volume weighted mean diameter D(4,3). The distribution statistics were expressed as the cumulative distribution of particle diameters (µm) at 10%, 25%, 50%(median), 75% and 90% of the total volume of the dust samples analyzed. This relationship was used to plot the cumulative distribution curves of particle diameters for weekly samples of both the solvent-based and the water-based pigment dust. For each week, the cumulative distribution curves of the two dust types were superimposed for comparison.

3.5.2 Multi-elemental Determinations

To determine the array of chemical elements absorbed by the dust samples, it was essential to perform a few trial runs of analyses by the ICP-AES under the specific optimised conditions. Guided by these preliminary results, major elements which were present in excessive concentrations were selected for further analyses. In this respect, the variations of each of these selected elements were analysed and discussed in relations to the dust types and sampling time on a weekly basis and/or average values of 12 weeks sampling duration. The relationships between the chemical compositions and concentrations of both the solvent-based and the water-based pigment dust were explored.

3.6 RELATIONSHIP BETWEEN PARTICLE SIZE DIAMETER AND CHEMICAL CONCENTRATIONS

Casual observations were made to relate these two aspects (as defined in the Objectives of this present study). The implications of this relationship were explored to dust pollution equipment and possibly towards human health.