

DISSERTATION

Optimized Determination of Elemental Concentrations in Airborne Particulate Matter Using X-ray Emission Techniques

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Thesis-related Publications

Part of the work presented in this thesis appears in the following publications and International Conference proceedings.

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2. Nikolai Dytlewski, Gunter Mank, Ulf Rosengard, **Samuel Bamford**, Andrzej Markowicz, Dariusz Wegrzynek, “*The International Atomic Energy Agency’s programme on utilization of accelerators*”, Nuclear Instruments and Methods (A), Vol. 562, 562 (2006) 650–655
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Abstract

Gravimetric and elemental concentration analyses have been carried out on airborne particulate matter sampled in an urban residential area. The data and derived information were generated from daily sampling of PM₁₀, PM_{2.5} and coarse particle fractions for a period of five months, including both winter and summer seasons. The aerosol-loaded filter samples were collected using the Gent sampler and the EU reference sampler LVS3 (KleinfILTERGERÄT) collocated at the same site. Whereas summer airborne particle mass concentrations were always below the PM₁₀ limit value of 50 µg/m³, winter mass concentrations had over twenty exceedances above the set limit value. Furthermore, coarse and fine particle fractions during summer were present in similar proportions at an average level of 10 µg/m³. On the other hand, winter particle fractions were predominantly in the fine fraction at more than twice the level of the coarse particle fractions. A field test investigation of the performance of the Gent sampler compared to the reference sampler showed that the Gent sampler does not qualify as an equivalent sampler according to the EU norm EN12341. However, by establishing the correlation equations between the two samplers for the various fractions, correction factors can be applied to the Gent sampler to make its readings comparable to the reference sampler. Much more information about the ambient atmospheric environment was obtained through the subsequent determination of elemental concentrations using X-ray emission techniques. The analytical techniques employed were the proton-induced X-ray emission (PIXE) analysis, and energy dispersive X-ray fluorescence (EDXRF) analysis. The optimized measurement conditions for PIXE were found to be at proton energy of 2 MeV, with 24 µm Mylar foil between sample and detector, and proton beam of 7 mm diameter. The PIXE quantitative method developed using the said conditions gave enhanced sensitivity for the low Z elements. The elements identified and quantified with PIXE analysis of the air filter samples were: Al, Si, S, Cl, K, Ca, Ti, Fe, Cu, and Zn. The EDXRF quantitative method was also optimized through a careful combination of secondary/polarizing targets and evaluation models. The EDXRF technique identified the same elements as by PIXE, and also Pb. Validation of the quantitative methods with the standard reference filter SRM 2783 gave reasonable agreement for most elements analysed, and for both techniques. The results obtained separately with the PIXE and XRF methods gave reasonable agreement for most of the elements. For other elements where agreement was not good enough between the two techniques, EDXRF showed a systematic bias. This bias when corrected for empirically, brought most of the elements into agreement. The elements Si, S, K, Ca, and Fe exhibited different concentration patterns for the different seasons, and served as possible indicators of sources of pollution in the area. Correlation tests performed on selected combination of elements, clearly pointed out some of the sources of pollution as emanating from dust and re-suspended dust particles, combustion from vehicles, and combustion from fossil fuels used for heating during winter. The quantitative procedures took into consideration the relevant needs and requirements for elemental concentration in air pollution studies. Consequently, the elemental concentration analysis gave additional information that could not have been possible simply with gravimetric analysis alone. A multi-stage, multi-orifice air impactor sampler "DEKATI" was modified to enable direct deposition of particulates on a reflector for subsequent analysis by TXRF.

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CHAPTER 1 GENERAL INTRODUCTION

1.1 The Atmospheric Environment

The Earth's atmosphere reaches over 560 kilometres from the surface of the Earth, and maybe divided into several distinct layers. The layer closest to the Earth's surface is referred to as the Troposphere, and extends from about 8 kilometres over the North and South Poles to 15 kilometres over the Equator. The Troposphere contains the largest percentage of the mass of the total atmosphere, and nearly all the earth's weather occurs there. Human beings and animals live within this layer, and its unstable nature (turbulent mixing) therefore makes tropospheric pollution very significant to the welfare of human beings and the ecosystem.

Environmental pollution issues continue to occupy the attention of governments, scientists, and concerned groups because of the adverse effects of pollutants on human health, ecology, ozone layer, visibility and climate. Pollutants are generated from both natural and anthropogenic sources, and manifest eventually in the terrestrial, aquatic, and atmospheric environment. However, the atmospheric environment is the media with far-reaching consequences and most susceptible to additional pollution from long-range transboundary pollutants. The atmosphere is a complex mixture of aerosols comprising mainly of gases and particulate matter. However, the focus of air quality research over the years has been on gas-phase species, with less effort placed on particle-phase characterization (1). "Particulate matter" (PM) is the generic term for a broad class of chemically and physically diverse substances that exist as discrete particles (liquid droplets or solids) over a wide range of sizes (2). Monitoring of airborne particulate matter is increasingly becoming an important issue due to population growth, urbanization and the emergence of mega-cities, industrialization, increasing mobility, public concern, and poverty. The properties of particulate matter vary greatly with time, region, meteorology, and source category. Hence, for air pollution assessment and effective management, it is vital to increase our understanding of the chemical properties of airborne particulate matter (APM) and their physical processes. Attempts therefore to provide a complete description of APM have included the study of their physical and chemical properties. Some of the important physical parameters of particles include:

- Number and number size distribution
- Mass and mass size distribution

- Surface area
- Shape
- Hygroscopicity
- Volatility
- Electrical charge

Some studies have been carried out on the significance of particle physical metrics, and their effects (3-7). Similarly, the important parameters considered in the chemical characterization (particle composition) of APM include:

- Elements
- Inorganic ions (sulphate, nitrate, and ammonium)
- Organic compounds (volatile and semi-volatile organic compounds)
- Carbonaceous compound (organic carbon and elemental/black carbon)

The above-mentioned parameters play different but collective role in affecting particle dynamics, behaviour and fate in the air, and also in the human respiratory tract. Hence, the set of parameters to be measured in any air pollution studies must be carefully selected in order to derive maximum information. This requirement consequently calls for an integrated approach to air pollution issues, where ambient monitoring is combined with emissions inventories and modelling as summarised in the schematics in Figure 1.

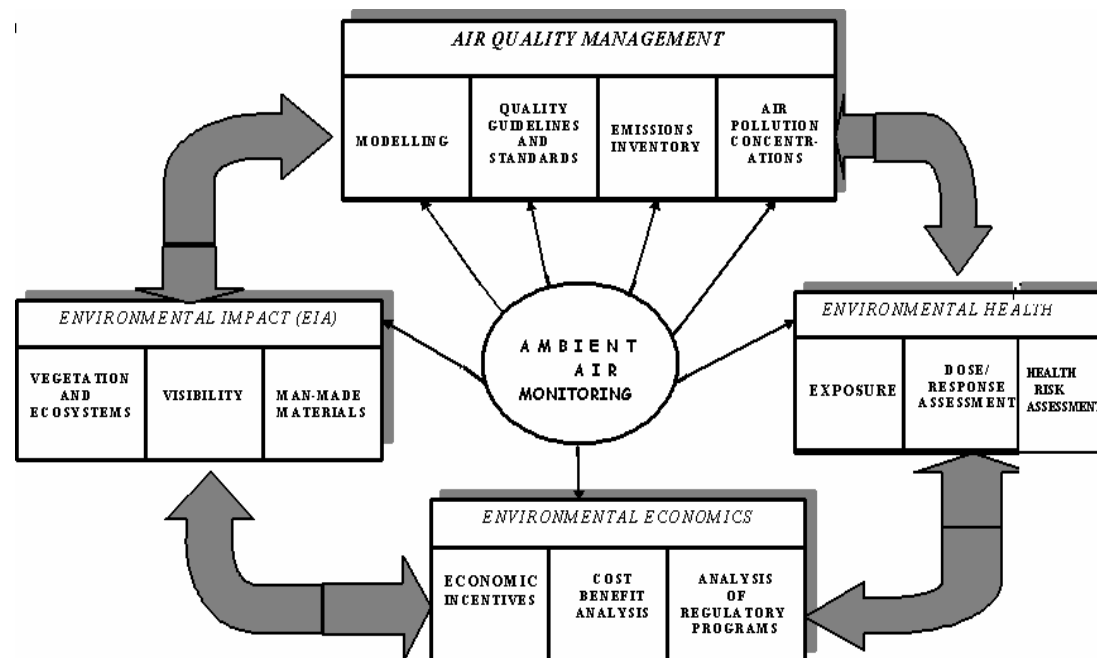


Figure 1 Ambient air monitoring objectives

This approach leads to the generation of data needed to characterize air quality, associated health and ecosystem impacts, develop control/mitigation strategies, study trends with time, and assess cost-effectiveness and progress of environmental protection programs.

Hence, the suite of measurements to be made in any monitoring program depends on the main goal of the study and the user-needs for the information. Ambient air monitoring is therefore a powerful tool and is utilized for one or more of the following objectives:

- To assess compliance with national ambient air quality standards
- To determine the impact of sources on ambient pollution levels
- To assess associated health and ecosystem impacts
- To observe pollution trends
- To determine the influence of long-range transboundary air pollutants
- To determine general background concentration levels
- To provide a data base for research/evaluation of
 - transportation planning
 - urban land-use
 - development and evaluation of abatement strategies
 - development and validation of emission and receptor models

Once the set of measurement parameters have been decided for a monitoring program, an equally important consideration are the air samplers and analytical tools to be used to generate the information required.

1.2. The current situation in APM analysis

1.2.1. Focus on PM mass concentration

Many environmental agencies charged with the responsibility of monitoring and managing atmospheric pollutants focus mostly on mass concentrations of airborne particulate matter. This situation is very predominant in many developing countries. This can be attributed to the fact that in setting standards for particulate matter, a size-specific indicator (PM_{10}) was chosen as the pollutant indicator. Such an indicator of the total mass of suspended PM of aerodynamic size less than or equal to $10\mu m$ include all the particles small enough to reach the tracheobronchial region, and penetrate even to the sensitive pulmonary region of the human respiratory tract (8). Consequently, most agencies having regulatory programs that seek to address issues

of compliance to air quality standards, have concentrated measurements on particle mass distribution and concentration. The smaller than 2.5 μm and the 2.5 to 10 μm size fractions are usually referred to as fine and coarse particulates respectively. Such measurements consider both primary particulates which are directly released into the atmosphere, and secondary particulates which are formed from atmospheric gases by absorption, condensation, and other processes. The USEPA maintains two separate ambient air quality standards for particulate matter. One standard deals with particles (PM_{10}) that are less than 10 micrometers (EAD) The second standard also addresses levels of “fine” particulates ($\text{PM}_{2.5}$) having particles less than 2.5 micrometers (EAD) (9 – 12). The European Union has also set its standard for PM_{10} , and is in the process of introducing a separate quality standard for fine particulate matter ($\text{PM}_{2.5}$) in the air (13 – 14). Despite the absence of similar official regulations in the other regions (Africa, Asia, and Latin-America) most countries have national regulations which are adoptions or adaptations of the air quality standards of either the USA or the European Union. It is worth noting however that, mass concentrations of airborne particulates may be the same in places, but effects of the particulates can be different. The toxic and polluting effects of PM are not influenced solely by particle size but also by its elemental and other chemical composition [15]. Mass concentration data alone (gravimetric analysis) is not sufficient in providing information for: (1) identifying sources of pollution, (2) apportioning contributions from the identified local sources, (3) determining influence from transboundary pollutants, and (4) determining contributions due to re-suspension of PM. Trace element concentrations of APM, is the additional data needed to derive the above-mentioned information. Nevertheless, the significance of trace element content in APM has unfortunately been underplayed. This additional information is already available from the same aerosol-loaded filters that were collected for gravimetric analysis. Hence, considering the effort and resources usually put into aerosol sampling, it is rather unfortunate that the available resources are often underutilized. An additional step of an appropriate analytical technique will furnish the much needed element concentrations in the APM. Trace element information is also needed for evaluation of health-related impact of APM.

1.2.2 Intercomparability of data

Some studies have already been done in different regions where both gravimetric and trace element analysis of APM in the atmosphere, have been carried out (10 – 12). However, even in such cases, additional problems exist in the intercomparability of results. Comparison and correlation of results is severely limited because of incompatible data sets. This situation arises from:

(a) The different types of aerosol environments studied

- traffic-influenced aerosols
- urban-influenced aerosols
- suburban background aerosols
- vegetation burning-influenced aerosols
- marine-influenced aerosols
- in-door aerosols

(b).The different sampling devices.

As a result of the diverse nature of the chemical and physical properties of particles in the atmosphere, there are many possible measurement procedures. The air samplers used for the collection of aerosols are varied, and employ different filters and collection techniques. These various design choices influence the particulates actually measured (16). Furthermore, one still has to grapple with sampling artefacts associated with the filter and deposited matter. Mass changes can occur due to loss of semi volatile components, such as certain organics and nitrates, through evaporation and sublimation during variable temperature and humidity conditions. Other contributing issues to such mass changes include adsorption/desorption of gaseous matter, gas to particle conversion, and chemical reactions. Consequently, different results can be obtained in sampling the same atmosphere due to the choice of air sampler used (17-18). Hence the need for a Standard Reference Sampler and Reference Method approach for PM_{10} and $PM_{2.5}$ as practised in the USA and Europe. Nevertheless, reference samplers suffer severe limitations in areas where the aerosol mass loadings are relatively low. In such situations the mass concentrations are close to detection limits, and sampling periods greater than twenty four hours are also required. This opens the door to other types of samplers, including sampling impactor samplers.

(c). The wide spectrum of parameters analysed

In examining the effects of air pollution, the parameters measured and monitored depend very much on the monitoring objectives, and the information to be derived from the monitoring data. Consequently, different data sets are generated thus limiting comparability of data. The parameters monitored include:

- total suspended particulates (TSP)
- size-fractionation (coarse, fine, and ultra fine)
- mass concentration
- chemical composition
- total number concentration
- trace elements
- single particles

(d). The varied analytical techniques

Variations due to different climatic environments and multiplicity of polluting sources lead to the generation of particles of different composition. Consequently, chemical characterization of APM is vital for pollution monitoring, assessment, management, and mitigation. The most important chemical properties of particles usually analysed are:

- Elemental composition
- Secondary inorganic ions
- Carbonaceous compounds
- Organic composition

The methods of analysis used may be categorised into Physical (instrumental) or Wet analytical techniques. The physical techniques include X-ray Fluorescence (XRF) Spectrometry, Proton Induced X-ray Emission (PIXE), Instrumental Neutron Activation Analysis (INAA), and Microscopy Analysis. Among the wet chemical analysis are techniques such as Ion Chromatography, Colorimetry, Atomic Absorption Spectrophotometry (AAS), Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICPAES), and Organic Analysis. A review of advances and challenges in analytical chemistry of the atmosphere has been done by M. F. Sipin et al (1). The above-mentioned (and other) analytical techniques employ different

physical principles, and have different sensitivities, resolutions, and analytical ranges. Hence results produced in utilizing such techniques for chemical characterization of APM cannot be easily compared.

(e) The inadequate availability of certified reference materials

In view of the diversity of air samplers and analytical techniques, the availability of appropriate certified filter standards would have gone a long way in facilitating comparability of data and results, through method validation and traceability using these standards. Unfortunately, there are very few suitable air filter standards available that serve the required needs like suitable elemental configuration, suitable concentration range, suitable substratum, acceptable analytical quality and completeness. One is therefore driven to collect standard-like specimens from different sources or create own sets of standard filters (19-20). Hence, issues of uncertainty estimation and accuracy in results of APM analysis have not as yet been resolved to the satisfaction of many practitioners in the business of PM monitoring and assessment.

1.3 Element measurement requirements and needs in APM

The two main sources of trace element release into the atmosphere are natural and human activities. Natural sources include soil dust, sea water spray, volcanic eruptions, vegetation and forest fires. Human activities such as mining, smelting, combustion of fossil fuels, waste incineration, industrial processes, agricultural operation, tyre and engine wear and cremation also release elements into the atmosphere. The majority of trace elements released from any source are generally associated with particulate material (21). The most common interest in elemental composition of particulate matter derives from concerns about health effects and the use of these elements for pollution source identification and apportionment. The trace elements of concern are those potentially harmful to the environment and human health. These trace elements are indicated in regulations such as the USEPA list of Hazardous Air Pollutants (HAPs) and the 1st and 4th Daughter Directives of the European Union's Framework Directives 96/62 /EC on ambient air quality assessment and management. Table 1.1.3.1 shows a list of elements of regulatory interest. Another category of trace elements are those that are needed, as trace element

signatures, for “fingerprinting” pollution sources. Such elements might be region specific, and their determination provides valuable information that is very significant in air pollution assessment, and mitigation. Table 1.1.3.2 also shows typical examples of such elements.

Table 1.1.3.1 Trace elements of Regulatory Interest

Element	Symbol	EPER	UK PI	US CAAA	US TRI
Number on list					
Arsenic	As	X	X	X	X
Cadmium	Cd	X	X	X	X
Chromium	Cr	X	X	X	X
Copper	Cu	X	X		X
Mercury	Hg	X	X	X	X
Nickel	Ni	X	X	X	X
Lead	Pb	X	X	X	X
Zinc	Zn	X	X		X
Antimony	Sb		X	X	X
Beryllium	Be		X	X	X
Boron	B		X		
Fluorine	F		X		
Manganese	Mn		X	X	X
Selenium	Se		X	X	X
Vanadium	V		X		X
Cobalt	Co			X	X
Barium	Ba				X
Silver	Ag				X
Thalium	Tl				X

EPER- European Pollutant Emissions Register

UK PI- United Kingdom Pollution Inventory

US CAAA- United States Clean Air Act Amendments (1990)/Air Toxics (HAPs)

US TRI- United States Toxic Release Inventory

Table 1.1.3.2 Trace elements of Interest in Pollution Source Identification and Apportionment

Element	Symbol	Sea Spray	Soil	Smoke/fires	Motor vehicles	Industry
Sodium	Na	X				X
Magnesium	Mg	X	X			X
Sulphur	S	X				X
Chlorine	Cl	X				
Calcium	Ca	X	X			X
Potassium	K	X		X		
Bromine	Br	X			X	
Aluminium	Al		X			X
Silicon	Si		X			X
Titanium	Ti		X			X
Iron	Fe		X			X
Nickel	Ni				X	
Carbon	C			X	X	X
Vanadium	V				X	X
Chromium	Cr					X
Manganese	Mn				X	X
Lead	Pb				X	X
Zinc	Zn				X	X
Copper	Cu					X
Strontium	Sr					X
Cadmium	Cd					X
Arsenic	As					X
Antimony	Sb				X	X

Since no single analytical technique is capable of detecting and quantifying all relevant inorganic and organic elements and compounds in the expected concentration ranges, a combination of complementary techniques are called for in compositional characterization of APM. Taking also into consideration the large numbers of samples that have to be analysed on routine basis, non-destructive analytical techniques offers a good option for elemental analysis. They have capability for simultaneous multi-elemental characterization, and sample preparation is simple and minimalistic.

1.4 Project Objectives and Strategy

Considering the foregoing review on the current situation in airborne particulate matter analysis, and the prevailing gaps and constraints in existing knowledge, the project objectives and approach may be summarised as follows:

1.4.1 Overall Objective

To develop methodologies that facilitates the generation of relevant, accurate, and comparable data on airborne particulate matter for air pollution assessment

1.4.2 Specific Objectives

1.4.2.1 To optimise the inherent strengths of selected energy dispersive x-ray emission methodologies, for the determination of element concentrations in airborne particulate matter.

1.4.2.2 To improve comparability of data generated by the GENT air sampler, through the assessment of its equivalence to the European reference sampler under EN12341.

1.4.2.3. To contribute to the improvement in the traceability of APM elemental results.

1.4.3 Project Strategy

In order to provide a framework which will facilitate the realization of the intended objectives, a work strategy was adopted as captured in Figure 2 below.

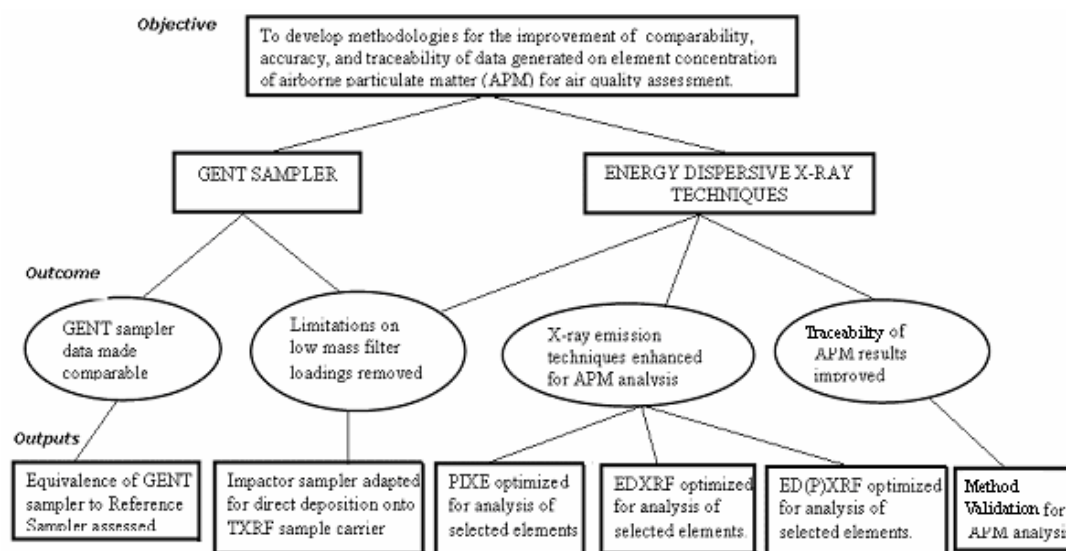


Figure 1.4 Project Strategy - Objective, Outcomes, and Outputs

Figure 2. Schematics showing the strategy for realization of project objectives

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CHAPTER 2: SAMPLING METHODS FOR AIRBORNE PARTICULATE MATTER

2.1 Introduction

There exists a variety of monitoring methods for the determination of mass concentrations of airborne particulate matter in ambient air. These methods involve either the gravimetric (manual) or continuous (automatic) methods of sampling. In the gravimetric methods, a pump system draws ambient air through a specially shaped inlet. The suspended particulate matter is inertially separated and then collected through an appropriate filter. These filters are conditioned and weighed in the laboratory, and can be subjected to physical or chemical analysis. The continuous methods, however, employ direct-reading instruments using different operating principles. They provide real-time concentrations. The different measuring techniques and instruments do give different values of ambient concentrations at the same location for the same PM. Consequently, regulatory agencies define precisely the type of particles to be measured, and designated instruments and methods to be used. Since particles being measured are irregularly shaped, an equivalent diameter is commonly used as a measurable index of the physical particle. For PM measurements and analysis, the frequently used diameter is the aerodynamic equivalent diameter. This is defined as the diameter of a standard density sphere (1000kg/m³ or 1g/cm³) having the same gravitational settling velocity as the particle being measured.

$$d_a = d_p \left(\frac{\rho_p}{\rho_0} \right)^{1/2} \quad (2.1)$$

Where d_a is the aerodynamic equivalent diameter (aed), d_p is the particle physical diameter, ρ_p is particle density, and ρ_0 is the standard particle density of 1000kg/m³ or 1g/cm³

Tropospheric aerosols are suspensions of small particles having aerodynamic equivalent diameters ranging from nanometers to micrometers. The range of diameters of common aerosol particles is between 0.01 and 100 μ m. The lower limit of 10 nm roughly corresponds to the transition from molecule to particle. Particles larger than 100 μ m normally do not remain suspended in air for a sufficient amount of time. Many studies have however shown that particles to be measured can be generally classified into two main size-based categories as fine and coarse particles (10). The most important particles with respect to atmospheric chemistry, physics, and health effects are in the 0.002-10 μ m range (2). The smaller than 2.5 μ m and the 2.5 to 10 μ m size fractions are referred to as fine and coarse particulates respectively. Figure 2.1 summarizes the particle size distributions and ranges of major concern in APM measurement and analysis (2). The organ in our body most sensitive to particle exposure is the respiratory system (3). The respiratory system can be divided into three regions from the point of view of PM sizes (Figure 2.2a). These are

1. Upper Airways region: includes nose, mouth, pharynx, and larynx
2. Tracheo-bronchial region: includes the lung airways from trachea to terminal bronchioles
3. Alveolar (pulmonary) region: includes alveoli sacs.

Hence, the particle sizes of concern have been designated to simulate the sizes of relevance as far as the human respiratory system is concerned. The American Conference of Governmental Industrial Hygienists (ACGIH) (40), the International Organization for Standardization (ISO) (5), and the European Standardization

Organization (Comité Européen de Normalisation, CEN) (2, 3) have adopted identical particle size-selective sampling conventions for inhalable, thoracic, and respirable aerosols (Figure 2.2). For pollution assessment, further compositional analysis is carried out on the coarse (2.5 to 10 μm) and fine (< 2.5 μm) size fractions to enable pollution source apportionment.

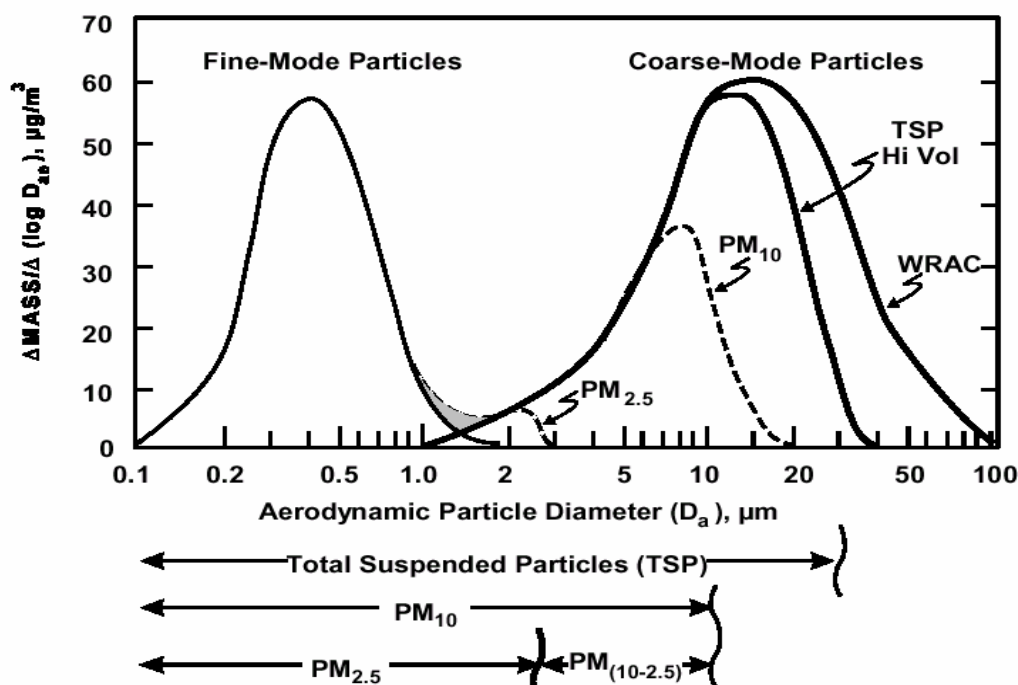


Figure 2.1 Coarse and Fine particle size ranges and distribution (2).

In human exposures by inhalation, three size-dependent particulate fractions are recognized. These determine where penetration and deposition occurs in the respiratory tract and a response is elicited. The inhalable fraction (aerodynamic diameter, $a_{\text{ed}} < 100 \mu\text{m}$) is during breathing; it is relevant to health effects anywhere in the respiratory tract. Particles greater than $10 \mu\text{m}$ are usually removed by the upper respiratory system. The thoracic fraction (the PM_{10} fraction) is the inhaled particle component which penetrates into the lung (*i.e.* the whole region below the larynx) and is important for asthma, bronchitis and lung cancer. Particles smaller than $5 \mu\text{m}$ are referred to as the respirable fraction and can penetrate deep into the alveolar region of the lung (*i.e.* includes the respiratory bronchioles, the alveolar ducts and sacs). PM that is deposited in the first two regions are caught in mucus and cleared by ciliary action. However, PM that is deposited in the alveoli region can dissolve and pass through the membrane into the blood or can be engulfed by macrophages. These lead to all kinds of adverse health effects.

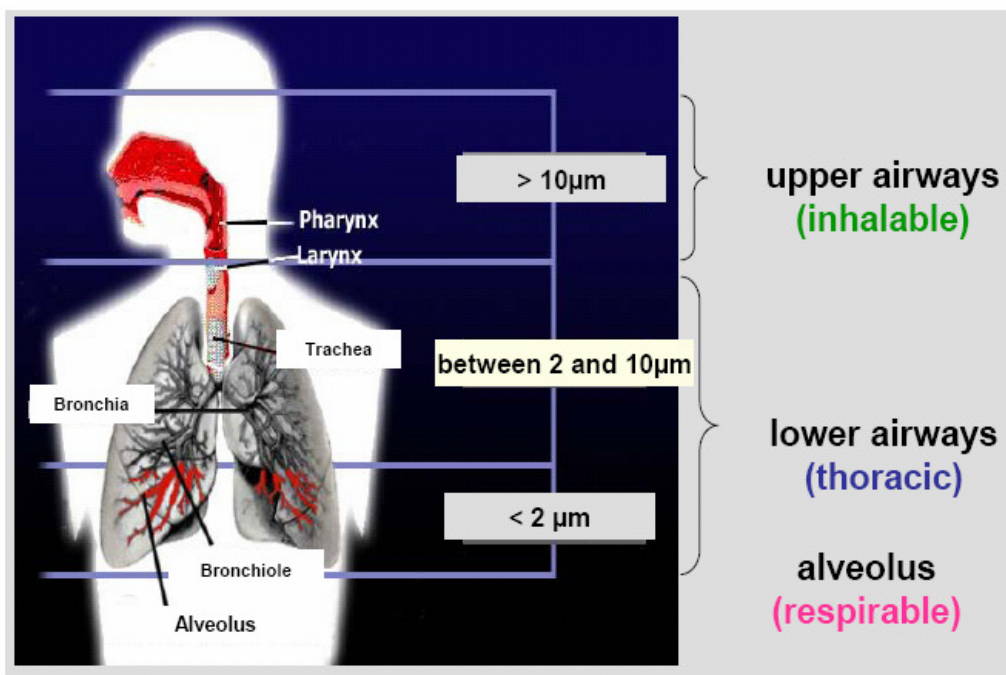


Figure 2.2a Respiratory system and particle deposition

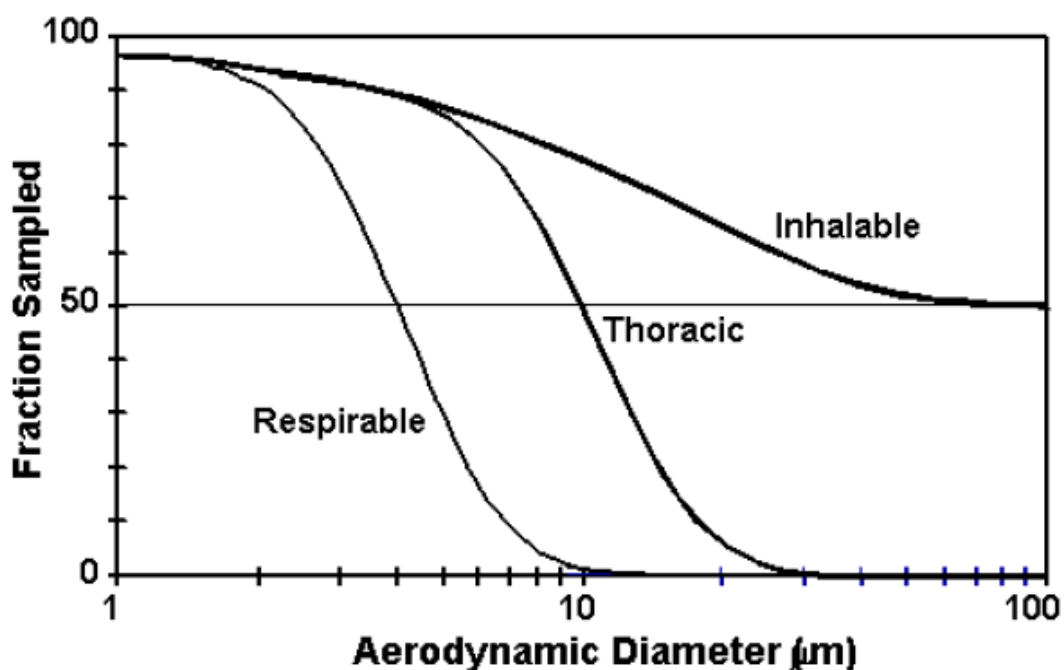


Figure 2.2b. ISO/ACGIH/CEN sampling conventions. An ideal sampler should have a sampling efficiency curve that matches one of these curves as closely as possible under all wind directions and velocities. The 50% cutpoints for the respirable and thoracic conventions are 4 and $10\mu\text{m}$ respectively

2.2 Reference and Equivalent methods

In order to generate data on airborne particulates that may be considered representative and applicable on a national or regional scale, national and international regulations/directives have been put in place. These regulations

essentially prescribe the particle size to be measured, the instrument to be used, how the monitor must be operated, and the data quality objectives. These requirements are intended to ensure that PM monitoring is carried out in a consistent and standardized way. This has led to the establishment of Reference and Equivalent methods in the USA and EU, which have served as the basis for methods existing in many other countries.

2.2.1 Reference Methods

The US EPA Federal Reference Methods (FRMs) have been specified for measurement, among others, of ambient PM₁₀ (6) and PM_{2.5} (7, 8). The limiting of sampling to particles <10 µm is justified by the wish to study only particles which have an effect on human health. The FRMs specify performance characteristics and operational requirements applicable to PM₁₀ and PM_{2.5} monitoring methods, and for PM_{2.5}, specify sampler design characteristics. The EPA PM-10 standard for environmental sampling specifies a sampler that has a 50% cutpoint (D₅₀) at 10 µm with a tolerance of ± 0.5 µm. This implies the aerodynamic equivalent diameter for which the efficiency of particle collection is 50%. With such a cutpoint, larger particles are still collected but with substantially decreasing efficiency but smaller particles are collected with increasing efficiency (up to 100%). The PM₁₀ regulation requires that for a sampler to be officially accepted as a PM₁₀ sampler, it must pass specified tests in a wind tunnel (6) and also meet additional specifications set forth in 40 CFR Part 53 (8). The intent was to allow flexibility in sampler design while maintaining a consistency in sampler performance. The FRM for particulates was updated to incorporate particles with aer less than 2.5 (Federal Register 1997). This PM_{2.5} regulation was set to similarly monitor the attainment of the national primary and secondary air quality standards for PM_{2.5}. However, in contrast to the 10µm cutpoint, the 2.5µm cutpoint occurs near a minimum in the particle mass distribution. This therefore minimizes differences between samplers with cutpoint biases. Both particulate samplers operate through gravimetric determination of airborne particles. They consist essentially of a sample inlet, collection medium (filter) and a flow regulated pump. Most filter based PM samplers utilize a size separation device to separate out PM of the size range of interest which is collected on a sample filter. The flow rate is controlled to a flow that will provide the correct PM size cut and capture an appropriate sample mass relative to the analytical detection limit, during the collection period of 24 hours. The most important variables in sampler design are: 1) properties of the size-selective inlet and sampler surfaces; 2) filter media and filter holders; and 3) flow movement and control.

In Europe, regulations for ambient air quality assessment and management are facilitated through the agency of the Environment Council of the European Commission. The Framework Directive of 1996 (9) defines and establishes objectives for ambient air quality, provides the basis for assessing the ambient air quality using common methods and criteria, in order to improve and maintain ambient air quality in the European Community. The Framework Directive is supported by four Daughter Directives which set the numerical limit values or target values, and alert thresholds for each of the identified pollutants. The Daughter Directives seek to harmonize monitoring strategies, measuring methods, calibration and quality assessment methods to arrive at comparable measurements throughout the EU and to provide for good public information. The First Daughter Directive (10) deals with limit values for NO_x, SO₂, Pb and PM₁₀ in ambient air, and came into force in 1999. The Directive requires that Action Plans for PM₁₀ be prepared, and general strategies for decreasing

concentrations of PM10 shall also aim to reduce concentrations of PM2.5. Table 2.1a and 2.1b summarizes the limit values for the airborne particulates.

Table 2.1a Limit values and indicative limit values for PM10, issued by European Union

A.1. Target	Averaging period	Limit value	Margin of tolerance	Date by which limit value is to be met
STAGE 1				
Protection of human health	24 hours	50 µg/m ³ PM10, not to be exceeded more than 35 times a calendar year	50 % of the entry in the force of this Directive, reducing on 1 January 2001 and every 12 months thereafter by equal annual percentages to reach 0 % by 1 January 2010	1 January 2005
Protection of human health	Calendar year	40 µg/m ³ PM10	20 % of the entry in the force of this Directive, reducing on 1 January 2001 and every 12 months thereafter by equal annual percentages to reach 0 % by 1 January 2010	1 January 2005
STAGE 2 (Indicative limit values to be reviewed in the light of further information)				
Protection of human health	24 hours	50 µg/m ³ PM10 not to be exceeded more than 7 times a calendar year	To be derived from data and to be equivalent to the Stage 1 limit value	1 January 2010
Protection of human health	Calendar year	20 µg/m ³ PM10	50 % on 1 January 2005 reducing every 12 months thereafter by equal annual percentages to reach 0 % by 1 January 2010	1 January 2010

The situation with PM2.5 particulates are as indicated in Table 2.1b

Table 2.1b Directives on PM2.5

PM _{2.5}	24 hours	No EU threshold but required to be measured and reported at representative locations.
	1 year	No EU threshold.

In 2005, the European Commission published the Thematic Strategy on Air Pollution (12), which was accompanied by a proposal for a Directive (13). The proposed Directive would consolidate four of the existing air quality Directives into one Directive, and introduce some changes that would also cover PM_{2.5} for the first time. For PM₁₀ measurements the reference method of the directive is described in CEN standard EN12341 (14), which essentially gives specifications of the size selective inlets or sampling heads to be used for sampling the PM₁₀ fraction of the particles. The standard refers to the collection of the particles on a quartz fibre filter at ambient temperature. The collected mass of particles is determined gravimetrically. The filters are conditioned before and after sampling under well-established temperature ($20 \pm 1^\circ\text{C}$) and relative humidity ($50 \pm 5\%$) conditions during 48 hours. For PM_{2.5} a reference method based on the gravimetric determination of the PM_{2.5} fraction is currently being standardised by CEN. There are several difficulties in the selection of an appropriate measurement method. It is impossible to generate a primary calibration standard of PM_{2.5}. Nevertheless, such a standard is needed to designate a reference size specific PM_{2.5} sampling head by convention. Furthermore, the possible loss of volatile particulate matter during sampling, which has been observed for PM₁₀, is known to be even more important for the PM_{2.5} fraction (15).

2.2.1.1. Reference Samplers

In the USA, a PM₁₀ Reference Sampler should meet the USEPA's performance specifications (8). This specifies a controlled flow wind tunnel, monodispersed fluorescently-tagged wet and dry aerosols, and an isokinetic nozzle aerosol sampling reference using 10 particle sizes and three wind speeds. This enables the determination of aerodynamic penetration through candidate PM₁₀ inlet. The regulation also essentially defines the cut-point d_{50} and slope associated with the PM₁₀ sampler. The penetration of ambient aerosols through the PM₁₀ inlet to the collection substrate is characterized over the ranges of operating conditions expected. This is used to determine the penetration efficiency or sampling effectiveness. The ambient PM₁₀ sampler penetration data curve should satisfactorily follow the thoracic convention (ideal PM₁₀ sampler penetration data EPA *CFR*, 2001e). For PM_{2.5} sampler performance characteristics, EPA's emphasis on the 2.5 μm cutpoint was more closely associated with separating the fine and coarse atmospheric aerosol modes than mimicking a respiratory deposition convention. EPA essentially defines the d_{50} and slope associated with the PM_{2.5} ambient air sampler in 40 *CFR*, Part 53. The d_{50} for the PM_{2.5} sampler is explicitly stated in the EPA standards as $2.5 \pm 0.2 \mu\text{m}$ aed. A number of PM samplers have been designated by the USEPA as reference samplers for the measurements of PM₁₀ and PM_{2.5}. Sampler inlets, however, may vary as to the method of fractionation. Inertial impaction, virtual impaction and cyclonic flow, are the commonly applied separation techniques used in most of these reference samplers (16 -18).

The EN 12341 standard refers to three different reference sampling devices: the Wide Range Aerosol Classifier (WRAC), the USEPA High Volume sampler (Sierra Andersen) and the Low Volume sampler (KleinfILTERgerät) (19).

2.2.2 Equivalent Methods

Due to the complex nature of particulate matter, testing the performance of PM monitoring methods is not a trivial issue. For comparability, collocation and

simultaneous measurements are made with the candidate method and a reference method for PM10 and PM2.5 methods. Comparability is shown for PM10 and PM2.5 methods when the linear regression parameters (slope, intercept, and correlation coefficient) describing the relationship meet the values specified in Table 2.2 below

Table 2.2 Some specifications for USEPA Federal Equivalent Method for PM sampling

SPECIFICATION	PM10	PM2.5	
		CLASS I	CLASS II
Precision of replicate measurements	5 µg/m3 or 7%	2 µg/m3 or 5%	2 µg/m3 or 5%
Slope of regression relationship	1±0.1	1±0.05	1±0.05
	0±5	0±1	0±1
Intercept of regression relationship, µg/m3			
Correlation of reference method and candidate method measurements	≥0.97	≥0.97	≥0.97

For methods for PM2.5, EPA defined three classes of candidate FEMs (Classes I, II, and III) based on the extent to which the method differs from the FRM, so that the nature and extent of the performance and comparability testing necessary can be more closely matched to the nature of the candidate method. Class I equivalent method is a filter-based method which is very similar to the sampler specified for reference methods, but with only minor deviations or modifications, as determined by EPA. Class II FEMs however have substantial modifications from that of a reference method. Classes I and II uses integrated sampling by filtration, followed by filter conditioning and gravimetric analysis. Class III equivalent methods are non-filter based methods, and includes alternative equivalent method samplers and continuous analyzers, based on designs and measurement principles different from those specified for reference methods. Any sampler associated with a Class II candidate equivalent method (Class II sampler) must meet all requirements for reference method samplers and Class I equivalent method samplers. In addition, Class II samplers are subject to additional tests and performance requirements of full wind tunnel test, loading test, and volatility test. Specific requirements for designation as a Class III FEM are not provided in the CFR because of the wide range of technologies that might be employed for PM2.5 mass measurement. As a result, specific Class III FEM testing and other requirements would be developed by EPA on a case-by-case basis. Class III FEMs may be required to undergo any or all of the testing required for validation as an FRM, Class I FEM, and Class II FEM. Tests may be at multiple locations and in different seasons, as well as additional testing specific to the sampling technology (20).

Reference and equivalent methods (for PM10 and PM2.5) are determined in the European Community in accordance to the EU Norm EN12341. The equivalence

is established essentially from field test measurements, by determining the degree of comparability between 1) two collocated specimens of candidate samplers (using uncertainty measurements), and 2) collocation of a candidate and reference sampler (using the so-called reference equivalence function). For comparability of candidate samplers, the test statistics of uncertainty at the 95 % confidence level should be $\leq 5 \mu\text{g}/\text{m}^3$ if the average concentrations obtained from the duplicate measurements are $\leq 100 \mu\text{g}/\text{m}^3$. On the other hand if the average concentrations are $> 100 \mu\text{g}/\text{m}^3$ then the said uncertainty must be $\leq 10 \%$. For comparability between candidate and reference sampler, the reference equivalence function should be bounded within a two-sided acceptance envelope of $\leq 10 \mu\text{g}/\text{m}^3$ if the reference concentration levels are $\leq 100 \mu\text{g}/\text{m}^3$ or within $\leq 10 \%$ at reference concentration levels $> 100 \mu\text{g}/\text{m}^3$.

2.2.2 1. Equivalent Samplers

PM10 and PM2.5 samplers designated as equivalent samplers fall broadly into two main categories. The first category is the filter-based manual samplers. Particle fractionation may be achieved either by inertial impaction, or by the use of cyclone particle size separators unto filter substrate. The other category of equivalent samplers can be described as automated or continuous samplers, applying different mechanism in the particle measurements. Most of them work either on the principle of the oscillating microbalance (Tapered Element Oscillating Microbalance (TEOM) sampler) or the absorption of beta radiation (Beta gauge samplers). These samplers enable the provision of on-line data with higher time resolution. A list of USEPA designated reference and equivalent methods/samplers are available on-line (21). Even though a compiled list is not similarly available for samplers to be used in the European Community, there exist individual test reports on some approved equivalent samplers in Europe (22, 23).

2.3 Air samplers used for this work

Three different types of air samplers were used for this work. The main sampler of interest is the GENT sampler, which is a low volume, filter-based sampler having a stacked filter unit for simultaneous, sequential collection of coarse and fine airborne particulates. The second sampler was the EU low volume reference sampler LVS3 (KleinfILTERgerat). It was used for the purpose of assessing the comparability of the GENT sampler to the EU reference method for PM10 and PM2.5. The third sampler used was the Dekati multi-stage impactor sampler, for simultaneous collection of PM10 and PM2.5 fractions. The sampler was adapted to investigate the possibility of direct deposition of airborne particulates unto suitable impaction substrate for subsequent elemental analysis with x-ray emission techniques.

2.3.1 The GENT sampler

The Gent Stacked Filter Unit (SFU) PM10 sampler was designed by the University of Ghent, under a contract from the International Atomic Energy Agency (IAEA). The sampler has been supplied to many Member State countries of the IAEA, and is used extensively in many regional and national projects of the IAEA Member States. The sampler system is described in detail by Maenhaut (24)]. The “Gent” SFU Unit is based on sequential filtration through two Nuclepore® filters with different pore sizes. It is equipped with a pre-impaction stage that acts as a PM10 inlet, and a stacked filter cassette produced by the Norwegian Institute for Air Research (NILU).

The filter cassette utilizes two 47-mm diameter Nuclepore polycarbonate filters with pore sizes of 8 μm and 0.4 μm that are placed in series. The first Nuclepore filter ("coarse") has a 8 μm nominal pore size, and is Apiezon-coated to prevent blow-off. At a flow rate of 15-16 lpm, this gives a 50% efficiency cut-off at 2 μm ead. The coarse filter collects the 2-10 μm and particle size fraction. The second filter is also a Nuclepore filter with a nominal pore size of 0.4, and collects the fine filter particles <2 μm and that passes through the first coarse filter. One of the samplers manufactured in Belgium was compared with one built to the same design in the U.S.A. (25), and the results showed relatively good agreement. Figures 2.3 a-b show the sampler system, and blown-up diagrams of the SFU. The air volume flowing through the sampling line can be derived from the rotameter or from the integrating volume meter. The volume meter gives a more accurate reading of the air volume sampled. In order to maintain the required volume flow rate between 15-16 lpm, the length of the POLY-FLO tubing connection between the SFU and pump should be shorter than 100m. The sample collection period can be operated manually or controlled by a programmable 24-hour time switch.

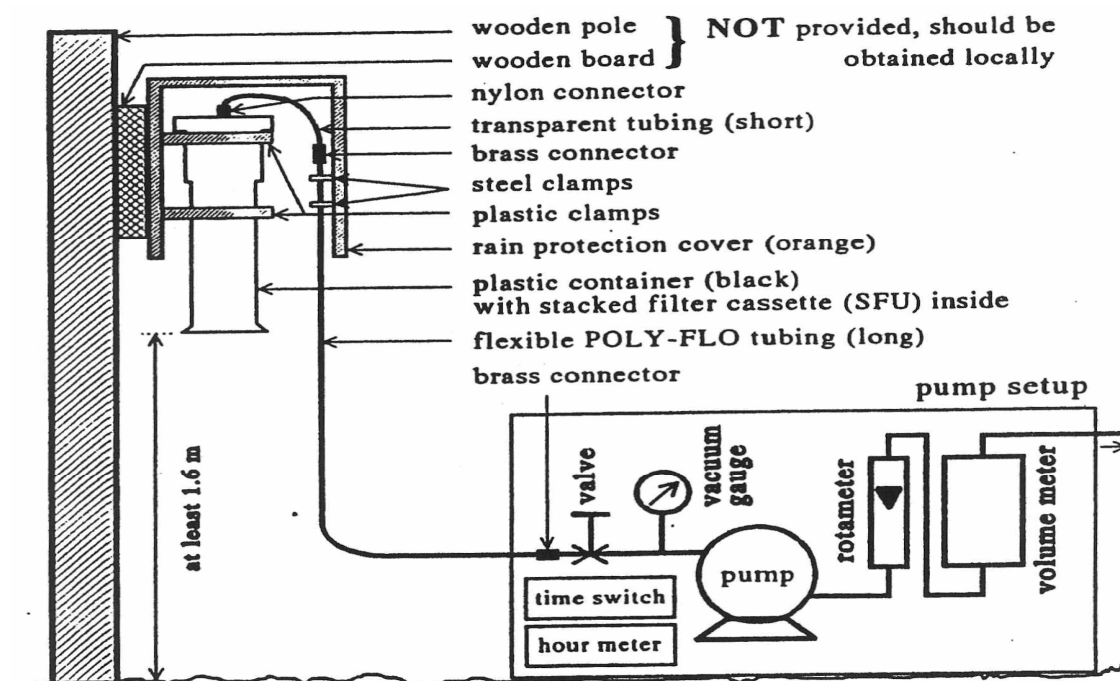


Figure 2.3 a. Schematic diagram of the SFU sampling line[24]

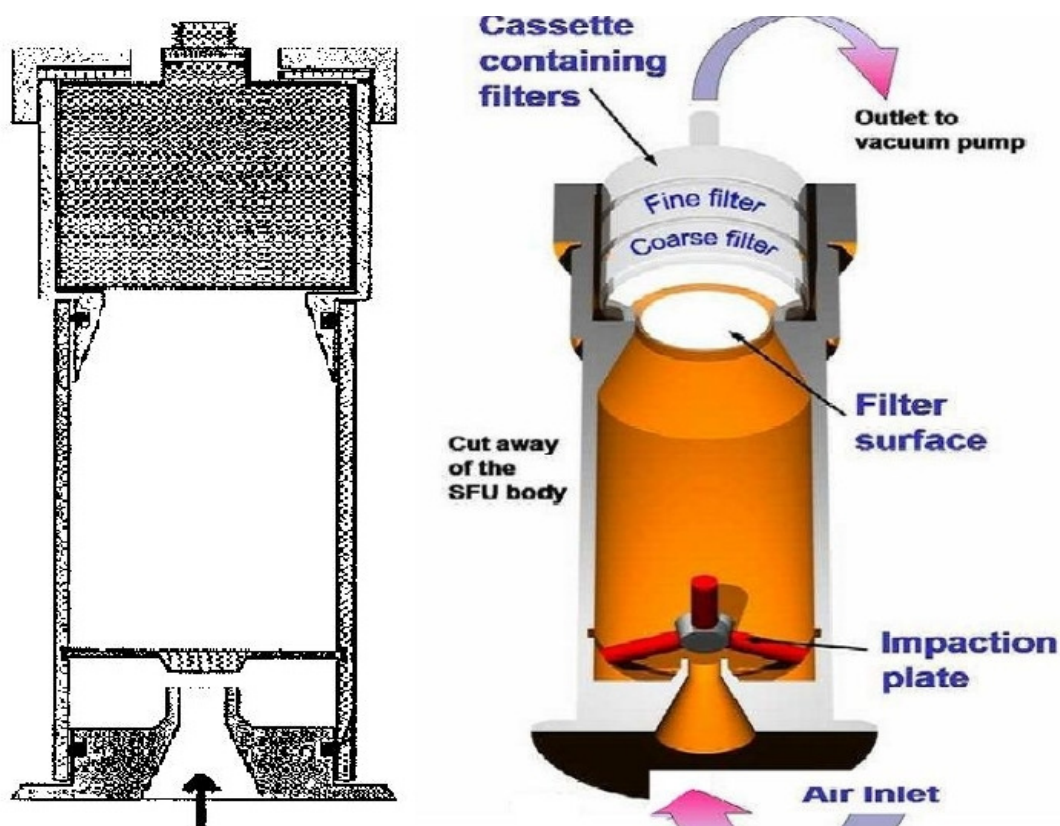


Figure 2.3b Blown-up cross-sectional view of the SFU Unit of the GENT sampler
2.3.2 The LVS3 Reference Sampler (Kleinflitergerät)

The flow-controlled LVS3 low-volume sampler used as reference sampler, is as shown in Figures 2.3c. The PM10 inlet is equipped with a preliminary separator at which particles with an aerodynamic diameter of more than 10 μm are separated out of the air sucked into the instrument, so that only the respirable fraction is collected on the filter. The sample inlet is according to the specification in European Standard EN 12341, Annex B.1. The PM10 inlet and the filter holder are screwed together to ensure gas-tight sampling. Both are outside the main sampling instrument and are connected to the sampling system by a straight tube. A sensor mounted on the tube measures the outside air temperature during sampling. The sampler also has a microprocessor and built-in software support. With this, temperature and the air pressure values are constantly recorded. The device consequently converts the collected air volume into so called standard conditions (0 °C and 101.3 kPa). This model is equipped with a 4 m³-vacuum pump, and the flow rate amounts to about 3.5 m³/h with a glass fibre filter inserted. It has changeable impaction unit for collection of different particulate fractions. After 24 hours of sampling, the filter is accordingly conditioned for gravimetric and other analysis.



Figure 2.3c. Kleinfiltergerät (LVS3) Reference sampler

2.3.3 The Dekati PM-10 Impactor Sampler

There exist significant limitations in the reference methods of sampling air particulates when the filter mass loadings are very low. In such cases, impactor samplers have been used for both size fractionation and subsequent elemental analysis. The Dekati PM-10 sampler is a multi-stage, multi-orifice cascade impactor which selectively collects airborne particles of different aerodynamic particle sizes. The 50% cutpoint (D50) of the sampler have been selected so that PM10, PM2.5 and PM1 concentrations can be determined simultaneously. Particles are collected on impactor substrates in four successive impactor stages. The first PM-10 stage removes particle larger than 10 microns off the particle stream. The second PM-2.5 stage collects particles smaller than 10 microns and larger than 2.5 microns. The third PM-1 stage collects particles smaller than 2.5 microns and larger than 1 micron. A back-up filter after the impaction stages constitutes the fourth stage, and collects all particles smaller than 1.0 μm . The impactor substrates are analysed gravimetrically or chemically after the measurement. Dekati PM-10 Impactors are available with flow rates of 10, 20, and 30 lpm. Figure 2.3d shows the Dekati PM-10 Impactor sampler, and a scheme of its operational principles.

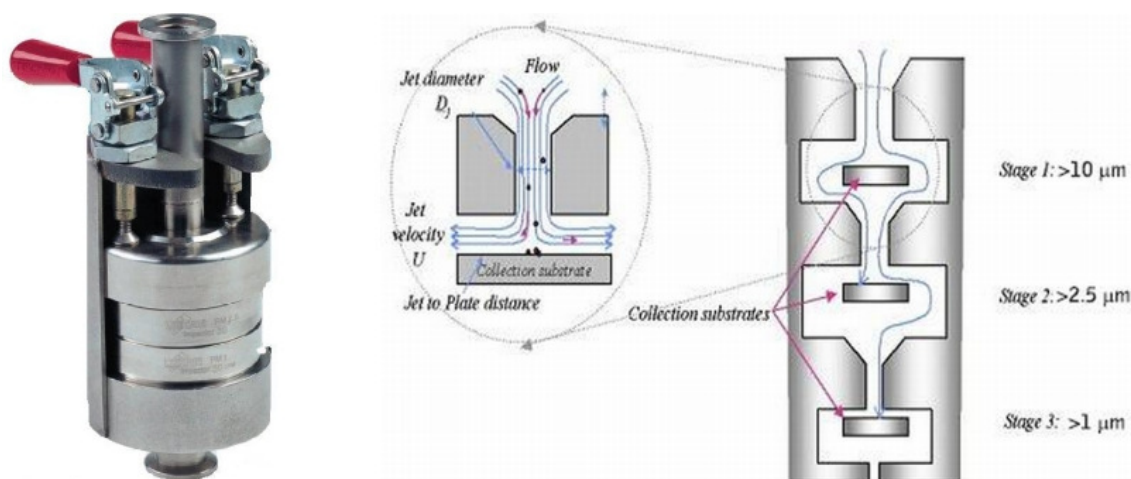


Figure 2.3d The Dekati PM-10 Impactor Sampler [26]

The Dekati PM-10 impactor sampler used in this work was modified to enable the deposition of particulate matter on a 30 mm impactor substrate, suitable for subsequent direct analysis by both TXRF and PIXE techniques.

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CHAPTER 3: ANALYTICAL TECHNIQUES FOR CHARACTERIZATION OF ELEMENTS IN AIRBORNE PARTICULATE MATTER

3.1 Introduction

Significant efforts are required (time, instrumentation, expertise, money) in aerosol sample collection and data generation. It is therefore unfortunate to focus mainly on mass concentration measurements in air pollution studies. Subsequent and additional determination of the chemical composition of aerosol particles is needful, and of interest in deriving maximum information from collected aerosols. This information helps essentially to: 1) identify potentially toxic components, 2).enable pollution source profiling and apportionment, and 3) augment the assessment of the effects of PM on health and welfare. In general, no single analytical method is suitable for measuring all chemical species of interest in airborne particulates. It requires a combination of methods to address the monitoring objectives, in an optimized manner. The analytical methods for characterization of chemical composition of airborne particles fall under two main categories. The first set of methods is laboratory-based, and carries off-line analysis on samples collected from the field (sampling sites). The other set of methods includes techniques which enable real time, on-line measurements. The parameters commonly determined include elements, water soluble ions, organics, and carbon. However, the interest in this work lies in the determination of elemental concentration of airborne particulate matter, for bulk particle characterization. Analytical techniques available for the determination of elemental concentrations in aerosol samples include (1-3):

- X-ray Fluorescence Spectrometry (XRF)
- Particle Induced X-ray Emission Spectrometry (PIXE)
- Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)
- Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
- Neutron Activation Analysis (INAA)
- Scanning Electron Microscopy (SEM/XRF)

The above techniques have the advantage of having simultaneous, multi-elemental capabilities. Some of these methods can be complemented by the use of single element techniques such as

- Flame Atomic Absorption Spectroscopy (FAAS)
- Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)
- Anodic Stripping Voltammetry (ASV)

Nevertheless, AAS, ICPAES, and ICPMS techniques require the digestion of the aerosol-loaded filter in an acidic solvent, and introduction of the dissolved sample to the instrument for analysis. However, due to the complex nature of ambient particles, it is difficult to achieve complete and thorough dissolution of the particles. Furthermore, the dissolution process also has the risk of introducing contaminants, and sample losses. These factors combine to reduce accuracy in the analysis of elemental concentrations requiring dissolution of the samples. Besides, for large quantities of samples, this sample preparation requirement is time-consuming, and

expensive. Consequently, non-destructive techniques are preferable in the analysis of elemental concentrations in airborne APM.

Even though INAA is a non-destructive method, it does not enjoy much patronage in its use in the routine analysis of APM. This can be attributed to the facts that the aerosol-loaded filter must be folded and sealed in a plastic holder, and then bombarded with a high neutron thermal flux. Consequently, the accessibility to a reactor facility becomes an issue. The neutron bombardments activate and transform elements into radioactive isotopes that emit gamma rays, which are discrete and characteristic of the emitting isotopes. The measured intensities of the gamma rays are proportional to the amounts of elements present. The folding of the filters and the radioactivity of the activated samples makes it difficult to reuse the samples for further analysis. In addition, INAA is not capable of determining certain important elements such as silicon (Si) nickel (Ni), tin (Sn) and lead (Pb). Detailed description of analysis of airborne particulates using neutron activation analysis can be found elsewhere (4)

PIXE and XRF (5,6) methods are the most widely used because they are relatively more accessible to many users, are non-destructive techniques, and require no sample preparation. Filters remain intact after analysis and can be used for additional analysis by other methods. PIXE and XRF techniques can quantify the concentration of elements with atomic numbers ranging from 11 (sodium) to 92 (uranium). These techniques have been made available to many Member State countries of the International Atomic Energy Agency through their Technical Cooperation program. In this work the analytical methods used for the determination of elemental concentration in the collected aerosol samples are:

1. Proton Induced X-ray Emission (PIXE) analysis
2. Energy Dispersive (Polarized) X-ray Fluorescence (ED(P)XRF) analysis

3.2 Proton Induced X-ray Emission (PIXE) method

The acronym PIXE originally indicated particle-induced X-ray emission. However, since most of the work done and reported used proton beams for irradiation, the acronym has implicitly been accepted as proton-induced X-ray emission (7). One of the common applications of most PIXE facilities is in the area of determination of elemental concentrations in airborne particulate matter (8-12). PIXE is one of the variants of X-ray emission techniques. In this technique a beam of energetic protons are accelerated onto a target (sample) of interest. This causes ionization and atomic excitation, leading to the ejection of inner-shell electrons from atoms in the target. The inner vacancies created are filled by outer shell electrons resulting in the emission of X-rays which are characteristic of the target's elemental composition and concentration. The X-ray spectrum is usually recorded in an energy dispersive mode using a Si(Li) detector. The energies of the emitted X-rays are used to identify the atoms or elements in the target, and the X-ray intensities used to determine the element concentration. The PIXE facility, like any accelerator-based facility, consists essentially of ion sources, an accelerator system, a beam transport system, end stations (scattering chambers), and computer control system as depicted in Figure 3.1 below:

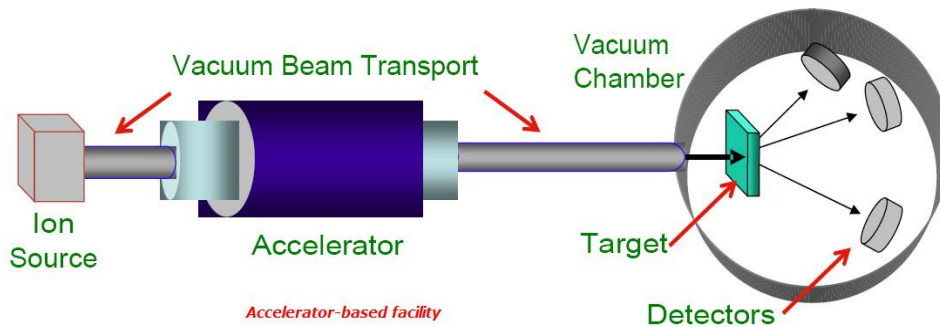


Figure 3.1 Essentials of an Accelerator-based Facility(13)

3.2.1 ***Ion sources***

The ion source is a device which serves the purpose of producing, focusing, accelerating, and emitting ions as a uniform and narrow beam. The ions may be either positive or negative ions produced from neutral atoms. There are essentially three types of ion sources: the duoplasmatron, the negative sputter ion source, and the radio frequency (RF) ion source. However, the facility used had only the duoplasmatron source installed. In the duoplasmatron configuration, a low pressure arc is produced between a cathode and an anode. The cathode filament emits electrons into a vacuum chamber containing small quantities of hydrogen gas (in the case of proton beam). The gas becomes ionized through interactions with the free electrons from the cathode, forming plasma. A very dense plasma is then created in the vicinity of the extraction aperture by means of a mechanical (conical intermediate electrode) as well as a magnetic constriction (using magnetic mirrors). Application of a highly negative potential to the extractor enables plasma penetration through the anode aperture, and the emission of proton ion beam. A Duoplasmatron ion source can produce either a positive or a negative ion beam depending on the placement of the intermediate electrode

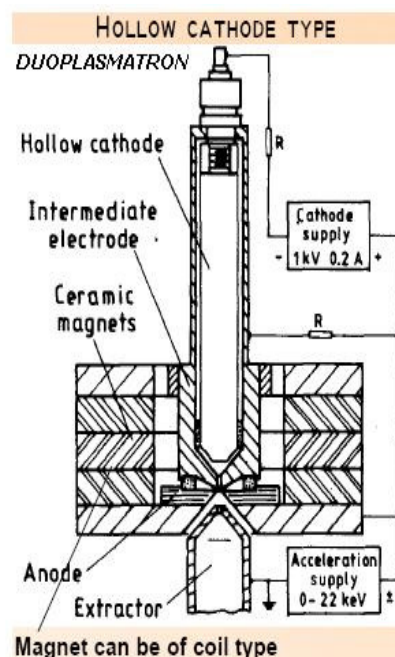


Figure 3.2 Duoplasmatron ion sources (14, 15)

3.2.2 Accelerator System

An accelerator facility is usually categorised by the voltage generating technique of its accelerator system. Figure 3.3 shows the schematic diagram and picture of the PIXE facility used in this work. It has links to two different accelerator systems: A Van de Graff accelerator and a Tandetron accelerator in tandem configuration.

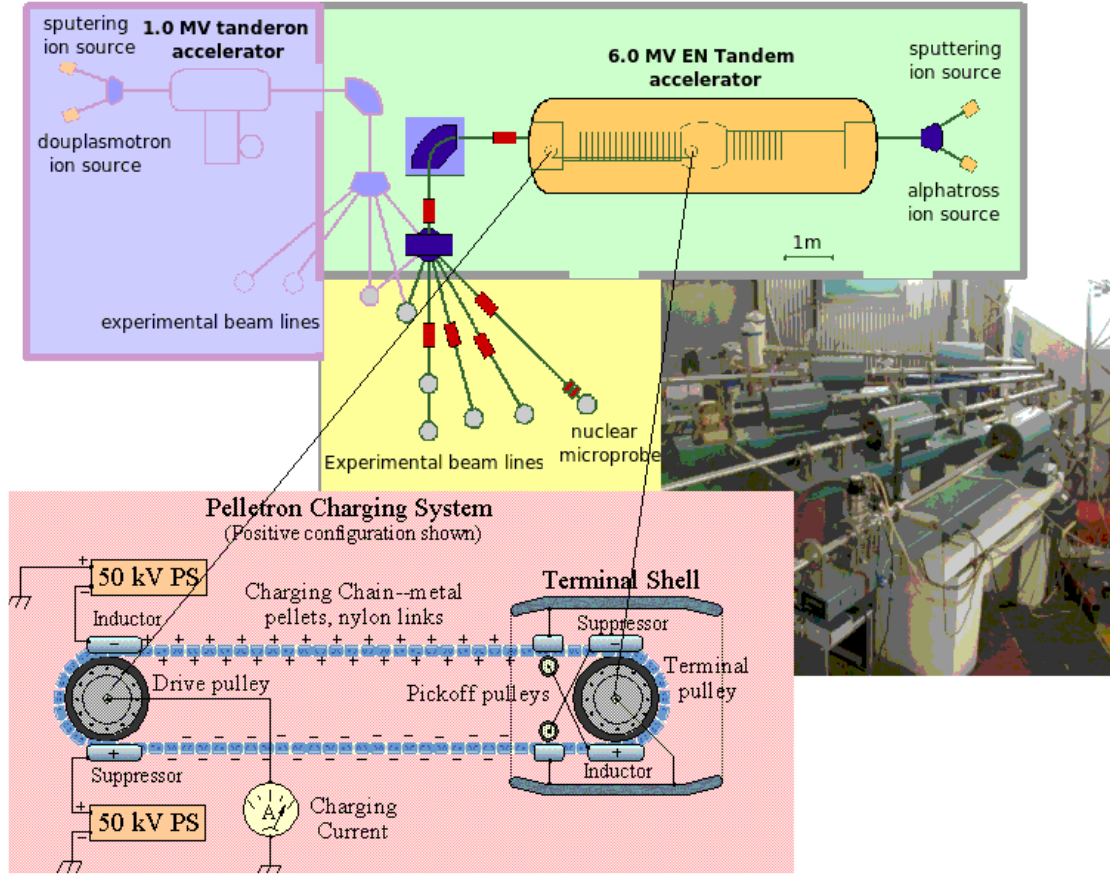


Figure 3.3 PIXE beamline linked to two accelerator systems

In the Tandem configuration, negative ions are extracted from the ion source, mass/energy analyzed by the low energy injection magnet and then injected into the accelerator. The accelerator structure is enclosed in a pressurized tank (SF₆) and contains corona rings to homogenize the electric field. The negative ions from the low energy end of the acceleration tube lose electrons, through charge exchange processes, in the stripper canal of the positively charged terminal at the centre of the accelerator system. The beam is now composed of positive ions which are accelerated a second time towards ground potential, along the high energy end of the acceleration tube. The final energy E of the particles will depend on the extraction voltage V of the ion source, the charge q of the particle and the terminal voltage of the accelerator V_T according to the equation:

$$E = q(V + V_T)$$

3.2.3 Ion Beam Transport System

The ion beam transport system serves the purpose of providing a focused beam with uniform energy. By means of, einzel lenses, injection magnets, slits, x and y electromagnetic steerers, and switching magnet, ions of the desired charge and uniform energy, are steered and focused into the different beam lines. A magnetic quadrupole lens is then employed to enhance the focusing capability of the beam line, and to bring suitably focused ion beam onto the target in the sample chamber. Differential pumping is included in the beam line so that the end station can be kept in the expected low pressure range. Close-up views of the ion beam transport system, and scattering chamber is shown in Figure 3.5



Figure 3.4 (a) scattering chamber

(b) ion beam transport system

3.2.4 Data Acquisition System

The Data acquisition system (DAS) and software for sample positioning, irradiation, and spectrum display is also shown in Figures 3.6a and 3.6b.

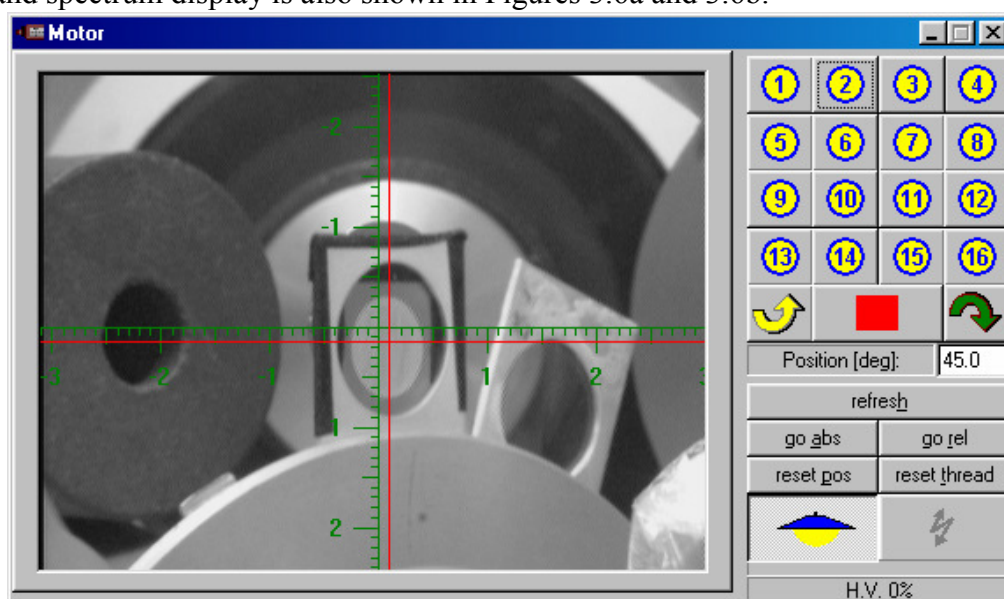


Figure 3.5a Remote-controlled sample positioning system

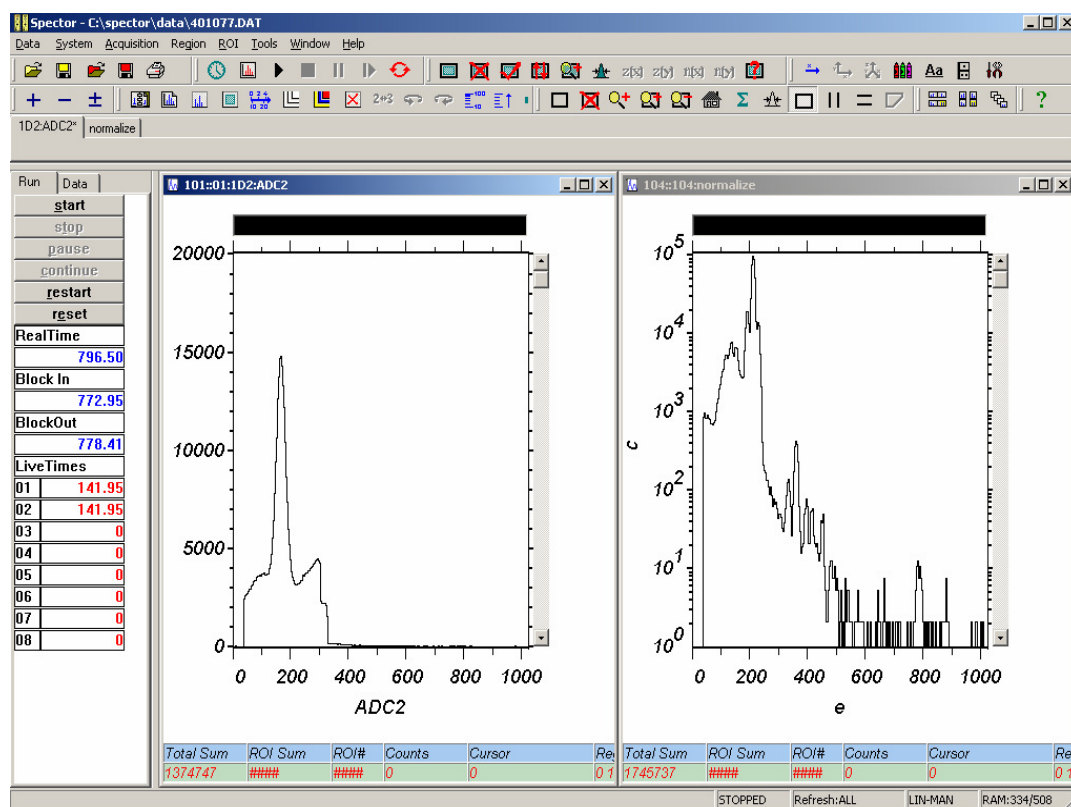


Figure 3.5b SPECTOR (16) – IAEA- developed software for the simultaneous multi-parameter spectrum accumulation and display (LHS=RBS spectrum; RHS=PIXE spectrum)

The DAS is a general-purpose, multi-parameter package featuring full sample holder control and spectrum acquisition software (SPECTOR). A motorized 16-position sample holder accomplishes the automatic sample positioning. The sixteen positions are separated by 22.5° , with fine step movements of $0.9^\circ/\text{step}$. A camera attached to the chamber and connected to a standard frame grabber supports remote video monitoring, and enables visual inspection and finer position adjustments. The system can interface up to 16 NIM ADCs and collect data by PHA or list mode. All system components are controlled by user-friendly software (SPECTOR) running under the MS Windows. The SPECTOR features high-level hardware control, data input/output, data sorting in 1- or 2-dimensional display, display manipulation tools, control of up to 4 motors, and definition of scan area in micro-beam applications. Details on the DAS, and its application on other nuclear-related measurement systems have been reported elsewhere (17, 18).

3.2.5 Spectrum Deconvolution and Analysis

In PIXE measurements, the primary goal is to determine the concentration of the elements of interest in the target. The concentration values are deduced essentially from the intensity of the measured x-ray line, and therefore require the accurate extraction of the spectra peak areas in the spectrum generated. There exist different routines for spectrum deconvolution and analysis. However, they generally extract the peak areas through modeling of the peak shapes and the background of the spectrum with appropriate functions and/or algorithms. A model is constructed and fitted to the experimental spectrum. When the fit is not satisfactory, the parameters for constructing the model spectrum are adjusted and fitting is repeated. This is basically

an iterative process to find the best values for the parameters. An intercomparison was carried out by the IAEA on seven PIXE spectrum analysis software packages (19, 20). The type of peak shape functions, fitting algorithms, background treatments, and database used are further described in an IAEA technical document (21).

PIXE analysis turns out to be simplest in the two extreme cases of thin and thick samples respectively (7). A sample is considered thin when the energy lost, δE , by a traversing proton of a few MeV (range of tens of microns) is negligible. In this case:

$$E = E_0 - \delta E \quad (\delta E \ll E_0)$$

A 'thin' sample depends on the incident proton energy and the sample/target matrix. On the other hand a sample is considered 'thick' if it is able to stop the incident proton beam entirely. From the X-ray spectrum produced after proton bombardment, a good X-ray yield must be calculated for all X-ray energies identified. The number of counts under the X-ray peak corresponding to the principal characteristic X-ray line of an element is called the X-ray yield (Y_v) for the v - line. It is expressed as:

$$Y_v = \frac{\Omega}{4\pi} \cdot N_p \cdot n_z \cdot \sigma_v \cdot \epsilon_v \quad (3.1)$$

Where

Ω = solid angle subtended by the detector at the target,

N_p = number of incident protons that hit the specimen,

n_z = number of sample atoms per unit area of the specimen, z is the atomic number of the element,

σ_v = production cross-section for v - line x-rays,

ϵ_v = detection efficiency for v - line x-rays

Considering that,

$$n_z = m_z \cdot \frac{N_{av}}{A_z} ; \quad \sigma_v = \sigma_z \cdot \omega_z \cdot b_z ; \quad \text{and} \quad Q_p = 1.6 \times 10^{-13} \cdot N_p$$

Where

m_z = concentration of element z in mass/unit area, N_{av} = Avogadro's number

A_z = atomic mass of the element, ω_z = the K or L fluorescence yield

σ_z = ionization cross-section for K, L, or M shell at proton energy E_0

b_z = the transition probability for K_α or L_α line

Q_p = proton beam charge in μC

Substituting and combining the equations above, equation (3.1) becomes

$$Y_v = S_v \cdot Q_p \cdot m_z \quad (3.2)$$

Where, S_v is referred to as the thin target sensitivity.

The thin target sensitivity (S_v) may be determined by the fundamental parameters approach using physics data from the database (all physics, no standards), or establishing a functional relationship of S_v with Z through experimental measurements of thin target standards. As a compromise approach between the above methods, the thin target sensitivity can also be determined by the measurement of a standard reference material. These SRMs need not be of similar matrix to the sample/target - (The GUPIX approach (22)). Q_p may also be determined either directly or indirectly. Direct determination for thin or thick and conducting specimen is achieved by coupling a Faraday cup to a charge integrator. For thick conducting specimen, the charge integrator may be coupled directly to the specimen holder. Alternatively, Q_p may be determined by measuring the number of protons back-

scattered from a thin film or the thin sample/target (Rutherford Back-scattered Spectrometry, RBS).

In order to reduce the low-energy brehmsstrahlung background, a filter of appropriate thickness is often placed between the specimen and the detector. If such a filter is used the equation (3.2) has to be modified by a transmission factor and becomes:

$$Y_v = S_v \cdot Q_p \cdot m_z \cdot T_f \quad (3.3)$$

Where, T_f is the filter transmission factor and is a function of X-ray energy.

Additionally, for the case of a thick and homogeneous target, equation (3.2) has to be modified by an integration factor which takes into account the proton attenuation ($E_0 - 0$), and matrix stopping power within the target (7, 23).

3.2.5.1 The *GUPIX* approach

Aerosol-loaded filters can be considered in most cases as thin targets in PIXE analysis. Consequently, the thin target formalism for PIXE analysis using the GUPIX software package (22) was utilized in the PIXE aspect of this work. The GUPIX software evaluates the X-ray yield of a given X-ray-line by non-linear least squares approach. The model spectrum takes the library of relative X-ray line intensities in the database and modifies them for relative absorption in target, detector efficiency, and transmission through filters. For thin targets, equation (3.3) is re-expressed in GUPIX as:

$$Y_v = S'_v \cdot Q_p \cdot m_z \cdot f_q \cdot \Omega \cdot \epsilon_v \cdot T_f \quad (3.4)$$

Where,

S'_v = theoretical yield per μC of charge per unit concentration per steradian

$f_q = 1$ (if Q is the measured beam charge) or

f_q = a factor converting Q to μC , if Q is a quantity proportional to beam charge

f_q and Ω is combined into an instrumental constant H , which is in principle independent of Z and target matrix (24). Equation (3.4) therefore becomes

$$Y_v = S'_v \cdot Q_p \cdot m_z \cdot H \cdot \epsilon_v \cdot T_f \quad (3.5)$$

The H value is measured by measuring thin film standards. The H -value should be a constant, provided that the database is accurate, the detector is well characterized, and beam charge is properly determined. Consequently the “ H -value standardisation technique” enables the conversion of X-ray intensities into concentration.

3.3 X-ray Fluorescence (XRF) spectrometry

X-ray emission techniques remain dominant in the multi-elemental analysis of ambient atmospheric particulates (25). In X-ray fluorescence analysis, samples to be analysed are irradiated with energetic particles or photons from either a radioisotope, x-ray tube or synchrotron radiation source. Fluorescent X-rays are subsequently emitted through charged particle or photon interaction with the electron cloud of an atom. The interaction leads to the ejection of one or more of the electrons from the inner shells of the atom, leaving the atom in an excited state. Electrons from higher

energy levels then fill the vacancies created by the ejection process, and the excess energy resulting from such a transition is dissipated either by emission of characteristic x-ray photons or Auger electrons. The emitted x-ray photons are unique to the element. The characteristic X-rays from the different elements are distinguished either by their wavelength, λ , (WDXRF) or by their energy E , (EDXRF), depending on the type of measuring equipment employed (26). In WDXRF spectrometry, the polychromatic beam emerging from a sample surface is dispersed into its monochromatic constituents by the use of an analyzing crystal according to Bragg's law. The wavelength for any measured line is computed from knowledge of the crystal parameters and diffraction angle. With EDXRF spectrometry, the x-rays are detected by high-resolution semi-conductor detectors with pulsed optical feedback to provide high count rate capabilities. Signal from the detector are processed by standard pulse processing electronics and the resulting spectrum displayed. Consequently, qualitative and quantitative analyses are carried out. Only energy dispersive X-ray (EDXRF) spectrometers were used in this work.

3.3 1 Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry

A typical EDXRF spectrometer comprises essentially of an X-ray excitation source, a sample chamber, X-ray photon detector, and associated electronics for data acquisition and analysis. In EDXRF analysis, the emitted X-ray photons detected, are processed and separated according to their energy.

This is achieved through pulse height analysis (PHA), since the electronic signals generated by the X-ray detector have pulses whose amplitude are proportional to the energies of the photons deposited in the detector. X-ray tube-based EDXRF equipment come in two main variants: the conventional EDXRF system, and the other system with additional polarizing targets (ED(P)PXRf). The principle of x-ray fluorescence analysis, using secondary target excitation method is as shown in figure 3.2.1. The Cartesian geometry of the source-sample-detector arrangement, coupled with polarized excitation provides optimum conditions for measurements. Multiple elements can be identified simultaneously and non-destructively. The electronic devices in the spectrometer process the analog signals, convert them to digital signals and store them in the multichannel analyzer MCA) for display and further data reduction and evaluation

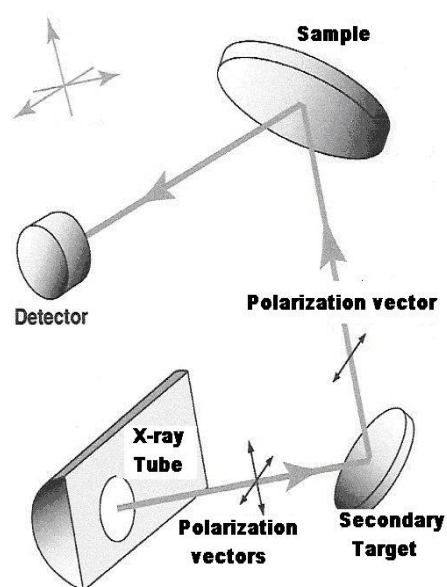


Figure 3.6 Secondary excitation mode

3.3 1.1 Conventional Tube-excited EDXRF spectrometer

Figure 3.7 shows a picture of a typical conventional EDXRF spectrometers. It comprises of an X-ray tube operated in a secondary target excitation mode. Both the tube anode and secondary targets can be changed to better suit samples to be analysed.. The sample chamber contains a sample holder which can accommodate wholly the 47mm (diameter) aerosol-loaded filters. The holder makes it possible to

present the same filter for analysis on different analytical facilities without having to cut up the filter, and also reduces the dangers of loss of material in presenting the sample for more than one analysis. The sample chamber can be evacuated to about 10^{-2} bar prior to analysis. This facilitates improvement in the sensitivity for low Z elemental analysis. The associated electronics for signal acquisition are Si(Li) detector, high voltage bias, spectroscopy amplifier, and analog-to-digital converter modules were all Canberra products. Fluorescent spectra generated are fitted with appropriate deconvolution software, enabling quantitative analysis to be carried out. Details of the derivation of the formalism for quantitative x-ray methods, and their different variants are described fully elsewhere (29-33).

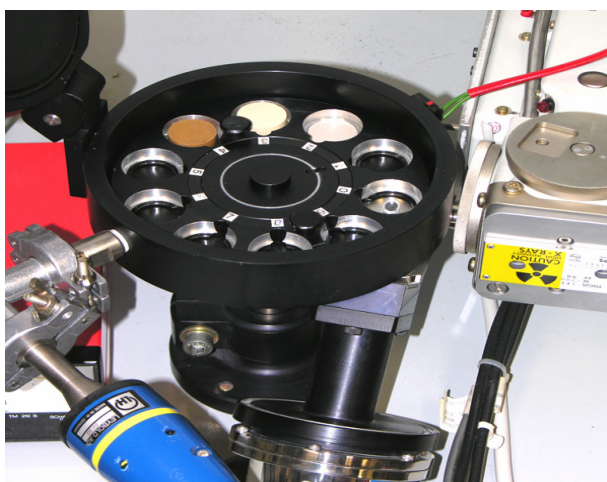


Figure 3.7 EDXRF spectrometer with Ag anode and Rh secondary target

3.3 2 Energy Dispersive Polarized X-ray Fluorescence (ED(P)XRF)spectrometry

The XRF spectrometer used in this work is the SPECTRO Xlab2000. This is a polarized XRF spectrometer, ED(P)XRF, and is fully software-controlled. It is equipped with a 400 W Palladium (Pd) end window tube, and a Si(Li) detector with a resolution of 148 eV (1000 cps Mn Ka). The spectrometer operates in the secondary excitation mode, making use of polarizers [Al_2O_3 Barkla polarizer and HOPG (Highly Oriented Pyrolytic Graphite) Bragg polarizer] and secondary targets (Al, Si, Ti, Co, Mo, and Pd). The polarizing and secondary targets, in combination with the Cartesian geometry of the source-sample-detector arrangement, provide a good signal-to-background ratio (34, 35). The sample chamber was operated under vacuum, and the specially constructed sample tray could accommodate 12 whole 47mm diameter nuclepore filters (automatic sample changer). Figure 3.8 shows the layout and working principle of the ED(P)XRF spectrometer used.

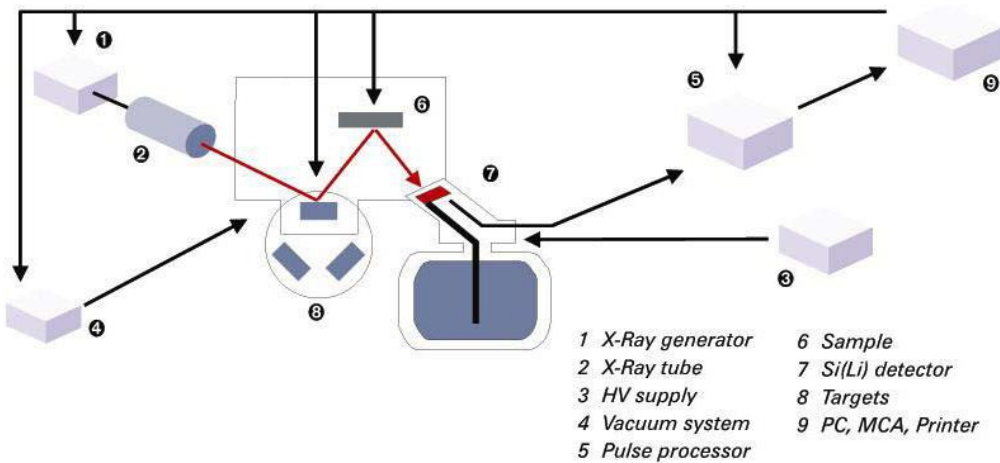


Figure 3.8 Schematic diagram of the ED(P)XRF spectrometer (figure: SPECTRO A.I)

3.3 2 1 Spectrum Fitting and Analysis (SPECTRO)

Spectrum deconvolution is necessary in order to determine the net X-ray intensities of each identified element in the sample. The SPECTRO software does spectrum fitting using the non-linear least squares approach, with correction of spectral artefacts from the detector and the sample. The X-ray intensities evaluated are also corrected for matrix effect, by means of matrix-dependent calculation of line ratios within a shell or between different shells. The software allows for the creation of a background spectrum from an experimental blank. This background spectrum is subtracted from each sample spectrum for the determination of elemental intensities. The Spectro Xlab2000 software has different quantitative calibration models. The models include the Fundamental Parameters' method (FPM), the Extended Compton Scattering (ECS) method, the SPECTRO method (combination of FPM and ECS), and Lucas-Tooth and Price (LTP) method (36). Aerosol-loaded filters can be considered as thin samples in most cases. Consequently the calibration of the spectrometer for the air filter analysis was done using thin film standards produced by the manufacturers (37, 38).

The basic formula used implies a linear relationship between the intensity and the concentration (39).

$$C_i = a_{i,0} + a_{i,1} \cdot I_i \quad (3.6)$$

whereby

C_i concentration of the element of interest

$a_{i,0}$ offset of the calibration curve

$a_{i,1}$ slope of the calibration curve

I_i net intensity of the element of interest

Taking into consideration matrix effects results in the following formula:

$$C_i = a_{i,0} + a_{i,1} \cdot I_i \cdot M \quad (3.7)$$

M correction term taken the matrix effects into account.

This matrix effect correction term can be realized by an internal standard Compton correction method, or can be calculated from mathematical models. The Compton scatter method is amenable to the determination of only or a few elements, whereas the mathematical correction methods imply the determination of all elements present.

3.3.2.2 Internal standard correction using Compton (incoherent) scatter method

The measured intensity of incoherent scatter may be used directly to compensate for matrix effects or indirectly for the determination of the effective mass absorption coefficient μ , which may then be used to correct for matrix effects. The compensation for matrix effects is based on a combination of sample preparation and experimental intensity data, and not on fundamental and experimental parameters.

The Compton scatter method can be expressed as:

$$C_{i,u} = (C_{i,r} \cdot \frac{I_{inc,r}}{I_{i,r}}) \cdot (\frac{I_{i,u}}{I_{inc,u}}) \quad (3.8)$$

where

$C_{i,u}$ concentration of the element of interest i of the unknown sample

$C_{i,r}$ concentration of the element of interest i of the calibration reference material

$I_{inc,r}$ intensity of the incoherent Compton line of the unknown sample

$I_{inc,u}$ intensity of the incoherent Compton line element of the calibration reference material

$I_{i,u}$ intensity of the element of interest i of the unknown sample

$I_{i,r}$ intensity of the element of interest i of the calibration reference material

The effective mass absorption coefficient μ is inversely proportional to the incoherent scattering. The mass absorption coefficient of multicomponent systems can be expressed as:

$$\mu = \sum_{i=1}^{i=k} \mu_i w_i \text{ where } \sum_{i=1}^{i=k} w_i = 1 \quad (3.9)$$

where

w_i the mass absorption coefficient of the component i

k the number of components

(2)

3.3.2.3 Fundamental or theoretical influence coefficient methods

The fundamental influence coefficients encompasses any mathematical expression relating emitted intensities and concentrations in which the influence coefficients are defined and derived explicitly in terms of fundamental parameters.

The calculation of the concentration from the intensities is performed by linear regression whereby the net intensities are corrected for the present matrix effects. For each element the concentration is calculated according to the following equation:

$$C_{i,u} = \left(\frac{C_{i,r}}{I_{i,r} (1 + \sum_j \alpha_{ij} C_{j,r})} \right) \cdot I_{i,u} \cdot M \quad (3.10)$$

$$C_{i,u} = \left(\frac{C_{i,r}}{I_{i,r} (1 + \sum_j \alpha_{ij} C_{j,r})} \right) \cdot I_{i,u} \cdot \left(1 + \sum_j \alpha_{ij} C_{j,u} \right) \quad (3.11)$$

whereby

$C_{i,u}$	concentration of the element of interest i of the unknown sample
$C_{i,r}$	concentration of the element of interest i of the calibration reference material
$I_{i,r}$	intensity of the element of interest i of the calibration reference material
$I_{i,u}$	intensity of the element of interest i of the unknown sample
$C_{j,r}$	concentration of the matrix element j of the calibration reference material
$C_{j,u}$	concentration of the matrix element j of the unknown sample
M	Matrix correction term
α_{ij}	The correction coefficient α_{ij} (called alphas) calculated from theory, although some approximations are involved.

Different type of alpha coefficient exists, but all of them are calculated without reference to experimental data, they are calculated using intensity data resulting from a fundamental parameter expression. The alpha coefficient is variable as a function of specimen composition. The calculation of the alphas is obtained by an iterative process.

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CHAPTER 4: EXPERIMENTAL MEASUREMENTS AND ANALYSIS

4.1 Gravimetric analysis

4.1.1 Sampling

Sampling and gravimetric analysis were carried out for PM10, PM2.5 (fine), and coarse fraction particulates in two different seasons (summer/winter), using the Gent and the reference samplers (LVS3) previously described in Chapter 2, sections 2.3.1 and 2.3.2 respectively. The PM10 particle fractions are particulates having sizes with aerodynamic equivalent diameter (a_{ed}) $\leq 10 \mu\text{m}$. The particulates with a_{ed} between $2.5 - 10 \mu\text{m}$, are referred to as the coarse fraction. The fine fraction particles are all those particulates with sizes $< 2.5 \mu\text{m}$. Consequently, for all practical purposes:

$$\text{PM10} = \text{coarse fraction} + \text{fine fraction (PM2.5)}$$

The sampling site was located at a residential area in Zagreb, Croatia, characterized by individual heating systems and moderate traffic density. 24 hour samples were collected during the periods July – September 2007, and December 2007 – January 2008. The filters employed for the collection of the particulates were preconditioned for 48 hours, before and after sampling, in the weighing room at 20°C and 30% relative humidity (CaCl_2). The Gent sampler used 47 mm diameter nuclepore filters at an average sampling flow rate around $1 \text{ m}^3/\text{h}$. The reference sampler, on the other hand, used a 47 mm diameter Whatman QM-A quartz microfibre filters at an average sampling rate of $2.3 \text{ m}^3/\text{h}$. The sampling was done by co-location of the samplers, in compliance to the European Standard EN 12341 [1].

4.1.2 Gravimetry

The gravimetric analysis was carried out using the standard gravimetric measurement method EN 14907 [2]. The measured mass concentrations expressed in $\mu\text{g}\text{m}^{-3}$ were calculated using equation (4.1):

$$C = \frac{m(l) - m(u)}{F \times t} \quad (4.1)$$

where

C = concentration in $\mu\text{g}\text{m}^{-3}$

$m(l)$ = loaded filter mass in μg

$m(u)$ = unloaded filter mass in μg

F = volume flow rate in m^3/h , normalized to 1 bar and 20°C

t = sampling time in hours

The Gent sampler measured the coarse and fine particulates directly. Consequently, its PM10 result was calculated by adding the values from the coarse and fine fractions. However, the reference sampler has separate PM10 and PM2.5 impactor heads, and therefore measures PM10 and PM2.5 (fine) particulates directly. The results of the coarse particulates for the reference sampler were therefore calculated by subtracting its PM10 mass concentration from that of the PM2.5. A Mettler Toledo MX5 Microbalance with a readability of 0.001mg , and a mesh for static discharge, was used

for mass measurements. Tables 4.1 and 4.2 show the mass concentrations of the particulates, measured simultaneously at the same sampling site by the Gent and the reference sampler (LVS3), for the different seasons.

Table 4.1

Table 4.1 Summer Particulates - mass concentrations (ugm-3)						
	Sven Leckel (LVS3)			GENT		
	PM10	PM25	Coarse	Coarse	PM2.5	PM10
7/16/2007	30.414	20.055	10.360	10.866	5.383	16.249
7/17/2007	36.054	20.906	15.148	16.983	13.609	30.592
7/18/2007	44.590	28.701	15.888	19.042	9.606	28.648
7/19/2007	58.485	36.389	22.096	28.547	9.612	38.159
7/20/2007	38.222	22.491	15.731	13.991	16.318	30.308
7/21/2007	30.822	18.889	11.932	13.468	8.045	21.513
7/22/2007	22.832	10.197	12.635	11.922	11.895	23.617
7/23/2007	34.617	17.527	17.089	19.540	13.631	33.171
7/24/2007	22.477	11.940	10.537	5.267	4.629	9.896
7/25/2007	13.972	9.288	4.684	5.285	6.911	12.195
7/26/2007	25.121	17.014	8.107	9.146	9.468	18.615
7/27/2007	24.574	17.161	7.413	6.414	6.558	12.972
7/28/2007	20.713	13.770	6.943	5.736	6.888	12.624
7/29/2007	12.879	9.557	3.322	3.417	5.714	9.132
7/30/2007	11.008	7.745	3.263	4.710	5.366	10.075
7/31/2007	12.907	9.261	3.646	4.511	9.379	13.890
8/1/2007	19.147	14.350	4.797	6.814	9.009	15.823
8/2/2007	35.794	25.076	10.718	8.719	12.478	21.196
8/3/2007	20.355	16.075	4.281	5.462	8.272	13.724
8/4/2007	16.720	11.801	4.918	5.117	6.520	11.637
8/5/2007	21.430	15.916	5.514	7.274	9.636	16.910
8/6/2007	34.138	26.589	7.548	10.223	21.266	31.489
8/7/2007	41.411	26.944	14.467	18.203	15.311	33.515
8/8/2007	37.509	27.894	9.615	12.601	17.364	29.965
8/9/2007	38.172	27.892	10.280	10.507	14.363	24.871
8/10/2007	25.385	21.074	4.312	5.274	7.824	13.098
8/11/2007	20.593	14.811	5.782	6.407	6.817	13.223
8/12/2007	24.983	17.708	7.276	11.746	8.268	20.015
8/13/2007	29.599	19.341	10.258	9.121	12.680	21.801
8/14/2007	30.189	23.695	6.494	7.525	13.574	21.099
8/15/2007	36.861	28.169	8.691	10.070	20.181	30.250
8/16/2007	34.718	25.293	9.424	9.976	20.081	30.057
8/17/2007	22.214	14.867	7.347	9.188	8.240	17.428
8/18/2007	21.809	16.454	5.355	6.569	9.322	15.891
8/19/2007	48.885	40.095	8.790	7.991	24.504	32.495
8/20/2007	28.565	22.024	6.541	8.422	12.982	21.404
8/21/2007	27.769	18.430	9.339	11.618	10.717	22.335
8/22/2007	30.634	21.218	9.416	10.825	13.103	23.927
8/23/2007	30.698	17.897	12.801	12.220	8.983	21.203
8/24/2007	34.747	21.605	13.142	11.752	12.755	24.506
8/25/2007	25.372	17.496	7.875	5.460	12.621	18.071
8/26/2007	29.185	18.998	10.187	8.413	11.477	19.890
8/27/2007	30.084	20.896	9.188	9.119	11.880	20.999
8/28/2007	33.487	25.033	8.454	6.433	13.595	20.028

Table 4.1 Continued

Table 4.1 Summer Particulates - mass concentrations (ugm-3)							
	Sven Leckel (LVS3)				GENT		
	PM10	PM25	Coarse		Coarse	PM2.5	PM10
8/29/2007	33.882	26.062	7.820		6.877	13.243	20.120
8/30/2007	28.436	21.423	7.013		7.170	9.100	16.271
9/1/2007	15.431	11.100	4.331		4.235	5.509	9.744
9/2/2007	18.370	11.448	6.923		8.176	6.864	15.040
9/3/2007	20.018	13.251	6.767		6.859	7.728	14.587
9/4/2007	12.725	8.963	3.762		3.861	3.351	7.213
9/5/2007	8.896	6.535	2.361		2.761	3.066	5.826
9/6/2007	9.766	7.335	2.432		3.322	3.172	6.494
9/7/2007	19.598	15.047	4.551		5.639	9.003	14.642
9/8/2007	17.735	10.195	7.540		7.111	7.130	14.241
9/9/2007	14.715	9.070	5.645		5.708	6.696	12.404
9/10/2007	16.934	11.015	5.919		6.880	6.750	13.630
9/11/2007	16.082	8.177	7.905		8.255	5.236	13.491
9/12/2007	16.306	9.603	6.703		6.596	5.999	12.595
9/13/2007	29.870	19.615	10.254		11.486	11.792	23.278
9/14/2007	33.374	20.801	12.573		12.384	11.192	23.576
9/15/2007	27.760	16.390	11.369		8.845	9.977	18.823
9/16/2007	36.240	24.067	12.173		10.423	14.883	25.306

Table 4.2

Table 4.2 Winter Particulates - mass concentrations (ugm-3)						
	Sven Leckel (LVS3)			GENT		
	PM10	PM25	Coarse	Coarse	PM2.5	PM10
12/3/2007	35.640	31.401	4.240	8.715	14.974	23.689
12/4/2007	42.643	35.941	6.702	13.166	21.892	35.057
12/5/2007	46.013	35.091	10.922	11.808	14.809	26.617
12/6/2007	69.653	57.244	12.410	17.988	37.647	55.636
12/7/2007	44.864	37.673	7.191	10.391	17.784	28.175
12/8/2007	18.890	13.748	5.142	7.569	11.942	19.511
12/9/2007	27.097	23.163	3.935	0.000	15.729	15.729
12/10/2007	38.625	34.107	4.518	4.094	20.539	24.633
12/11/2007	52.319	44.534	7.784	8.326	14.048	22.375
12/12/2007	8.843	6.731	2.111	1.715	1.911	3.626
12/13/2007	14.297	10.841	3.456	1.488	12.170	13.658
12/14/2007	26.682	25.642	1.041	2.454	19.835	22.289
12/15/2007	21.318	18.979	2.339	2.628	14.778	17.406
12/16/2007	35.545	29.065	6.480	7.371	22.880	30.252
12/17/2007	72.980	64.618	8.362	13.539	45.726	59.265
12/18/2007	68.024	61.400	6.624	12.147	30.407	42.555
12/19/2007	57.196	41.827	15.369	11.874	15.135	27.009
12/20/2007	65.041	48.585	16.456	14.904	5.801	20.705
12/22/2007	54.467	52.260	2.207	5.737	34.873	40.610
12/23/2007	66.756	61.668	5.088	6.400	36.481	42.881
12/24/2007	103.184	90.688	12.496	14.840	51.666	66.506
12/25/2007	50.551	45.114	5.437	6.631	28.932	35.563
12/26/2007	35.419	28.122	7.297	8.376	20.081	28.466
12/28/2007	54.646	48.835	5.811	8.677	10.236	18.913
12/29/2007	71.187	66.330	4.857	10.630	45.547	56.178
12/30/2007	10.679	9.007	1.673	9.883	19.785	29.669
12/31/2007	62.027	58.229	3.798	6.653	19.051	25.704
1/1/2008	61.609	58.200	3.409	7.122	29.470	36.592
1/2/2008	110.798	97.479	13.319	24.940	12.038	36.978
1/3/2008	135.918	126.951	8.966	16.002	63.560	79.562
1/4/2008	157.927	147.451	10.476	22.983	64.335	87.318
1/5/2008	130.390	115.760	14.630	12.854	43.517	56.371
1/6/2008	89.677	57.411	32.266	17.498	56.685	74.183
1/7/2008	106.430	86.382	20.049	14.575	7.568	22.143
1/8/2008	76.902	53.500	23.402	25.020	36.481	61.501
1/9/2008	82.183	72.007	10.176	15.774	41.733	57.507
1/10/2008	31.213	27.060	4.153	10.558	2.438	12.996
1/11/2008	60.026	54.639	5.388	10.427	26.330	36.757
1/12/2008	39.938	33.484	6.454	7.639	0.919	8.558
1/13/2008	66.817	56.125	10.692	17.477	32.639	50.116
1/14/2008	36.500	29.336	7.164	8.212	2.585	10.796
1/16/2008	61.697	54.487	7.210	6.723	31.497	38.220
1/17/2008	61.242	53.627	7.616	11.660	10.252	21.913
1/18/2008	58.824	50.473	8.351	13.586	27.498	41.083

Figures 4.1 – 4.4 show overview of the mass concentrations during the investigating period, and also for the different seasons;

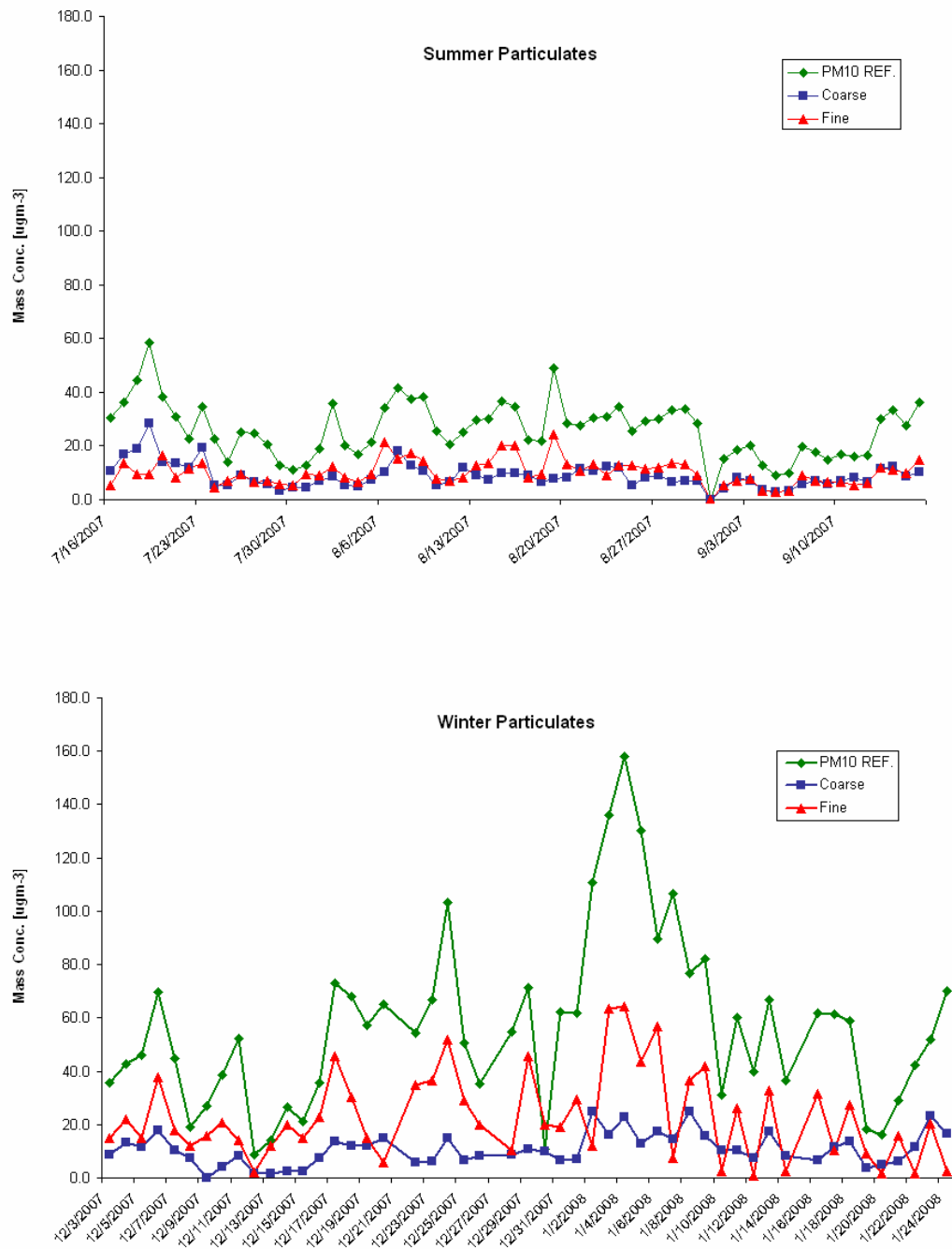


Figure 4.1 Particle mass concentrations for the summer and winter Seasons

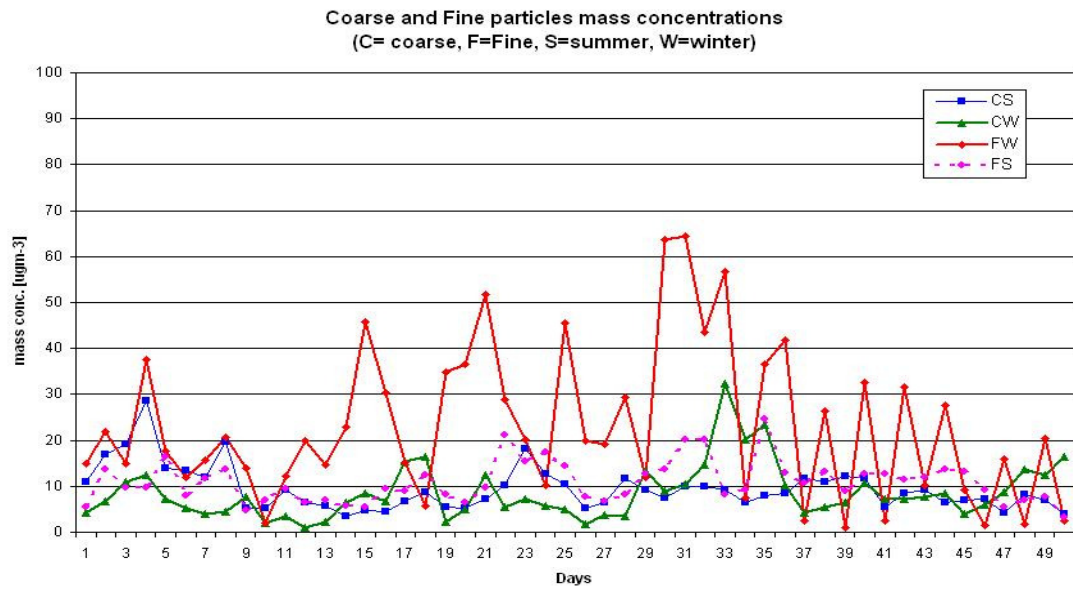


Figure 4.2 Particle mass concentrations during the investigation period

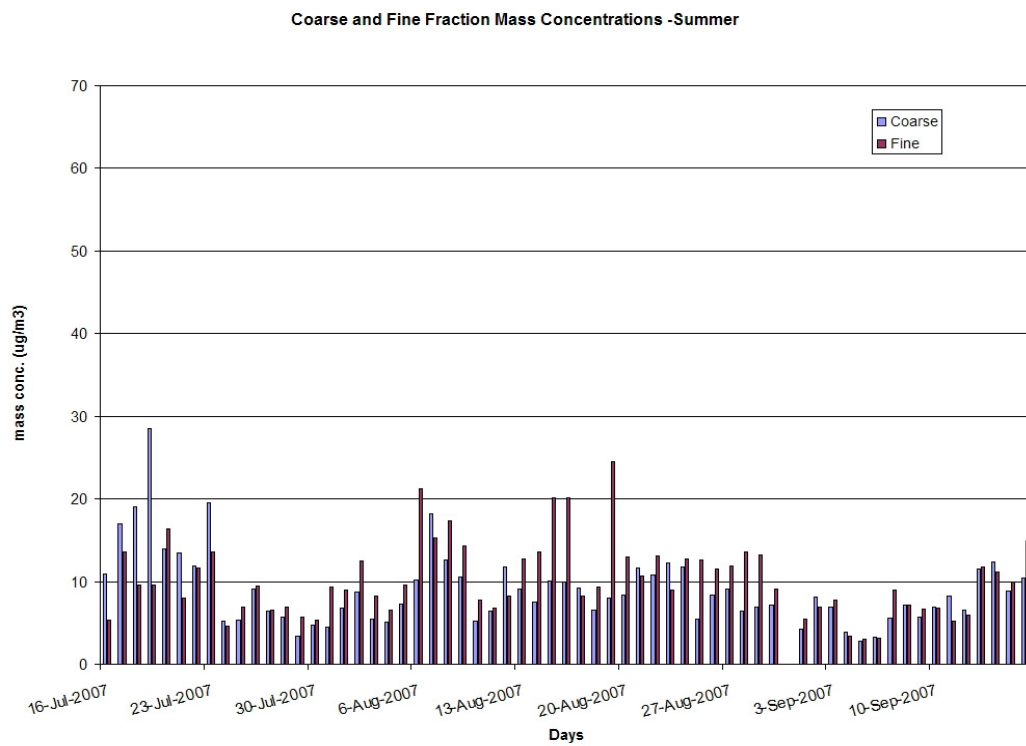


Figure 4.3 Coarse and Fine Fraction Particulates during Summer

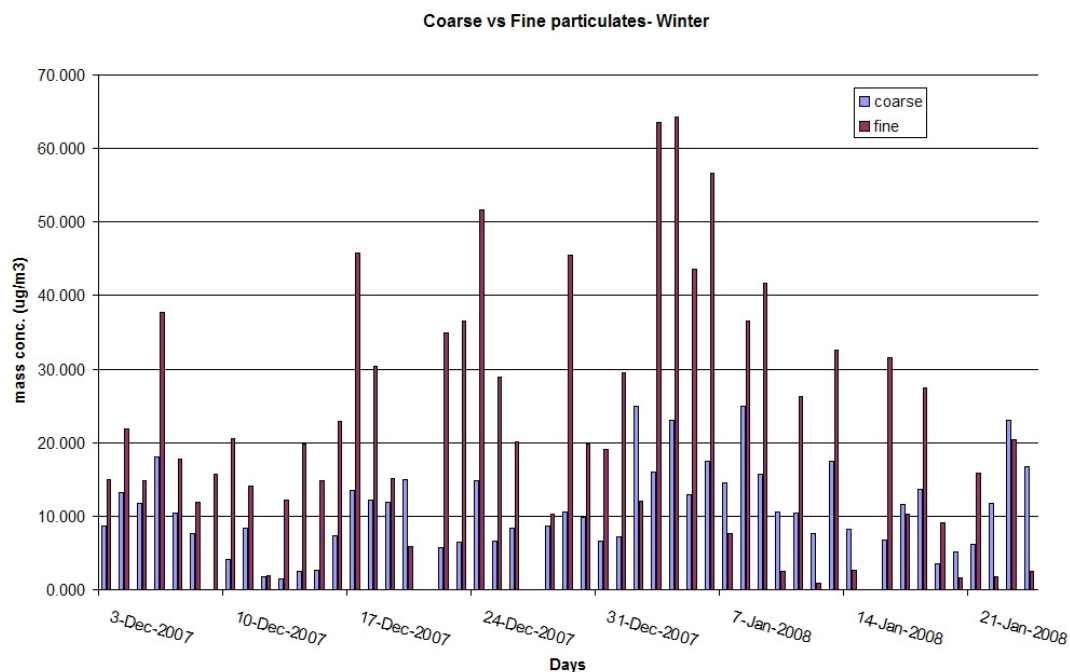


Figure 4.4 Coarse and Fine Fraction Particulates during Winter

A statistical summary of the mass concentrations of the different particle fractions collected during the summer and winter periods has been provided in Table 4.3 below.

Table 4.3 Particle Mass Concentration Results

Particle Mass concentration in $\mu\text{g m}^{-3}$ – 2007/2008				
	Summer (Jul - Sept)		Winter (Dec – Jan)	
	<i>Coarse</i>	<i>Fine</i>	<i>Coarse</i>	<i>Fine</i>
Average	9	10.3	10.9	23.1
Median	8.2	9.4	10.4	19.8
Standard Deviation	4.5	4.5	5.8	16.5
Minimum	2.7	3.1	1.5	0.9
Maximum	28.5	24.5	25	64.3
Number of sample pairs	62		49	

4.2. Field Test Investigation of Equivalence of Gent Sampler

The EN12341 standard [1] serves the purpose of harmonizing PM10 monitoring within the framework of the European Union Council Directive 96/62/EC [3], and the first daughter directive [4]. This standard enables the establishment of the equivalence of a candidate sampler, to the standard reference sampler, by means of a prescribed protocol in a field test under ambient conditions. The reference equivalence is assessed either through the (a) comparability of candidate samplers, or (b) comparability of candidate and reference sampler (i.e co-location of the candidate and the reference sampler). In the case of comparability with the reference instrument, it is required that the reference equivalence function, describing the relations between the mass concentrations of the candidate and the reference samplers, satisfies the following conditions:

- co-location of the candidate and the reference sampler
- reference equivalent function bounded within a two-side acceptance envelope, over the relevant concentration range:
 $\leq 10 \mu\text{g}/\text{m}^3$ if the reference concentrations X_i are $\leq 100 \mu\text{g}/\text{m}^3$, or
 $\leq 10 \%$ with respect to the reference concentrations X_i , if the reference concentrations are $> 100 \mu\text{g}/\text{m}^3$.
- the number of paired samples collected between each of the samplers during the comparison exercise, for the computation of the reference equivalent function, shall be at least forty (40).
- The computed relationship $y=f(x)$ between the candidate (y) and the reference (x) concentration values (by linear regression analysis) lies within the two-sided acceptance envelope, and its variance coefficient $R^2 \geq 0.95$.

The Gent sampler was co-located with the Reference sampler throughout the period of the investigations for both seasons. Figures 4.5 and 4.6 show the resulting correlations obtained.

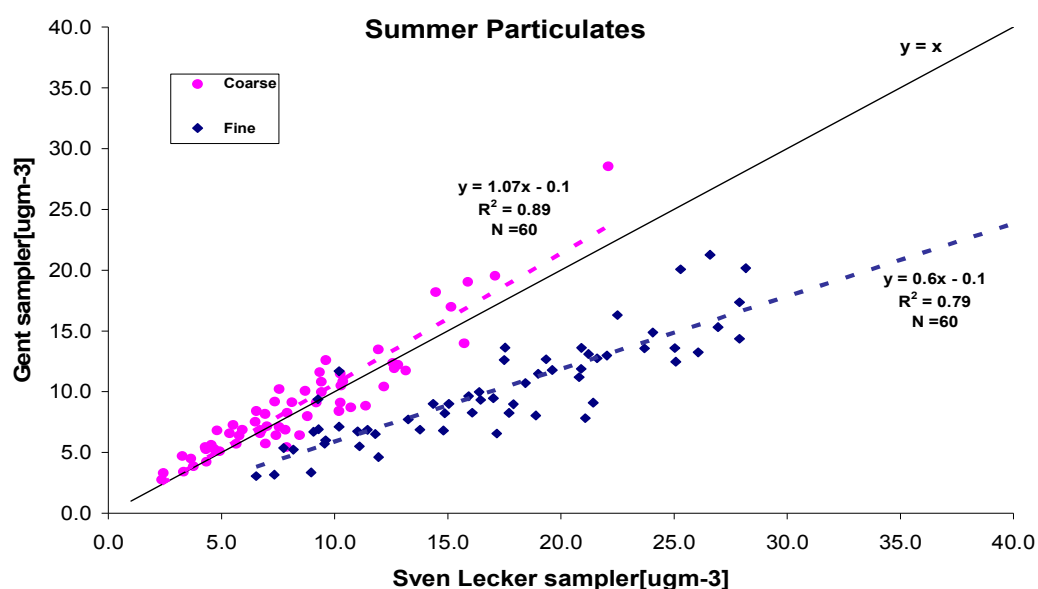


Figure 4.5. Co-location of Gent and Reference Samplers – Summer Season

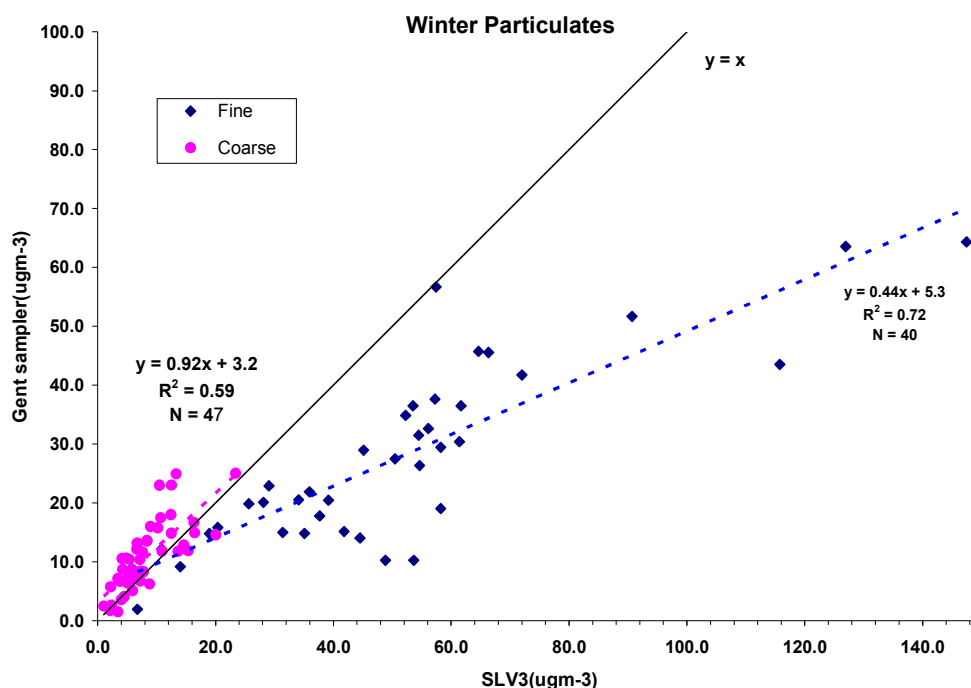


Figure 4.6 Co-location of Gent and Reference Samplers – Winter Season

It can be seen from the above figures (4.5 and 4.6) that the Gent sampler, when operated in its usual mode as a stacked filter unit, did not meet the requirements for an equivalent sampler under the EU norm EN12341. There was however a good correlation of its coarse particle fractions with that calculated from the reference sampler measurements for both summer and winter particulates, and for concentrations approaching $30 \mu\text{g m}^{-3}$. The fine particle fractions however showed poor correlation, particularly for the winter particulates. This may be attributed to the fact that fine fraction particles in Gent samplers have their effective cut-off at $2.2 \mu\text{m}$ and not $2.5 \mu\text{m}$ [5-7]. In addition, for concentrations greater than $30 \mu\text{g m}^{-3}$, high mass loadings of the first filter (coarse filter) seems to affect the efficiency of collection of the PM 2.5 stage in the stacked filter unit. The good correlation between the coarse fractions of the samplers indicates that the PM10 inlet (pre-impaction) of the Gent sampler is comparable to the PM10 head of the reference sampler. A similar observation was also made in the work reported in reference 8. The unresolved differences lie mainly in the PM2.5 fraction at high mass concentrations. Few studies have been carried out involving intercomparison of other samplers with the Gent sampler (5, 8-10). There is therefore the need to continue investigations in this direction in order to enable users of the Gent sampler utilize the same data generated in meeting other national or international statutory obligations and requirements.

4.3 Elemental Composition Analysis

4.3.1 Energy Dispersive (Polarized) X-ray Fluorescence (ED(P)XRF) Analysis

4.3.1.1 Quantitative Method Development

The spectrometer used in this work is the SPECTRO Xlab2000, which has been described in Chapter 3. The spectrometer has the possibility of excitation from eight secondary targets. Namely: Ti, Al, Al₂O₃, Si, Mo, Pd, HOPG, and Co. A quantitative method is developed through the combination of different targets and evaluation models. The excitation, measurement conditions, and evaluation models chosen in the development of the quantitative procedure took into consideration the relevant needs and requirements for elemental concentration in air pollution studies. Table 4.3 gives the excitation sources (secondary targets) used, the measurement conditions, the elements analyzed by each of the four secondary targets selected, and which X-ray line (K_{α} , K_{β} , L_{α} , L_{β}) is utilized in the computation of concentration.

Table 4.4 Measurement conditions selected for the elemental determination of the aerosol-loaded filters

Periodic Table of the Elements

Legend:

- Ti secondary target (20kV, 15.0mA, 300s)
- Mo secondary target (40kV, 7.5mA, 300s)
- Al₂O₃ polarizing target (50kV, 5.0mA, 500s)
- Co secondary target (30kV, 10.0mA, 300s)

Measurement conditions and elemental concentration determination using the ED(P)XRF spectrometer

Each sample is sequentially measured by all the four secondary targets before the sample- changer presents another loaded filter. In the measurement methods developed for the analysis of the air filters, X-ray irradiation of the samples was implemented in the following order: Mo secondary target, Al₂O₃ polarizer, Co secondary target, and Ti secondary target.

4.3.1.2 Evaluation Models

Two evaluation models were considered in the development of the quantitative method for the analysis of the air filters. These are the fundamental parameters' method, and the Lucas-Tooth and Price method. The quantitative methods developed using these models have been referred to as "Mem-fp" and "Mem-lt". The methods

were developed using filter standards prepared and provided by the Manufacturer of the SpectroXlab2000 spectrometer (11). These multi-element standards cover elements from Na – Pb in different concentration ranges, and a calibration standard has a minimum of seven elements. In all twelve standard filters were used in the development of the quantitative methods.

4.3.1.2.1 Fundamental Parameters' (FP) Method

When applied to air filters, the equation for the FP method reduces to

$$I_i = G'_o \times \varepsilon(E_i) \times K_i(E_o) \times C_i \quad (4.1)$$

where

I_i = measured net intensity of analyte i,

C_i = concentration of the analyte i,

G'_o = is an instrumental constant,

ε = detection efficiency,

K_i = product of all the fundamental parameters for the analyte i.

The above equation assumes that the aerosol-loaded filters can be regarded as thin samples, and therefore require no matrix corrections. Hence a linear relationship is expected, and on re-arrangement of equation 4.1 one obtains:

$$C_i = H_i \times I_i \quad (4.2)$$

where,

H_i = Calibration factor

4.3.1.2.2 Lucas-Tooth and Price (LTP) Method

The above method, which is an empirical influence coefficients' method, is based on intensities only and can be represented with the equation 4.3 below:

$$C_i = a_{i,0} + a_{ii} I_i \cdot (1 + \sum_j (a_{ij} I_j)) \quad (4.3)$$

The coefficients are derived by calculating the best possible fit between measured intensities and concentrations of a given set of standards (12), such that $\sum \Delta^2$ is minimum.

$$\text{Where } \Delta = \frac{C_i - C_{ix}}{I_i} \quad \text{and } C_{ix} \text{ is the calculated concentration of the analyte}$$

i.

The concentrations evaluated using equation 4.4 are also given in ng/cm² and must be similarly converted to ng/m³ using equation 4.3.

4.3.1.3 Validation of Quantitative methods

The methods “Mem-fp” and “Mem-lt” were subsequently analysed using two sets of the standard reference material of “Air Particulate on Filter Media” SRM 2783. Tables 4.5 show typical results of replicate analysis of the standard reference material.

Table 4.5 Validation results for “Mem-fp” method

Validation of the method "Mem-fp" on the ED(P)XRF spectrometer using SRM 2783 air filter standard													
Sample/Concentration (ng/cm ²)											Meas.	Certified	Meas/Cert
Element	sx000457	sx000458	sx000525	sx000526	sx000527	sx000527	sx000527	sx000528	sx000528	sx000528	Value*	Value	
Mg	720	414	546	531	583	550	555	482	511	582	547	865	0.63
Al	1820	1647	1767	1717	1768	1757	1784	1739	1706	1706	1741	2330	0.75
Si	5953	5259	5864	5634	5764	5821	5847	5622	5660	5637	5706	5884	0.97
K	488.8	379.4	453.8	425.6	457.9	432.6	466.7	439.2	405	405.4	435	530	0.82
Ca	1410	1223	1381	1333	1363	1351	1354	1284	1310	1310	1331	1325	1.01
Ti	168.1	146.5	166.5	160.8	164.8	159	163.6	158.2	162.7	163.2	161	150	1.08
Cr	24.8	23.1	24.4	26.2	24.2	26.4	24.6	26.4	26.7	26	25.3	13.5	1.87
Mn	39.3	35.7	39	36.4	37.5	37.2	39.1	36.4	36.9	37.9	37.5	32.1	1.17
Fe	2638	2363	2543	2490	2516	2550	2550	2513	2528	2520	2521	2660	0.95
Ni	26.5	21.4	23	24.3	22.5	24.1	19.5	25.2	25.5	19.7	23.2	6.8	3.4
Cu	64.1	59.8	63.3	65.1	60	58.5	60	60.5	57.7	57.9	60.7	40.6	1.49
Zn	265.7	226.7	244.3	244.4	236	241.6	240.6	244	238.3	242.9	242.5	180	1.35
Pb	58.4	44.8	45.1	47.8	49.6	44	45.7	52.1	46.1	47.2	48	31.8	1.51
Meas. Value* = average value													
Mem-fp = fundamental parameters' approach													

Also shown in Figures 4.7 and 4.8 are comparisons of the validation results of the two methods with the reference standard.

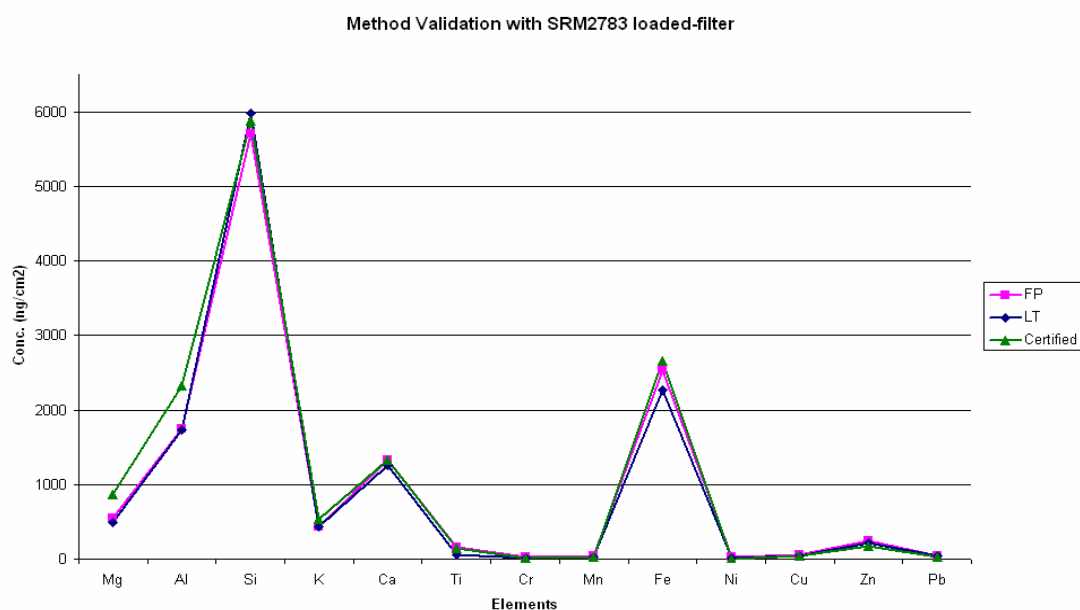


Figure 4.7 Validation of the quantitative methods developed for analysis of air filters on the ED(P)XRF spectrometer using SRM 2783 standard filter

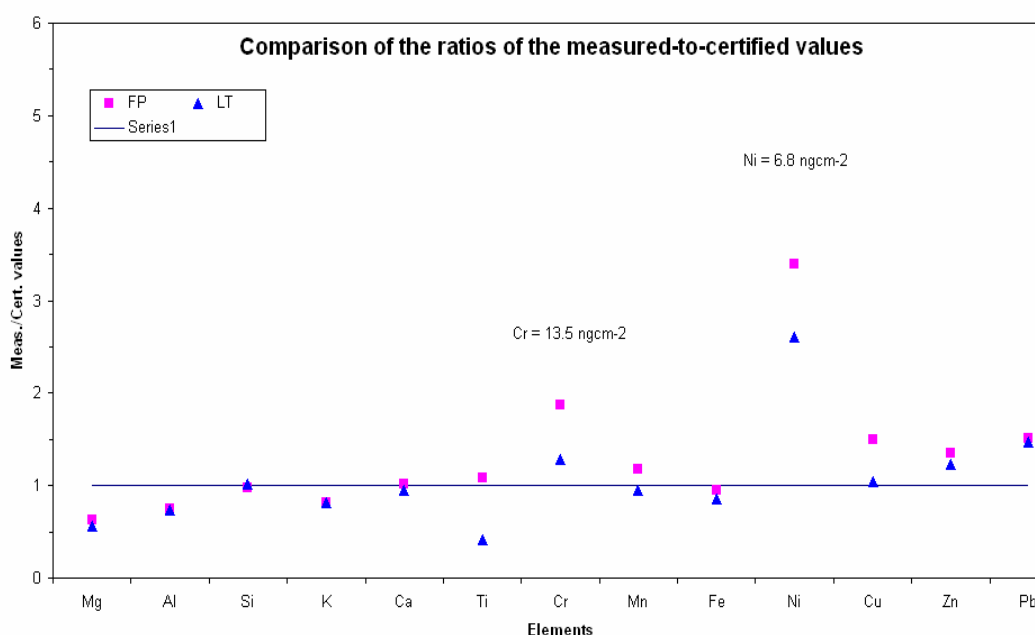


Figure 4.8 Comparison of the ratios of measured results to the certified values(SRM2783).

There was good agreement between the measured values and the certified values for most of the elements determined. There was, however, poor agreement for the elements Cr, Ni, and Cu. This may be attributed to the relatively low concentration values in the case of Cr and Ni. On the basis of the validation results obtained, quantitative values evaluated for the elements Cr, Ni and Cu in the samples collected must be regarded only as indicative values. Furthermore, the method “Mem-fp” was adopted for the subsequent analysis of the collected samples because of its better performance for the significant elements, and the versatility of the fundamental parameters’ approach as compared to empirical coefficient methods.

4.3.1.4 Elemental Concentrations

In air filter analysis, concentrations values using any of the methods are given in ng/cm^2 . These values must be expressed in ng/m^3 , and were computed as follows:

$$C_{vol} = \frac{C_i \times A_{filter}}{F \times t} \quad (4.4)$$

where

F = volume flow rate in m^3/h , normalized to 1 bar and 20°C

t = sampling time in hours

A_{filter} = area of particulate deposition on the loaded nuclepore filter

Whiles F and t are measured values, A_{filter} must be evaluated.

4.3.1.4.1 Evaluation of A_{filter}

Two different approaches were used in the evaluation of area of deposition of the particulates on the nuclepore filter. One of the techniques was a digital approach using ImageJ software (13), and the other was a manual technique of physical measurements of filter diameter.

ImageJ is a public domain Java-based image processing and analysis software. It can display, edit, analyze, process, save and print 8-bit, 16-bit and 32-bit images. It can also read many image formats including TIFF, GIF, JPEG, BMP, DICOM, FITS and "raw". For this evaluation an image of a typical aerosol-loaded filter was taken together with a measurement scale using a digital camera. The image was then imported into the ImageJ. The attached scale makes it possible to perform spatial calibration to relate pixel values to real world dimensional measurements in units such as millimeters. Two different algorithms were used in evaluating the diameter and area of deposition on the filter. The "Elliptical" algorithm employs a fitting with an ellipse, whose major and minor diameters are manipulated until the best perimeter fit to the area (by visual inspection), is obtained. The "Particles" algorithm employs similar evaluation automatically, using a linear combination of particles until the edges of the image on the artifact (in this case, the deposited area) are found and outlined. The results are indicated below in Figure 4. 9 and Tables 4.6a and 4.6b

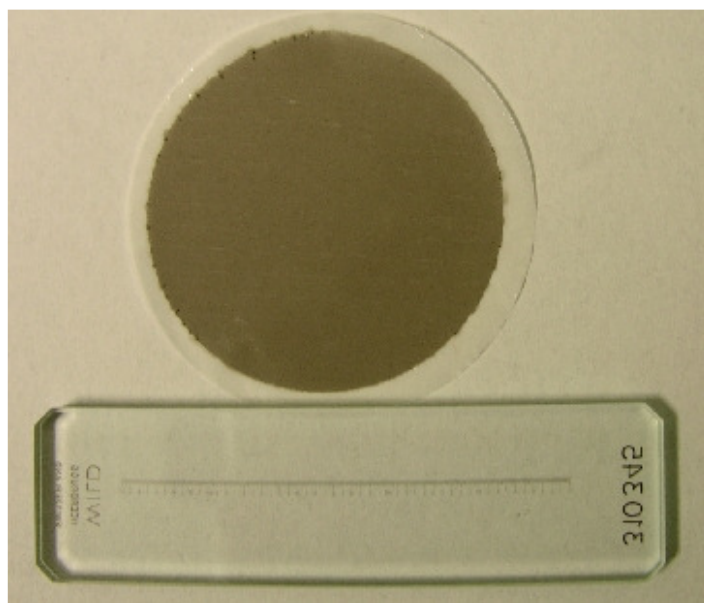


Figure 4.9 Digital evaluation of area of deposition using the software ImageJ

Table 4.6a Digital Evaluation of Area of Particulate Deposition

Elliptical	Area	Perimeter.	Major	Minor
1	12.254	12.409	3.968	3.932
2	13.229	12.893	4.116	4.092
Particles	Area	Perimeter.	Major	Minor
1	13.07	16.09	4.115	4.044
Average	12.85		4.06	4.02
STDEV	0.52		0.09	0.08

Table 4.6b Manual Evaluation of Area of Particulate Deposition

	DIAMETER	AREA
Filter #	4.046	12.85706
1	4.067	12.99087
2	4.084	13.0997
3	4.132	13.40944
4	4.056	12.92069
5	4.116	13.30579
6	4.083	13.09329
7	4.038	12.80627
8	4.047	12.86342
9	4.061	12.95257
10	4.062	12.95895
11	4.055	12.91432
12	4.04	12.81895
13	4.055	12.91432
14	4.114	13.29286
15	4.047	12.86342
16	4.042	12.83165
17	4.074	13.03563
18	4.15	13.52652
19	4.038	12.80627
AVG	4.07	13.01
STDEV	0.01	0.21

4.3.1.4.2 XRF Spectra of Aerosol-loaded Filters

Typical X-ray spectra from the ED(P)XRF spectrometer, of nuclepore blank filter and aerosol-loaded filter samples, are shown in Figures 4.10 and 4.11 respectively.

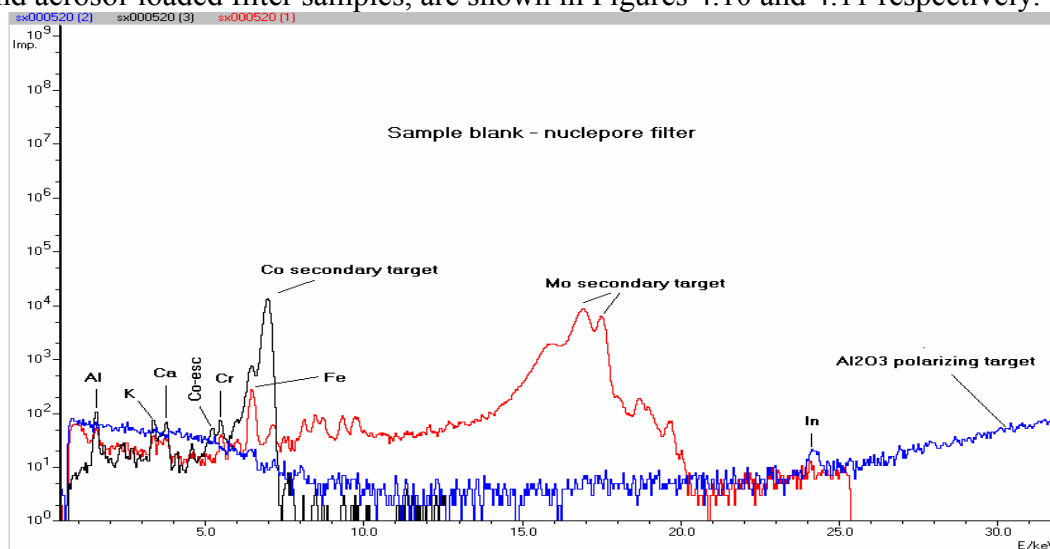


Figure 4.10 XRF spectra of blank nuclepore filter using different secondary targets

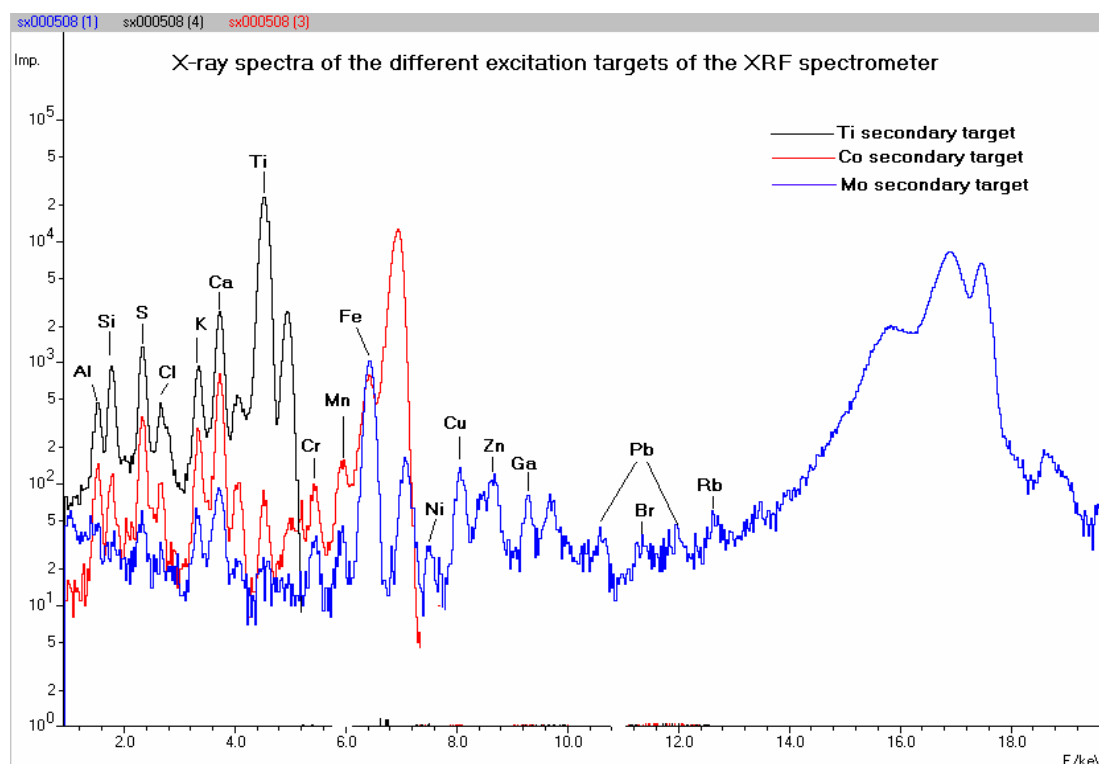


Figure 4.11 Expanded view of XRF spectra of an aerosol-loaded filter showing the elements excited by the different secondary targets.

Using the selected secondary targets, the coarse and fine filter samples collected during the winter and summer seasons were irradiated and analysed. The following elements were identified and quantified: Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb. The Al_2O_3 polarizing target was set up to determine the elements Ag, Cd, In, Sn, and Sb by their $K\alpha$ X-rays. However, apart from In which was identified as an interference element from the instrumental blank, none of the afore-mentioned elements were detected in any of the samples. Consequently only spectra from the other targets will be featured in this work. Figures 4.12 and 4.13 show typical spectra of the loaded filters for the different seasons. A typical table of results of elemental concentration values determined for the collected samples is shown in Table 4.7.

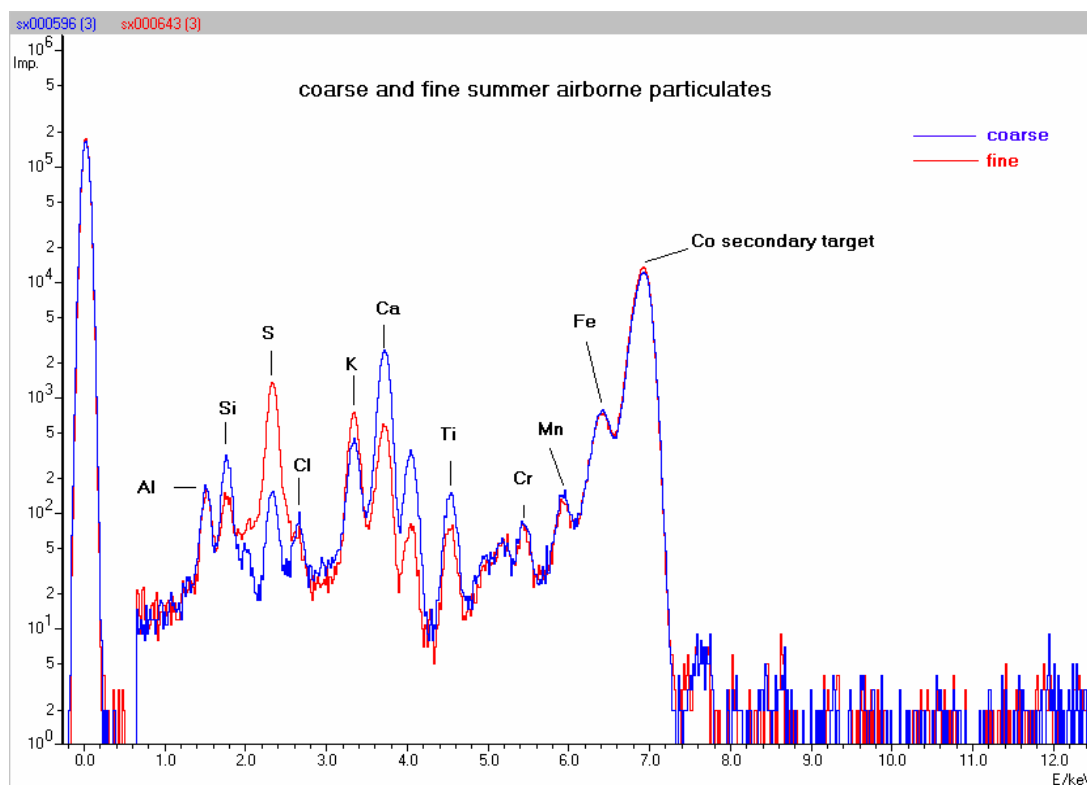


Figure 4.12 XRF spectrum of a set of filters loaded with coarse and fine particle fractions

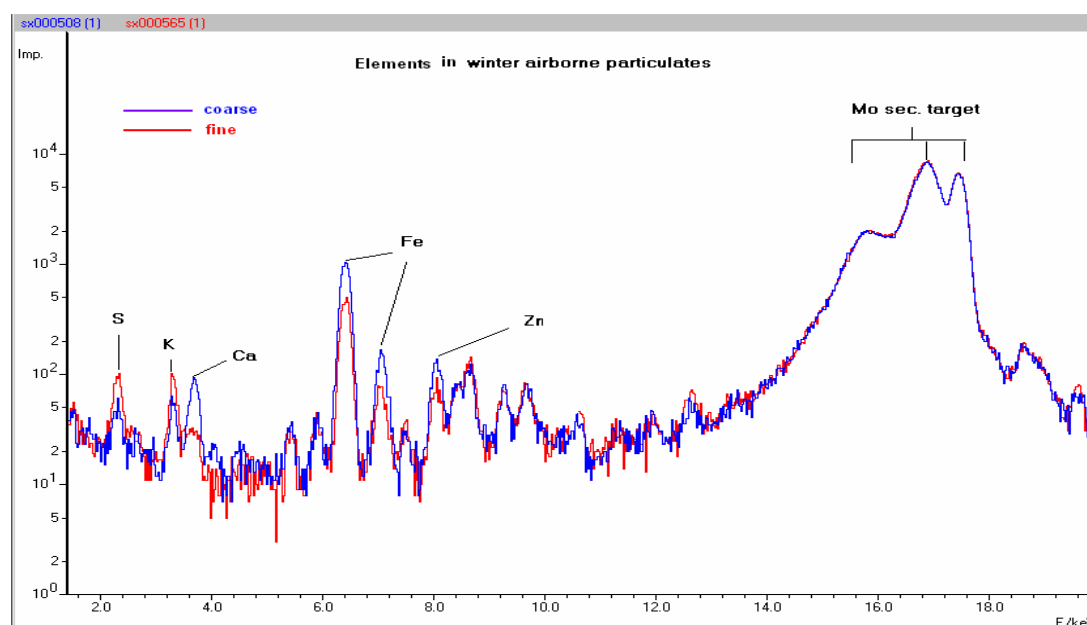


Figure 4.13 XRF spectrum of a set of filters with coarse and fine particle fractions (Mo-secondary target)

Table 4.7 Elemental concentration values of coarse particle fractions during winter

Coarse Particulates Collected in Winter during the months of December 2007/January 2008															
Element	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb	
Sample	Concentrations expressed in ng/m ³														
12/3/2007	255.65	349.18	48.16	96.42	24.08	99.94	10.84	6.98	10.93	373.75	10.26	34.00	46.53	11.73	
12/4/2007	299.61	433.56	56.21	259.30	28.11	336.20	15.01	8.49	13.21	496.91	12.20	39.97	49.47	14.17	
12/5/2007	302.92	472.74	50.08	1206.38	25.04	418.95	14.02	7.06	10.57	407.13	9.61	30.80	34.50	6.61	
12/6/2007	391.69	715.78	63.18	1603.41	31.59	1013.34	26.60	9.92	16.17	637.45	10.68	43.72	50.48	8.71	
12/7/2007	282.54	429.18	50.67	1126.91	25.34	372.02	13.38	7.65	10.24	354.69	9.17	35.17	33.95	5.99	
12/8/2007	292.77	440.78	54.04	84.51	27.02	242.46	13.24	6.86	7.02	275.05	8.65	23.83	31.77	4.53	
12/9/2007	295.64	407.23	57.49	57.49	28.75	78.54	7.93	6.55	7.13	166.73	10.06	23.86	30.82	5.84	
12/10/2007	320.13	415.19	60.47	60.47	30.24	60.89	9.61	8.28	7.32	180.81	9.98	31.75	38.94	7.38	
12/11/2007	290.86	455.37	48.86	48.86	24.43	334.74	15.20	6.79	7.38	217.42	8.89	22.08	28.00	6.06	
12/12/2007	207.49	194.79	43.47	43.47	21.74	21.74	4.35	4.43	4.35	8.69	6.74	12.52	17.95	3.87	
12/13/2007	247.73	288.45	45.91	45.91	22.95	22.95	6.24	5.19	4.59	50.96	7.07	14.97	22.91	4.55	
12/16/2007	280.57	319.10	57.34	57.34	28.67	28.67	4.19	6.54	4.76	22.65	13.82	22.19	40.48	10.45	
12/17/2007	266.52	339.33	55.36	323.77	27.68	27.68	6.26	6.70	4.82	33.33	9.52	21.04	32.39	6.72	
12/18/2007	318.12	460.35	57.94	776.33	28.97	281.16	11.76	7.24	8.17	241.01	10.02	25.49	34.65	6.77	
12/19/2007	440.09	745.93	75.50	1487.34	37.75	589.88	29.60	9.74	12.99	420.53	12.76	31.26	52.85	12.21	
12/20/2007	511.43	672.72	98.77	98.77	49.39	141.14	16.69	13.53	11.65	289.40	22.82	39.71	56.30	7.43	
12/22/2007	258.13	302.07	531.06	49.31	24.65	24.65	6.02	6.16	5.92	138.07	11.64	18.74	30.33	6.22	
12/23/2007	249.28	340.43	951.76	47.95	23.97	23.97	3.74	5.75	4.12	31.36	9.73	16.97	29.39	5.51	
12/24/2007	434.11	402.75	89.36	89.36	44.68	44.68	7.42	10.01	6.08	8.31	14.39	28.60	41.28	8.37	
12/25/2007	328.67	330.69	69.38	69.38	34.69	34.69	4.86	7.70	4.58	30.81	11.80	18.39	33.79	7.83	
12/26/2007	402.46	389.42	165.00	78.50	39.25	39.25	6.59	8.71	6.59	73.63	14.05	19.47	43.72	7.62	
12/28/2007	371.73	443.49	72.85	72.85	36.42	36.42	7.50	8.67	7.14	125.29	14.20	29.43	36.50	8.46	
12/30/2007	231.43	294.64	421.71	46.07	23.04	23.04	5.02	6.13	5.44	88.46	12.21	16.54	26.35	5.05	
12/31/2007	582.68	578.14	107.98	107.98	53.99	53.99	14.58	11.66	10.80	90.92	16.74	50.54	56.69	13.33	
1/1/2008	248.52	250.97	47.12	47.12	23.56	23.56	4.85	5.51	4.29	30.20	7.12	14.89	22.90	4.76	
1/2/2008	251.32	309.00	50.73	50.73	25.37	25.37	6.80	6.04	5.83	96.89	7.15	18.42	30.18	8.91	
1/3/2008	301.71	398.76	57.39	57.39	28.70	28.70	7.52	7.06	5.51	111.34	9.70	15.95	27.20	6.36	
1/4/2008	279.47	452.94	2106.64	45.29	27.54	22.65	7.20	5.44	5.98	164.87	11.10	16.71	32.43	7.56	
1/5/2008	369.31	445.92	883.17	72.27	36.14	36.14	7.37	8.60	5.64	57.53	12.65	27.54	48.06	9.30	
1/6/2008	392.92	484.61	346.16	76.53	38.27	38.27	9.57	9.80	7.81	205.11	12.78	33.29	42.17	9.65	
1/7/2008	300.50	361.71	57.31	57.31	28.66	28.66	8.37	7.97	7.79	211.49	9.40	31.58	40.98	6.39	
1/8/2008	486.46	545.73	99.77	99.77	49.88	49.88	11.67	13.07	9.78	229.46	17.76	36.71	56.07	9.22	
1/9/2008	250.93	326.20	172.38	49.75	24.87	24.87	7.46	6.17	7.56	161.68	8.56	25.17	36.81	7.35	
1/11/2008	482.10	744.74	88.13	88.13	44.07	44.07	18.07	12.78	17.80	565.82	15.60	57.11	60.11	14.83	
1/12/2008	247.31	347.81	48.20	241.72	24.10	24.10	6.12	6.46	8.39	320.53	10.70	30.22	30.99	5.76	
1/13/2008	319.48	359.86	61.19	61.19	30.60	30.60	6.30	7.95	6.36	113.81	9.42	24.90	35.80	8.52	
1/14/2008	217.13	342.12	40.73	80.60	20.36	121.78	9.04	5.13	6.60	234.60	6.80	18.41	23.26	4.19	
1/16/2008	295.81	595.87	47.10	234.96	23.55	640.62	19.03	7.44	13.00	531.81	8.43	33.59	35.33	5.32	
1/17/2008	397.59	583.63	63.30	172.37	31.65	482.86	15.76	9.56	14.69	501.34	11.01	47.67	48.23	6.56	
1/19/2008	302.51	421.91	56.53	77.90	28.27	53.03	10.06	7.41	7.80	168.47	10.35	29.74	38.39	7.87	
1/20/2008	324.32	457.73	55.77	55.77	27.89	285.44	16.40	7.81	12.83	370.33	9.59	31.73	36.87	6.07	
1/21/2008	336.45	666.08	54.20	54.20	27.10	701.85	22.22	7.91	12.52	506.74	9.86	43.30	38.97	6.44	
1/22/2008	247.05	353.79	45.63	45.63	22.82	132.97	8.62	5.02	5.38	114.08	7.89	18.44	21.45	4.28	
1/23/2008	307.55	501.24	52.71	91.66	26.35	338.75	13.33	6.06	7.64	211.88	7.22	21.08	29.57	4.17	

Figures 4.14a and 4.14b show a global view of the temporal variation of elemental concentrations during the summer seasons.

Figure 4.14a

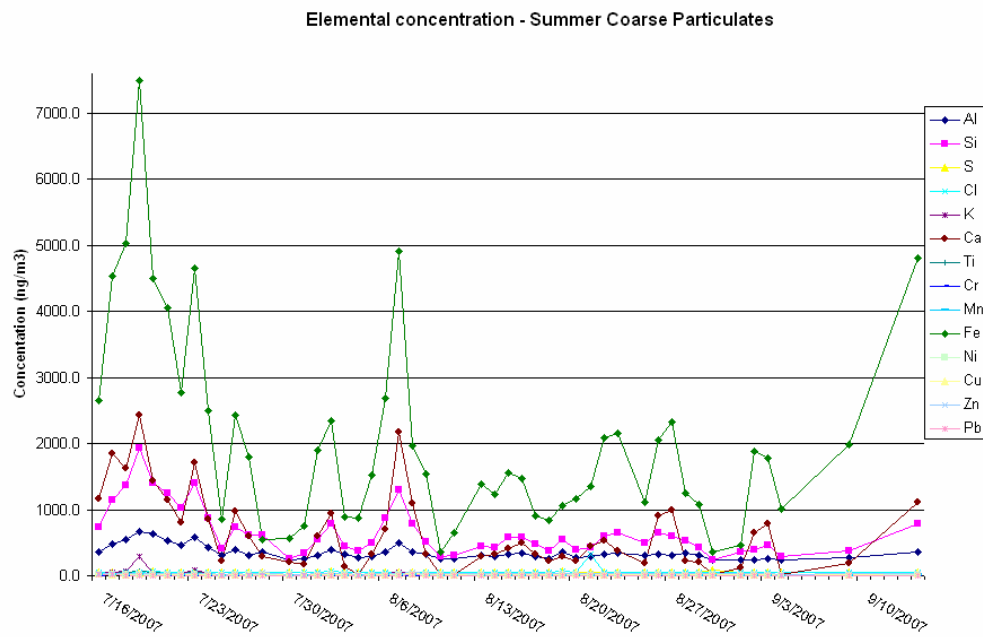
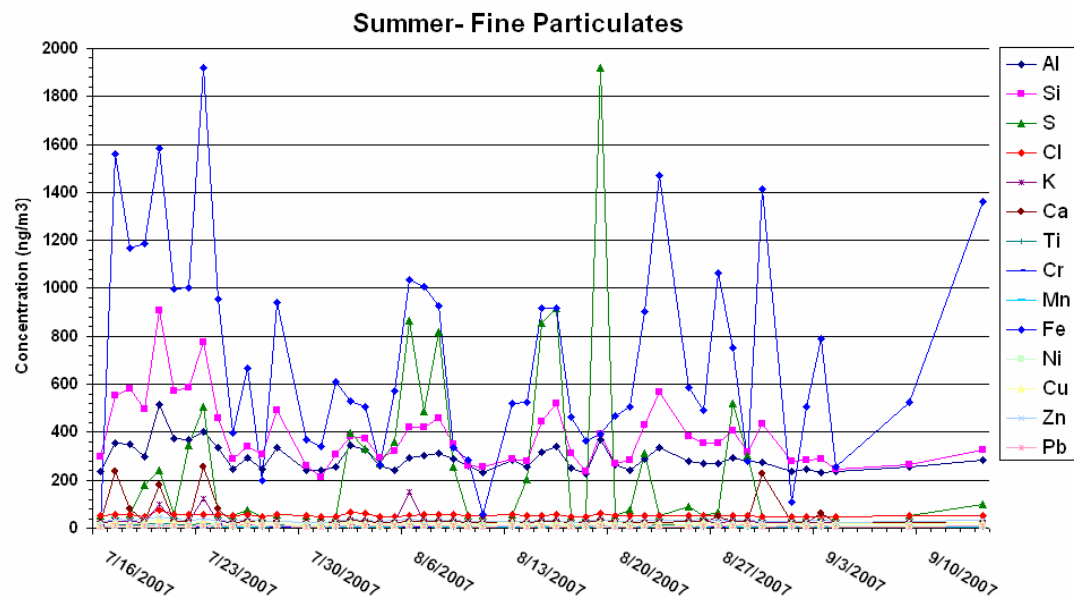


Figure 4.14b



Figures 4.15a and 4.15b show a global view of the temporal variation of elemental concentrations during the winter season.

Figure 4.15a

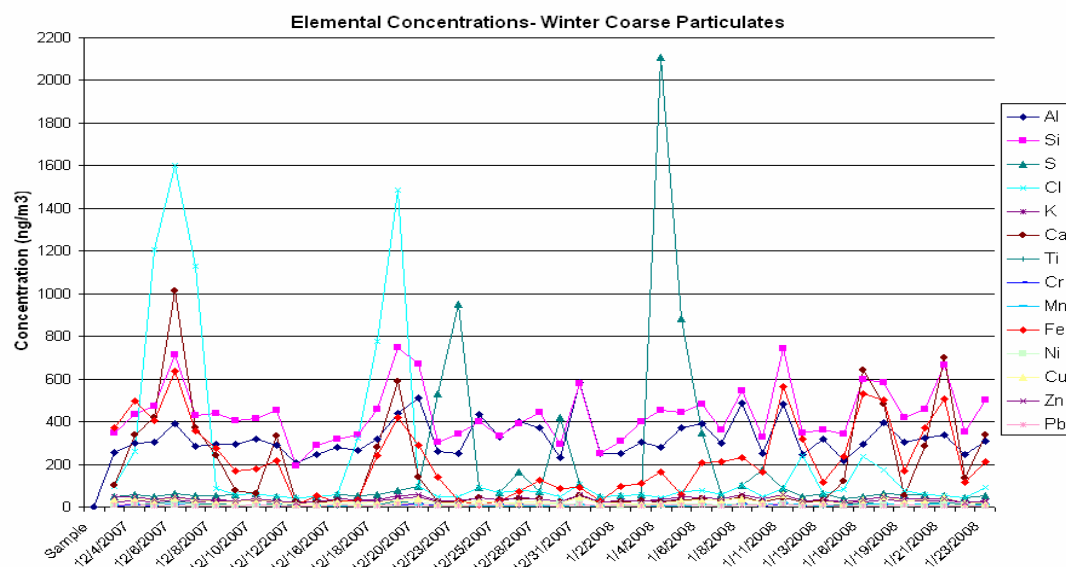
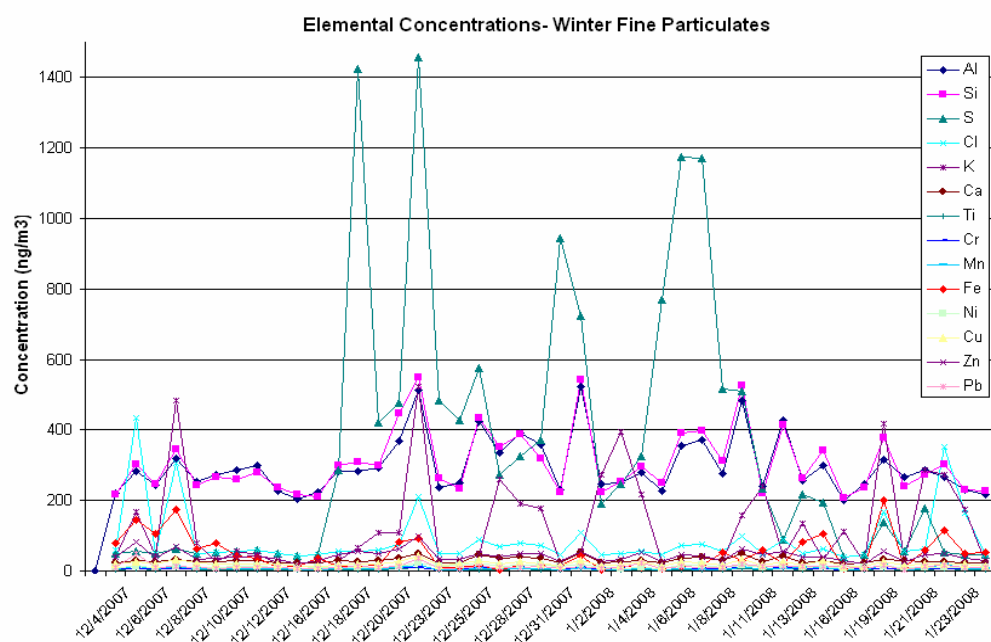


Figure 4.15b



4.3.1.5 Results and Discussions

The following elements were identified and quantified for the aerosol-loaded filters collected for the summer and winter seasons: Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb. Through a careful study of the X-ray spectra obtained for the different particle size fractions in the different seasons, one can glean additional information that could not have been possible simply with gravimetric analysis. For example, the elements Si, S, K, Ca, and Fe exhibit different concentration patterns for the different

seasons and can serve as possible indicators of sources of pollution in the area. Correlation tests were therefore carried out on a combination of elements. A strong correlation points to the elements originating from the same source and serves as a “give-away” of the particular polluting source. Figures 4.16 – 4.18 show some results of selected correlation tests performed.

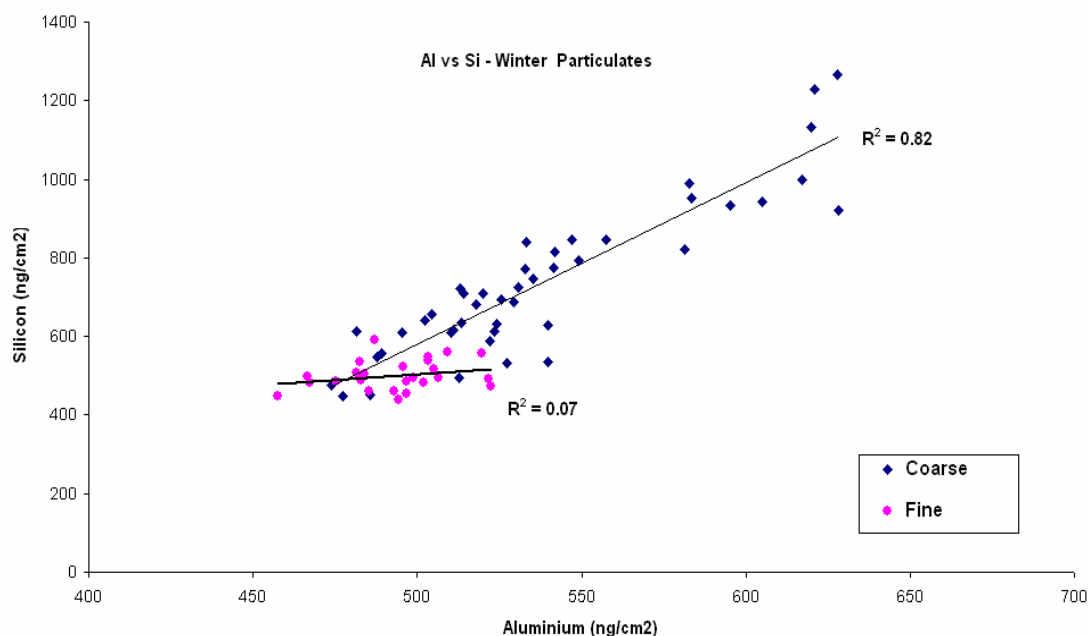


Figure 4.16 Correlation between Aluminium and Silicon concentrations

Aluminium and silicon are typical elemental signatures of particulates originating from the soil (dust). The fact that the correlation is poor in the fine fraction means that the Al and Si are predominantly in the coarse fraction. This is expected for dust or resuspended dust particulates.

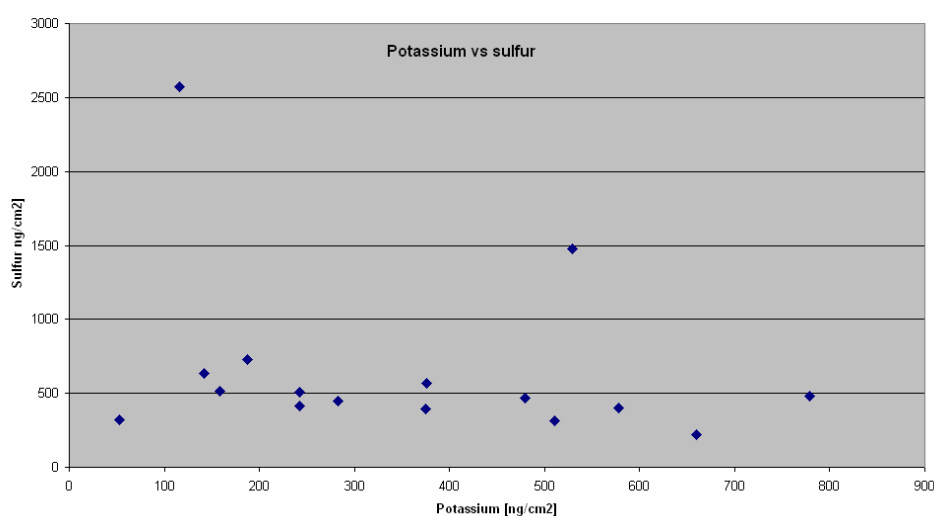


Figure 4.17 Correlation between K and S concentrations in the Fine Fractions (Winter)

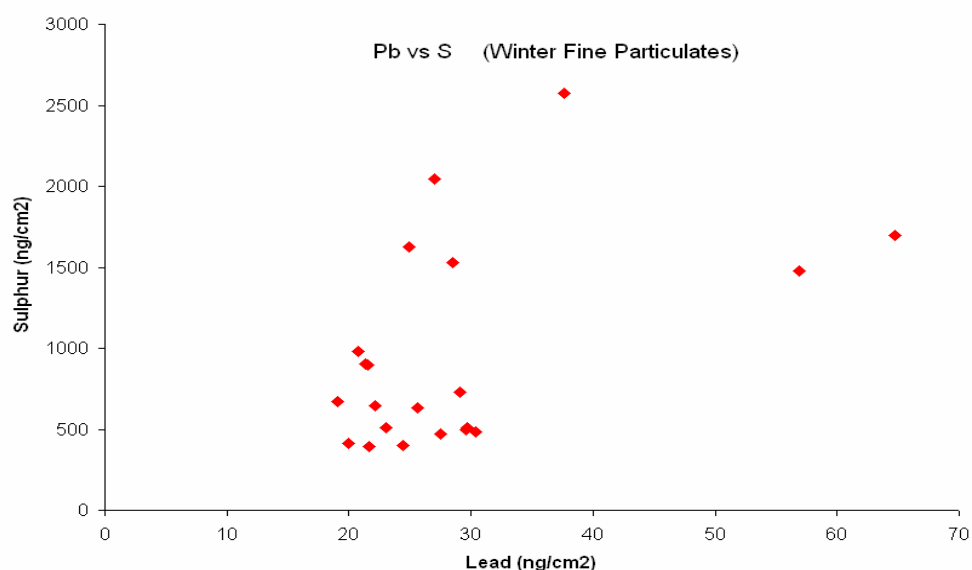


Figure 4.18 Correlation between Pb and S concentrations in the Fine Fractions (Winter)

Figure 4. 17 shows that no correlation exists between the concentration values of K and S determined in the fine fraction particles during winter. This fact indicates that the elements come from separate sources. On the other hand, Figure 4.18 shows that, the correlation between Pb and S concentrations in the fine fractions collected during the winter season points to two separate sources. Local information obtained leads to the identification of leaded-fuel from automobiles, and fossil-fuel based residential heating systems as the culprits for the Pb and S concentrations in the airborne particulates.

4.3.2 Proton-Induced X-ray Emission (PIXE) Analysis

The PIXE experimental set-up, which comprised of a PIXE/RBS beam line with links to two different accelerator systems (A Van de Graff accelerator and a Tandatron accelerator in tandem configuration), has been described in Chapter 3 of this thesis.

4.3.2.1 Optimization and Validation of Quantitative Method

Experimental measurements were undertaken to investigate the influence of filter (absorber) material, beam energy, and beam size, on PIXE analysis of selected filters. This was done under the following conditions, and through the analysis of sub samples of an international intercomparison air filter sample 1295:

- with 50 μm Kapton filter (as absorber between sample and detector)
- with 24 μm Mylar filter (as absorber between sample and detector)
- at 3 MeV and 5mm/7mm diameter beam size
- at 2 MeV and 5mm/7mm diameter beam size

The results obtained are shown in the Figure 4.19 , Figure 4.20 and Table 4.8 below

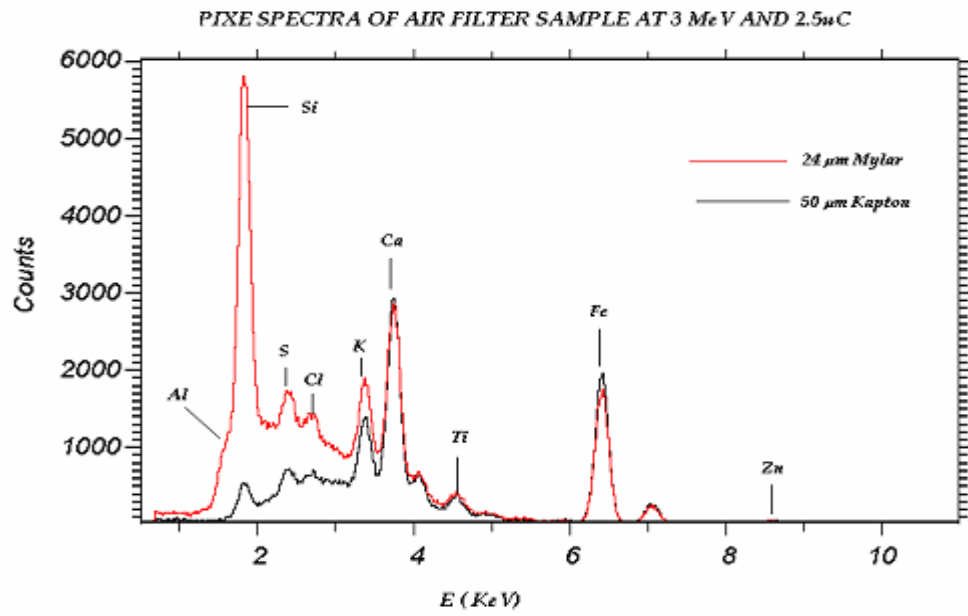


Figure 4.19 Comparison of Kapton and Mylar absorbers between sample and detector

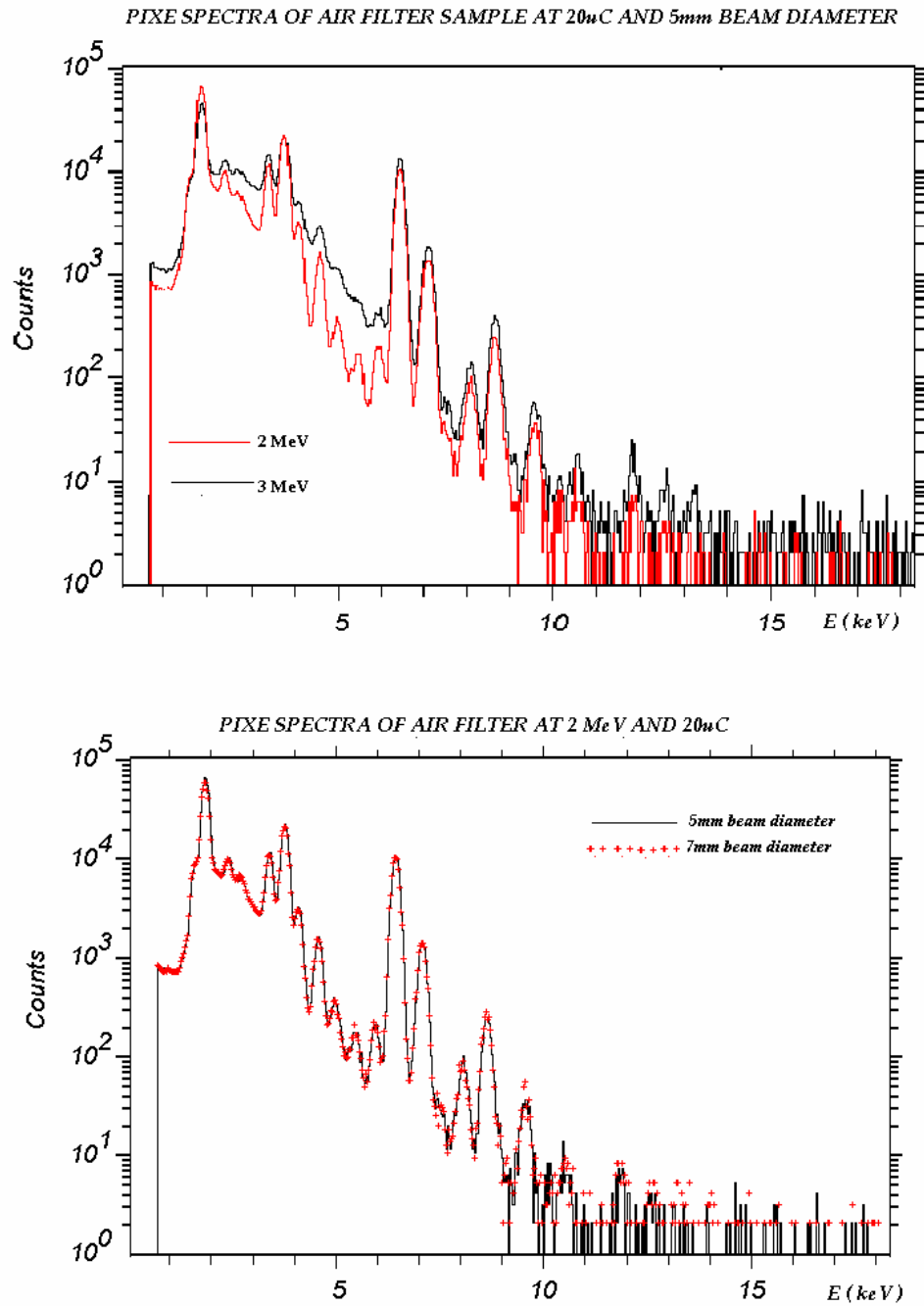


Figure 2

Figure 4.20 Top picture: Comparison of PIXE analysis of air filter at 2 and 3MeV proton energy respectively. Bottom Picture: Comparison of PIXE analysis of air filter at 2 MeV but with 5 and 7 mm proton beam diameters respectively.

Table 4.8 Air filter sample 1295 using Mylar absorber at 2 and 3 MeV beam energy

ELEMENT Sym	AREA(counts)		INTENSITY RATIO	% FIT ERROR	
	3 MeV	2 MeV	2MeV/3MeV	3 MeV	2 MeV
Mg	2592	2865	1.11	18.04	13.2
Al	57481	68975	1.2	1.47	1.06
Si	405986	593748	1.46	0.36	0.25
P	25156	22288	0.88	3.85	3.53
S	41341	44761	1.08	2.56	1.78
Cl	16212	12955	0.8	3.43	2.94
K	62227	64731	1.04	0.67	0.74
Ca	125710	141243	1.12	0.71	0.59
Ti	10721	9604	0.89	2.12	1.49
Cr	948	591	0.62	9.79	7.77
Mn	1148	1092	0.95	7.59	4.71
Fe	99295	77190	0.78	0.47	0.49
Ni	202	152	0.75	17.41	15.85
Cu	761	481	0.63	5.91	7.2
Zn	3041	1880	0.62	2.11	2.49
Br	121	35	0.29	13.56	26.64
Pb	119	63	0.53	15.59	19.46

Figure 4.19 shows that for the analysis of aerosol-loaded filters, it is preferable to use mylar foils as an absorber/filter between the sample and the detector. The mylar foils more successfully reduces low energy background without sacrificing the determination of light Z elements. It can be seen also from Figure 4.18 that irradiating the filters with different proton beam diameters of 5 mm and 7 mm did not make any observable impact. However, better signal to background ratios are obtained when the filters are irradiated with proton energy of 2 MeV than with 3 MeV protons. This is reflected in the higher counts obtained particularly for the light Z elements with 2 MeV protons as seen in Table 4.8. To determine the quantitative calibration factor H for the system, two standard reference samples NBS 147 and NBS1550 were used. Table 4.9 shows the results of the quantitative calibration of the PIXE set-up at proton energies of 2 MeV and 3 MeV, and for different conditions of filter/absorber material between sample and detector.

Table 4.9 Quantitative Calibration for PIXE Analysis of Aerosol-loaded Filters

Spectrum	Reference Sample	Proton energy	Foil	Element	Measured Conc.	Certified Conc.
307019	NBS 147	3 MeV	50um Kapton	Si	19.7	21.7
				Ca	11.6	12.1
				V	2.78	2.8
				Mn	2.98	2.8
				Co	0.64	0.61
				Cu	1.50	1.50
401053	NBS 147	3 MeV	None	Si	22.3	21.7
				Ca	11.6	12.1
				V	2.80	2.8
				Mn	2.91	2.8
				Co	0.64	0.61
				Cu	1.50	1.50
401051	NBS 147	2 MeV	24um Mylar	Si	21.1	21.7
				Ca	11.4	12.1
				V	2.78	2.8
				Mn	2.91	2.8
				Co	0.62	0.61
				Cu	1.58	1.50
401052	NBS 1550	2 MeV	24um Mylar	Si	22.1	22.1
				K	10.6	11.7
				Ti	7.95	8.2
				Fe	9.29	9.2
				Zn	4.22	4.1
				Pb	9.18/7.13	7.6

On the basis of the afore-mentioned results in Section 4.3.2.1, the following measurement conditions were adopted for optimized analysis of the collected air filter samples, with a focus on enhancing sensitivity for low Z elements:

Proton energy = 2MeV
 Filter/Absorber = 24um Mylar
 Beam diameter = 7 mm

The optimized quantitative calibration was subsequently validated by analyzing the air filter standard SRM 2783. The results are shown in Table 4.10

Table 4.10 SRM 2783 #240 AIR PARTICULATE ON FILTER MEDIA					
ELEMENT	Measured Conc. (ng)	Stat. Uncert. (ng)	Certified value	LOD (ng)	Meas./Cert value
Al	17103	347	<i>23210 ± 530</i>	308	0.74
Si	57886	98	<i>58600 ± 1600</i>	99	0.98
S	9572	15	<i>1050 ± 260</i>	44	0.91
K	5272	24	<i>5280 ± 520</i>	31	0.99
Ca	13464	39	<i>13200 ± 1700</i>	34	1.01
Ti	1601	16	<i>1490 ± 240</i>	18	1.07
V	52	15	<i>48.5 ± 6.0</i>	36	1.06
Cr	196	11	<i>135 ± 25</i>	21	1.45
Mn	374	14	<i>320 ± 12</i>	23	1.16
Fe	29941	90	<i>26500 ± 1600</i>	26	1.13
Cu	506	27	<i>404 ± 42</i>	37	1.25
Zn	2214	45	<i>1790 ± 130</i>	23	1.24

4.3.2.2 Design and Construction of Air Filter Sample Holder

In many situations where a sample is to be analysed with different techniques, sub-portions of the samples are taken (or cut in the case of air filters) and presented for analysis. In the case of nuclepore filters there is a serious risk of loss of material during sub-sample preparations, due to the nature of the filters. Besides, the representativeness of the sub-sample to the main sample cannot be assured. Consequently, to maintain the integrity of the samples in-between presentations to different analytical techniques, anew sample wheel and holder was designed and constructed for the IAEA's PIXE/RBS scattering chamber. The new design enables the mounting of whole 47mm nuclepore filters in the scattering chamber conveniently, and efficiently. In this way, the filters can be loaded and retrieved for other purposes without loss in material during sample handling and presentation. Materials used for the construction are aluminum sheet for the wheel and 47 mm Millipore petrislides for the holders. The design dimensions and the constructed sample holder are shown in Figures 4.21a and 4.21b

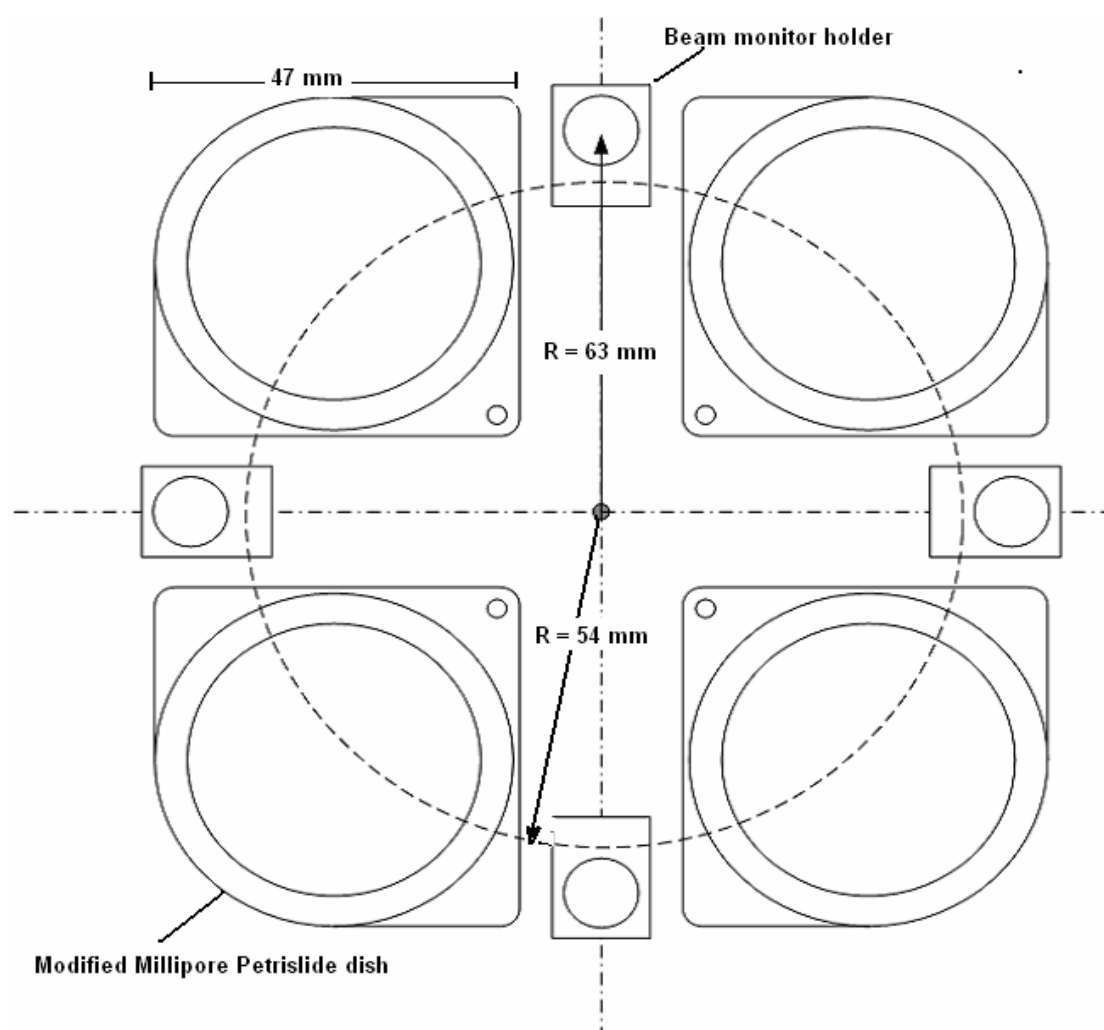
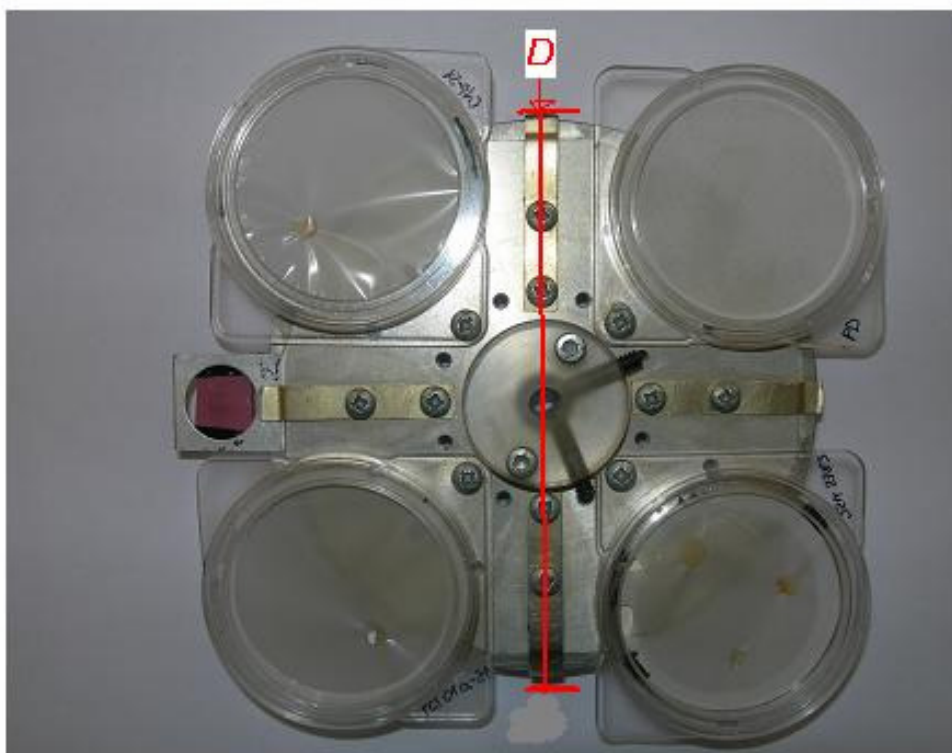


Figure 4.21a Design of air filter sample holder for the PIXE scattering chamber

Figure 4.21b Construction of the air filter sample holder for the PIXE scattering chamber



4.3.2.3 PIXE Spectra and Analysis of Air Filters

The air filter samples were irradiated with 2 MeV protons at a current of 5nA and a total charge of 10 μ C. Elements identified were Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb. Figure 4.22 and 4.23 show the PIXE spectra of the blank filters and standard reference filter respectively. Figure 4.24 is a typical sample spectra showing the significance of elemental concentrations in the different particle size fractions. Table 4.11 shows the elemental concentrations of some selected filters. As observed in the case of ED(P)XRF analysis, the overlapped PIXE spectra of both the coarse and fine particle fractions also show distinguishing elements that can serve as indicators for pollution source identification, and seasonal differences.

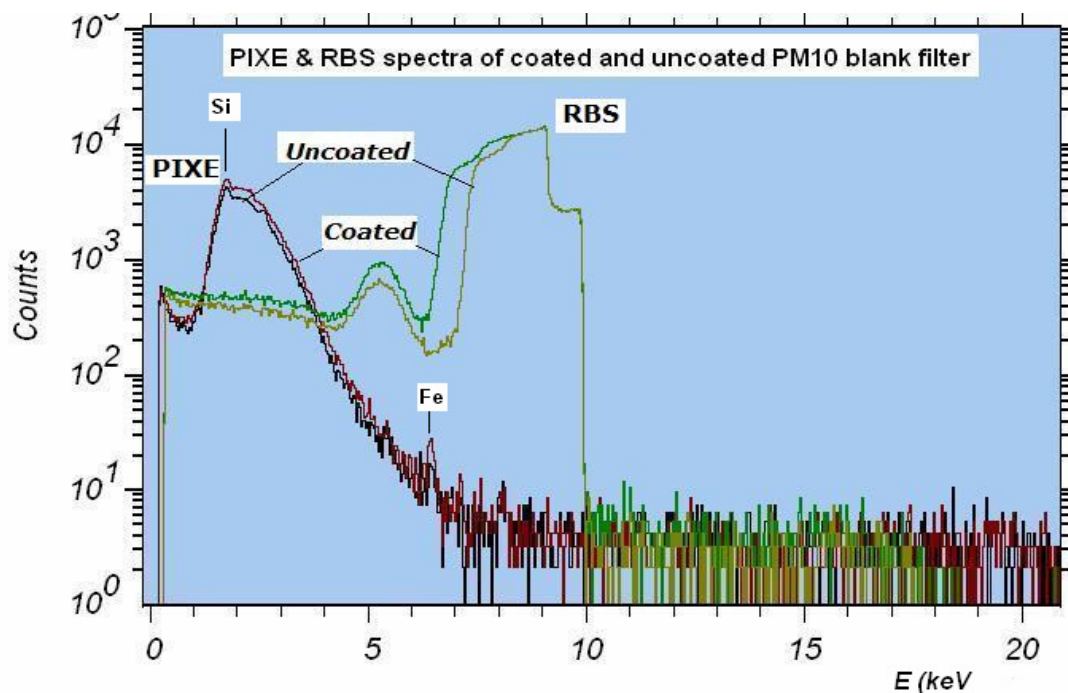


Figure 4.22 PIXE and RBS spectra of blank Nuclepore filters

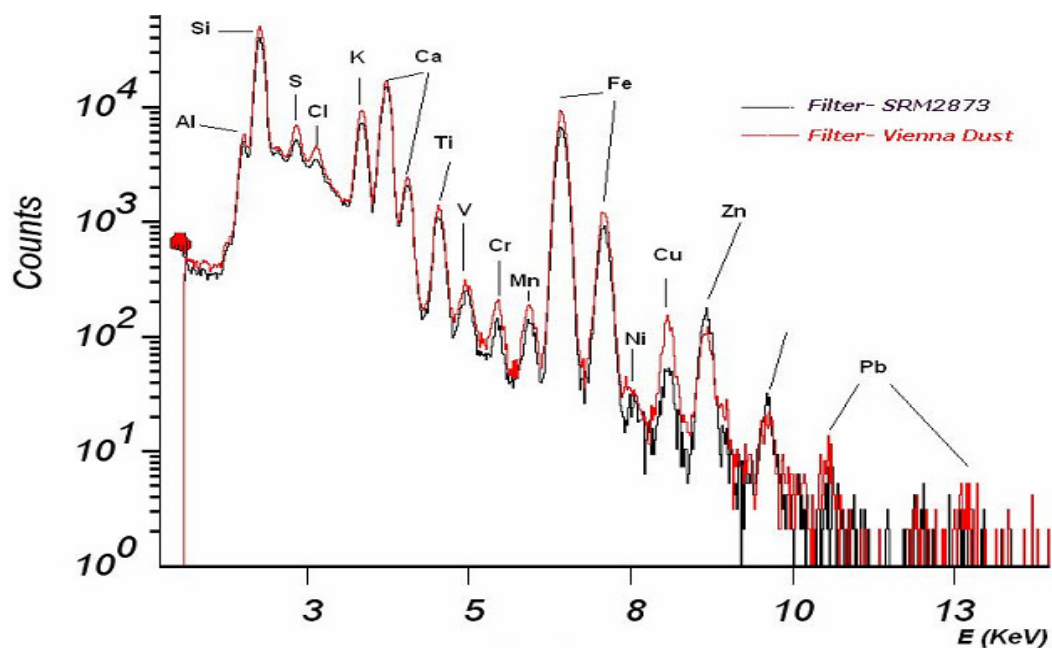


Figure 4.22 PIXE spectra of air filters from Vienna Dust and SRM 2873

Figure 4.23 PIXE spectra of air filter standard SRM2783 and IAEA Proficiency Test filter (Vienna Dust).

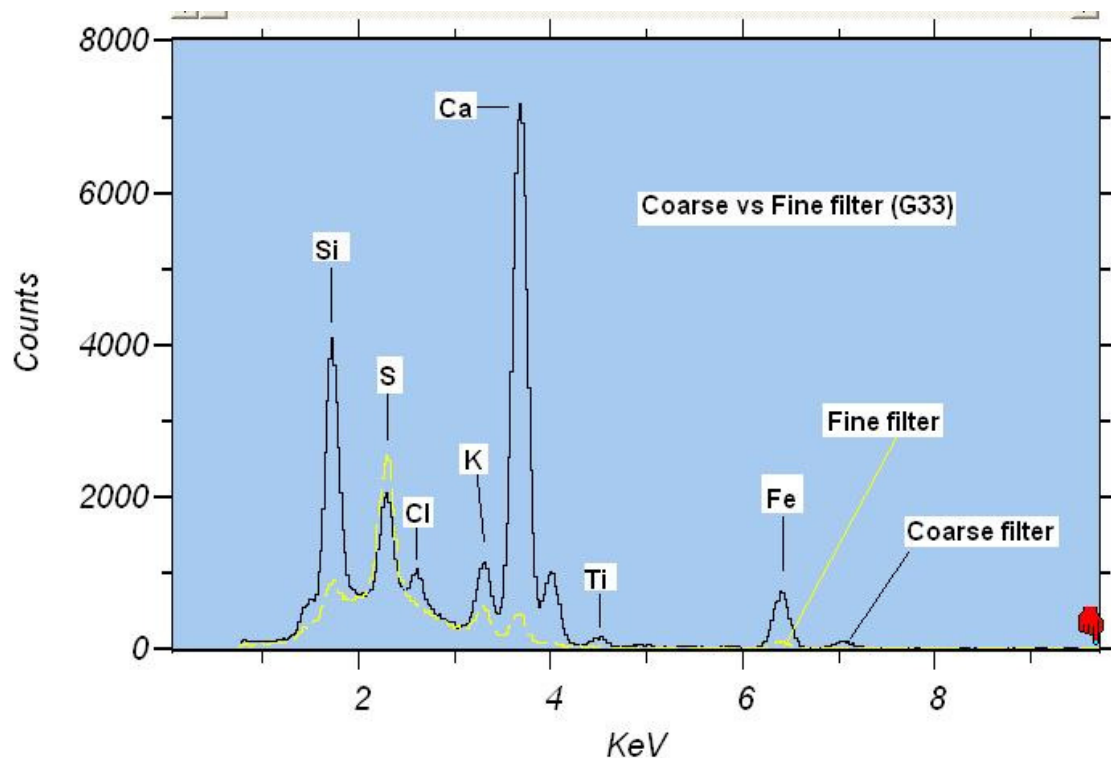


Figure 4.24 PIXE spectra of coarse and fine airborne particle fractions

Table 4.11 Results of selected summer samples (ng/cm²)

Sample	Al	Si	S	Cl	K	Ca	Ti	FeK	Cu	Zn
G61 Fine	111.7	352.5	1108	24.3	137.4	210	11.4	410.6	21.3	39.4
G61 Coarse	520.1	1582.1	270.8	93.2	186.2	1803	54.9	1240	34.2	38.9
G56 Fine	22.4	152.6	490.7	14.2	59.6	95.1	4.2	223.2	10	16.9
G56 Coarse	100.2	493.9	101.5	36.6	98.8	548.7	10.9	503.3	25.4	17
G51 Fine	30.5	146.7	401.7	12.2	56	44.5	5.3	111.4	5.8	11.1
G51 Coarse	84.9	360.7	91	79.8	88.6	236.3	7.1	337.4	17.2	12.1
G48 Fine	75.2	248.2	790.6	11.6	70	109.5	6.9	136	4	20.8
G48 Coarse	129	516	89.8	40.1	74.8	438.7	10.9	216.1	11.2	17.7
G46 Fine	< 27	136.7	1022.4	26.9	79.1	41.5	< 3	122	8.2	23.5
G46 Coarse	185.6	593	289.6	58.9	140.6	599.9	15.6	361.5	18.6	13.2
G45 Fine	56.9	224	1430.5	18.2	121.9	65.5	5.5	116.3	7.9	25.2
G45 Coarse	54.8	372.6	224.6	52.6	117.7	578	17.5	337.8	15	15.6
G36 Fine	45.9	199.2	1161.9	27.2	91.8	90.8	8.8	170.1	< 4	13.5
G36 Coarse	154.8	530.2	144.4	76.3	95.3	508.9	12.1	321.7	18.2	14.5
G34 Fine	47.3	211.2	780.3	12.4	99.7	125.9	7.6	125.9	3.9	13.3
G34Coarse	289.6	820	93.5	40.8	101	662.9	16.5	289.4	5.4	8.6

4.3.2.4 Results and Discussions

The results of PIXE analysis of some selected summer samples show that the elements Al, Si, Cl, Ca, and Fe occur predominantly in the coarse fraction of the summer particles. On the other hand, the element S showed predominant presence in the fine particle fractions. A comparison of the analysis of the standard filter sample SRM2783 by both PIXE and XRF techniques has been presented in Figure 4.25 below. Also shown in Figures 4.26 – 4.27 are a comparison of the results of PIXE and XRF analysis of the selected samples reported in Table 4.11. There existed a bias in the XRF results leading to higher values compared to that of PIXE. However, after correction of the XRF results with empirically derived functions, good agreement was established between the PIXE and XRF results. The correction functions were derived from the measured-to-certified ratio values for the SRM2783 standard for each element. The systematic shifts in the results were calculated by least square computation of the differences between the XRF and PIXE values. Hence the correction function is of the form: (See Table 4.12)

$$\text{XRF}_{\text{corr}} = (\text{XRF}_{\text{raw}} * \text{CF}) \pm \text{SHIFT}$$

corr = corrected value, raw = raw data, SHIFT = computed shift
CF = correction factor

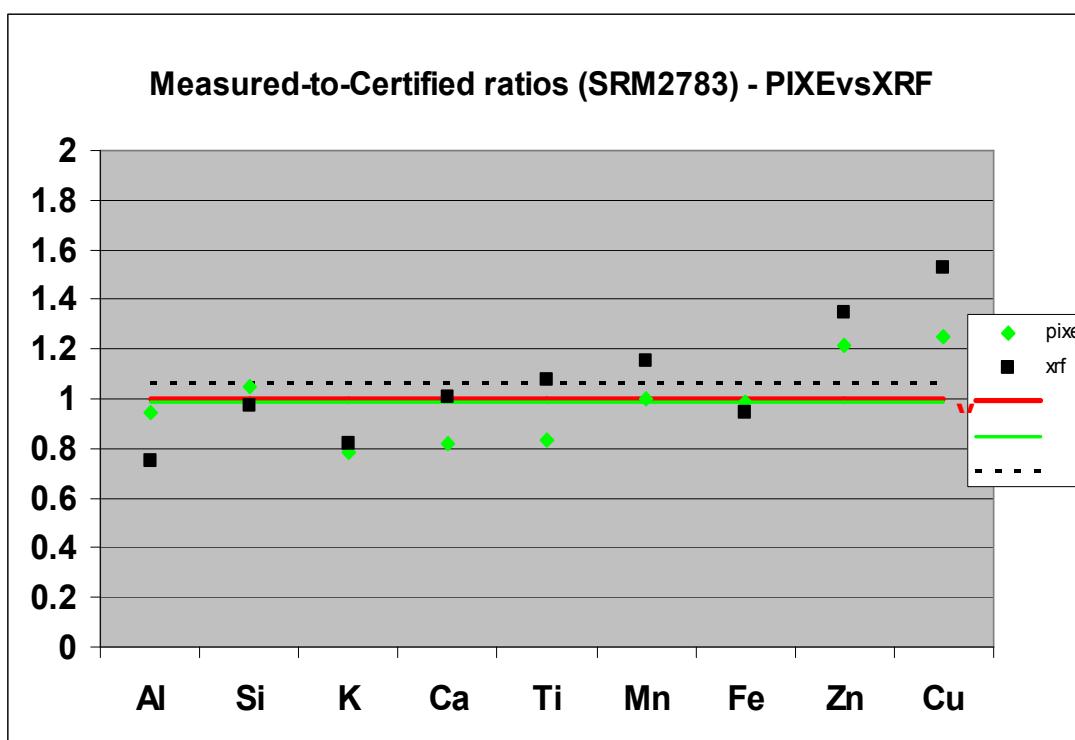


Figure 4.25 Comparison of measurement results of standard reference filter SRM2783 by PIXE and XRF

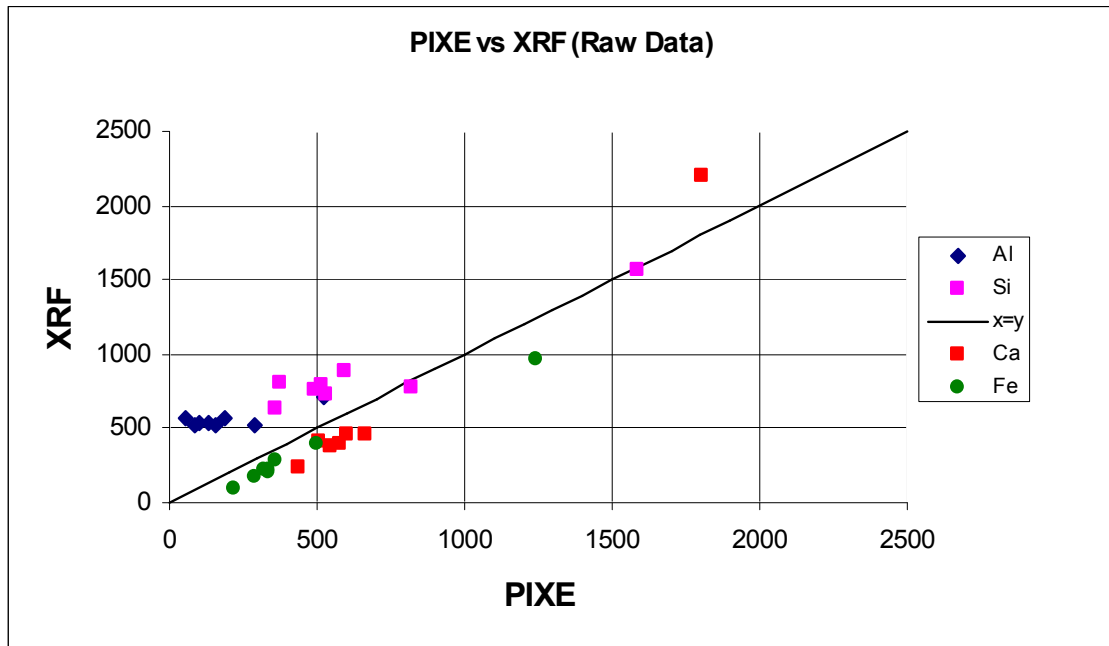


Figure 4.25 Comparison of PIXE and XRF analysis of elemental concentrations (ng/cm²) in some selected summer samples

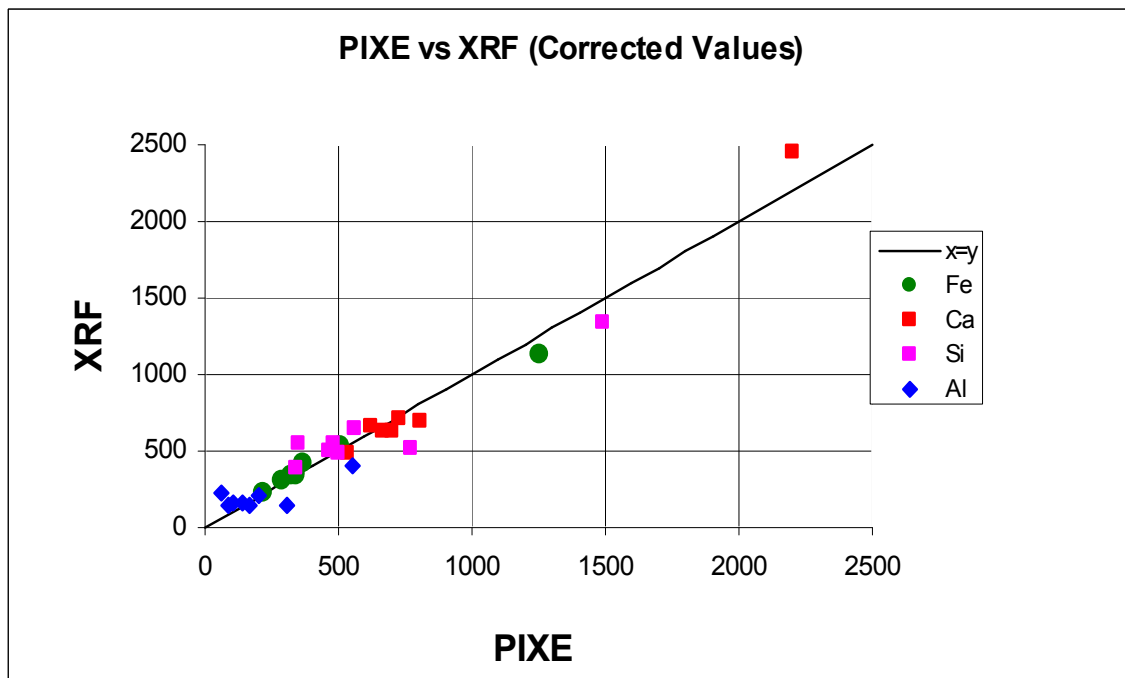


Figure 4.26 Comparison of PIXE and XRF analysis of elemental concentrations (ng/cm²) in some selected summer samples after corrections to XRF results

Table 4.12 Derived Correction parameters for XRF results

Element	Correction Factor	Calculated Shift
Al	1.35	-554
Si	1.01	-255
Ca	1.00	244
Ti	0.93	1
Fe	1.05	120
Cu	0.66	-14
Zn	0.75	-31

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CHAPTER 5. DEVELOPMENT OF A TECHNIQUE FOR DEPOSITING AIRBORNE PARTICULATE MATTER ON IMPACTOR SUBSTRATE FOR DIRECT TXRF/PIXE ANALYSIS

5.1. INTRODUCTION

In most air pollution studies, the recommended approach to sampling airborne particulates is by air filtration. Consequently, reference samplers and methods have been prescribed for the sampling of PM₁₀ and PM_{2.5} particle size fractions (1- 4). There exist, however, significant limitations in the reference methods of sampling air particulates when sampling in remote or unpolluted atmospheric environments. In such cases, mass concentrations are so low that sampling for even more than 24 hours still results in low mass loadings on the filter. Under these conditions, most analytical techniques employed for elemental composition determination do not have enough sensitivity. The analytes of interest exist at the level or less than the level of the detection limits of the techniques. Many analysts therefore resort to preconcentration of the analyte prior to analysis. This approach, however, poses the risk of introducing analyte contamination during the preconcentration process. Besides, it is not cost effective when dealing with large number of collected samples and for routine analysis. A better alternative is the combination of sampling with an air impactor sampler, followed by analysis with total reflection X-ray (TXRF) spectrometry or proton induced X-ray emission (PIXE) spectrometry. This enables both size fractionation and multielemental determination in the range of ng m^{-3} , in a relatively shorter time of sampling. Such a combination has already been used and reported on (5 – 9). All these works involved the use of single-orifice impactor samplers with multistages. The differences were in the number of stages, the range of sizes segregated, the flow rates, and the impaction substrates used. Impactor substrates used for direct deposition in these studies, included quartz carriers (siliconized/unsiliconized), glassy carbon, and Plexiglas (Vaseline-coated). In those studies where parallel sampling was done using the reference method, the impactor samplers were found to underestimate the concentration values. This was attributed essentially to bounce-off effects, and wall losses between stages

This project work was consequently undertaken in order to carry out:

- (1) investigation for a candidate material suitable as and impactor substrate in a multi-orifice impactor sampler
- (2) the development of a technique for depositing airborne particulate matter on an impactor substrate for subsequent analysis by both TXRF and PIXE techniques.

The impaction sampler used in this work is the Dekati PM-10 sampler. The equivalence of this sampler to the EU reference sampler has already been established, and the sampler has only three stages. These stages are nevertheless, the stages for the separation of coarse, fine and finer particles $< 1 \mu\text{m}$. It is a multi-orifice impactor sampler, and very few works have been carried out on direct impaction using multi-orifice impactors. The materials investigated as candidates for the impactor substrate were Plexiglas and silicon wafer. These were investigated considering their appropriateness for use as carriers in TXRF spectrometers, and analysis with both PIXE and TXRF techniques.

5.2. IMPACTOR AIR SAMPLER

5.2.1 Theoretical Considerations

The performance of impactor samplers are governed essentially by their Stokes number and other design parameters such as Reynolds number, nozzle-to-plate distance, throat length of the impactor, and diameter of the impaction plate. The Stokes number is a dimensionless number that gives an indication as to how particles moving in a fluid will behave, and therefore determines the collection efficiency of a jet. It is given as (10):

$$\text{Stk} = \frac{\rho_p d_p^2 C_c v_o}{9\mu W} = \frac{4\rho_p C_c d_p^2 Q}{9\pi\mu W^3} \quad - (1) -$$

ρ_p = the particle density (g/cm³),

d_p = the diameter of the particle (μm),

W = the nozzle diameter (cm),

V_0 = the jet velocity (cm/sec),

Q = the sampler flow rate

C_c = the Cunningham's slip correction.

μ = the viscosity of the flow medium

Stokes number is related to particle diameter and is consequently influenced by the desired particle cut-off point (Dp_{50} - the aerodynamic diameter at which half the particles are removed). This determines the size fractionation stages in the impactor sampler. Reynolds number is related to the velocity, and thus to the flow rate. In other words for more flow (larger sample) one needs to increase R-number value. For round jets this range is between 500 and 3000. However, once the upper limit (3000) is reached the only solution is to introduce a second jet, and further on until you reach the wanted flow rate through the sampler. Hence, multi-orifice jets offer the advantage of collecting relatively more particulates in a relative short time, at lower flow rates, and with lower pressure difference compared to single-orifice impactors.

The 50% collection efficiency cut-off for a multi-orifice impactor is therefore calculated from the equation (10):

$$d_{p50} = \sqrt{\frac{9\pi Stk_{50} \mu W^3 N_i}{4C_c \rho_p Q}} \quad - (2) -$$

where

N_i = number of jets

The key impactor design parameters and the principle of impaction are illustrated in Figure 1.

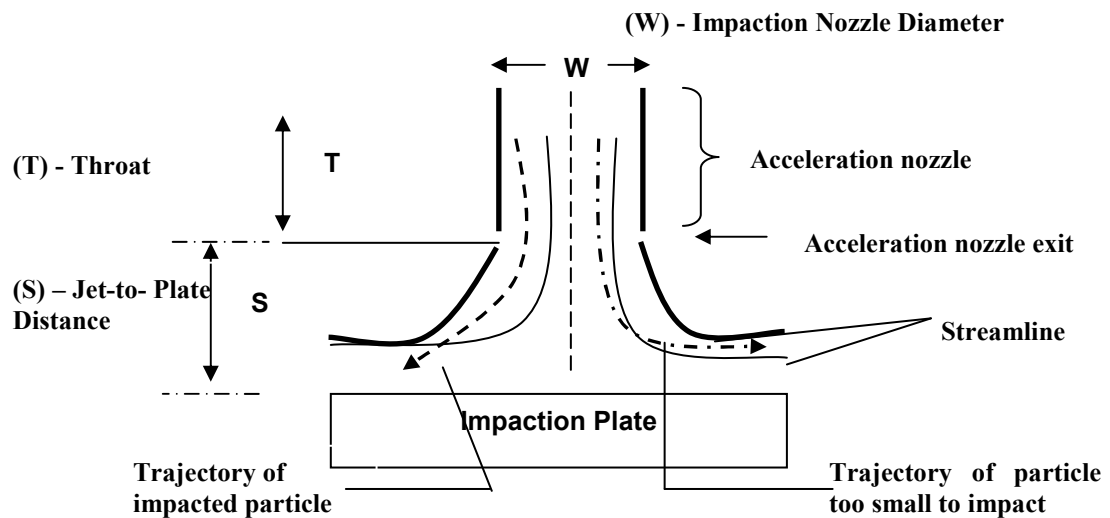


Figure 1. Principle of impaction

The Dekati PM-10 sampler used in this project selectively collects airborne particles of different aerodynamic particle sizes. The 50% cut-point (D50) of the sampler has been selected so that PM₁₀, PM_{2.5} and PM₁ concentrations can be determined simultaneously. Particles are collected on impactor substrates in four successive impactor stages. The first PM-10 stage removes particle larger than 10 microns off the particle stream. The second PM-2.5 stage collects particles smaller than 10 microns and larger than 2.5 microns. The third PM-1 stage collects particles smaller than 2.5 microns and larger than 1 micron. A back-up filter after the impaction stages constitutes the fourth stage, and collects all particles smaller than 1.0 μm . Dekati PM-10 impactors are available with flow rates of 10, 20, and 30 lpm. The impactor used in the project operated at 10 lpm and is shown in Figure 2.

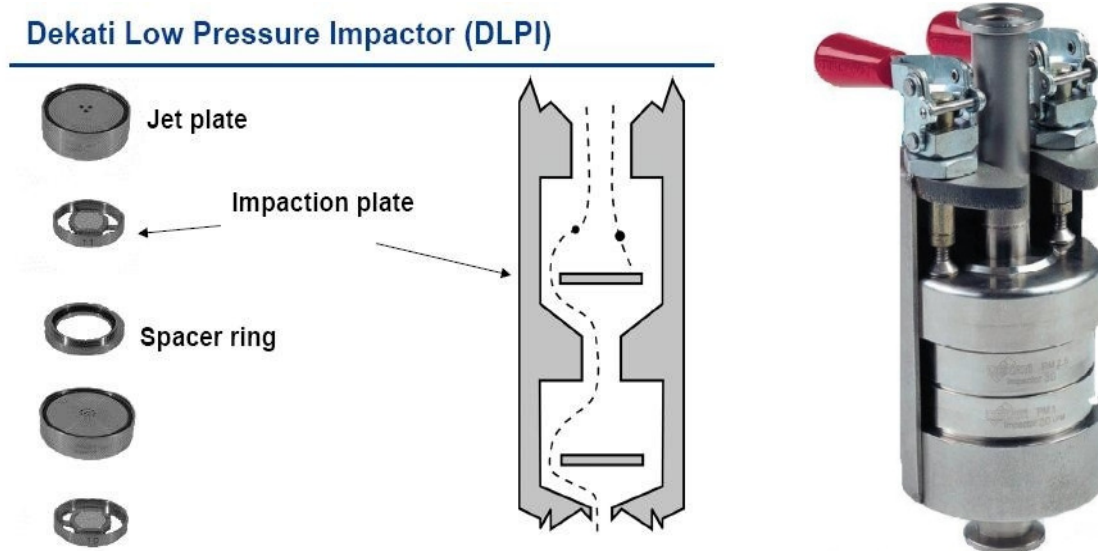


Figure 2. Setup of Dekati PM₁₀ Impactor Sampler (11)

5.2.2 Impactor Modifications

In the conventional operation of impactor samplers, the impaction surfaces are usually covered with an appropriate filter, which is digested and analyzed by TXRF or other analytical techniques. For direct deposition on the impactor substrate, there was the need to modify the impaction system such that the aerodynamic characteristics of the sampler are not affected. Since the same particle size fractions are to be sampled, aerodynamic considerations therefore required that the same Jet-to-Plate distance S (refer Figure 1) is ensured. Hence precise mechanical modifications were carried out

on the original impactor source holder in order to be able to hold a reflector/impactor of 30mm in diameter and 4mm thickness, while maintaining the same distance S from the Jet.

Figure 3 shows the original and the modified impactors (with Plexiglas spacer and substrate)

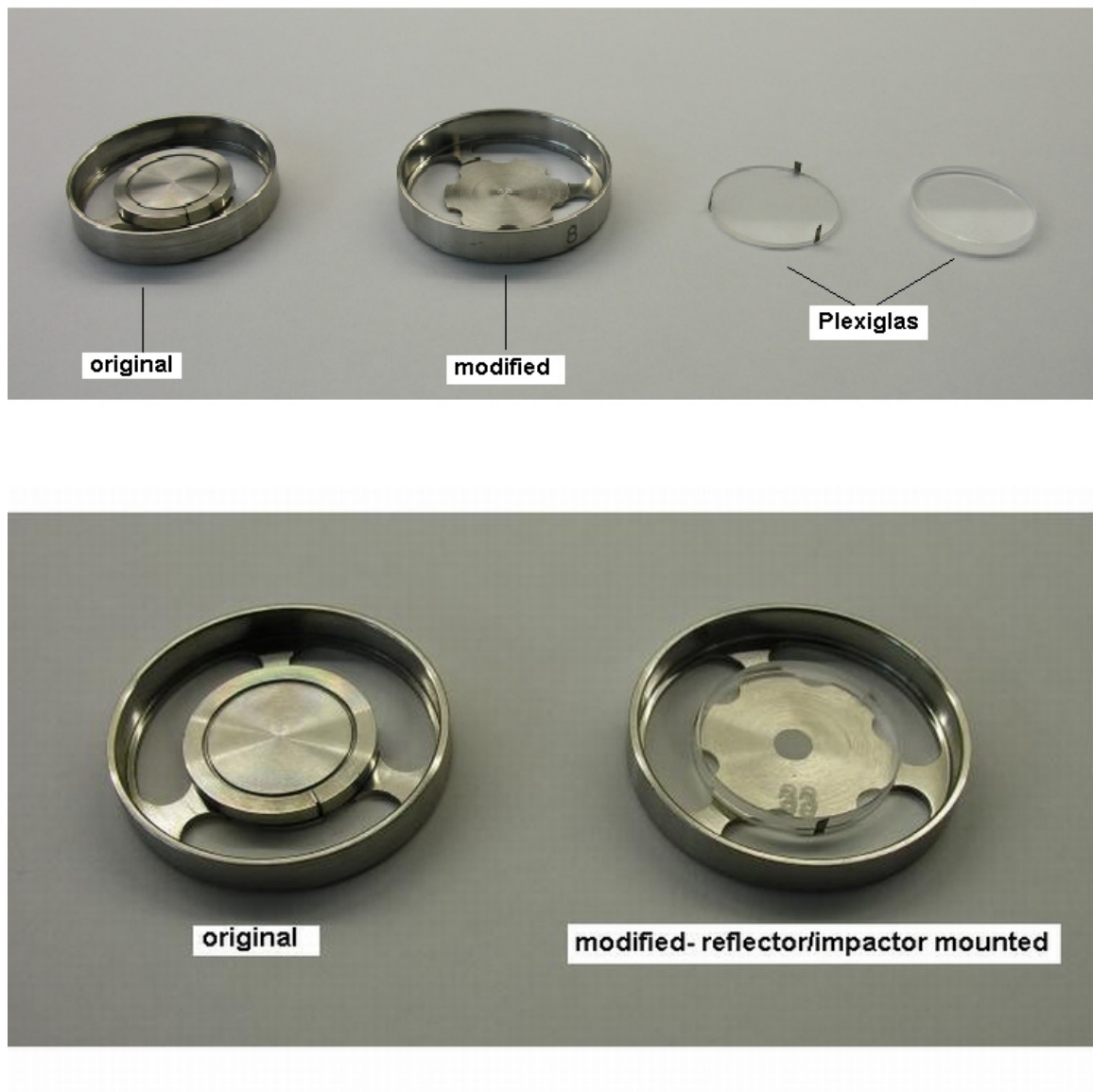


Figure 3. Modifications carried out on the original impactation system

5.2.3 Candidate Impactor Substrate

In TXRF spectrometers a carrier is needed to serve as a sample support as well as a totally reflecting mirror. The material to be used as the carrier should have the following characteristics.

- Machinable to a perfectly flat and smooth surface
- Immune to aggressive chemicals and mechanical stresses
- Free of fluorescence lines over the energy range of interest
- Free of contamination
- Hydrophobic
- Available at reasonable price
- High reflectivity under operating conditions

Table 1 gives an overview of different carrier material that could possibly serve as a candidate impactor substrate in the project work.

Table 1. Important Properties of Various Materials Used as Sample Carriers (12)

Carrier Material	Plexiglas	Glassy Carbon	Boron Nitride	Quartz Glass
Critical angle for Mo-K α	0.08	0.08	0.10	0.10
Reflectivity at 0.07°	99.8%	99.8%	99.9%	99.4%
Flatness	Good	Fair	Good	Excellent
Purity	Good	Fair	Good	Excellent
Fluorescence	None	None	None	Silicon
Resistance	Insufficient	Good	Excellent	Good
Cleaning	Not needed	Difficult	Easy	Easy
Price for one	\$0.10	\$30	\$60	\$28

Some of the above and other materials such as sapphire and polished silicon have been investigated and reported on (13 – 16). Considering Table 1 above and the cited references, two materials were chosen as candidate impactor substrates for study in this project. The major factors aside for their suitability as carriers were commercial availability, and cost. The selected materials were the Plexiglass or Perspex, and Si

wafer. These candidate materials also have to meet the requirements for analysis by TXRF and PIXE.

5.3. ANALYTICAL TECHNIQUES

5.3.1 Total Reflection X-ray Spectrometry

When X-rays are incident on a suitable reflector at glancing angles less than the critical angle for the reflector, the X-rays undergo total external reflection. If a sample of interest is located at the point of incidence, the sample will be excited by both the incident and the reflected X-rays. Furthermore, there will be minimal penetration into the substrate owing to the total reflection. These processes lead to a higher sensitivity in TXRF analysis even for minute samples, due to the increased fluorescent excitation and reduced background photons. An estimate for the critical angle for total reflection is given as:

$$\alpha_{\text{crit}} = \frac{1.65}{E} \sqrt{\frac{Z\rho}{A}}$$

where

Z = atomic number of reflector medium

A = mass number of reflector medium

ρ = density of reflector in g cm^{-3}

E = incident photon energy in keV

Also shown in Figure 4 is a schematic diagram for TXRF setup.

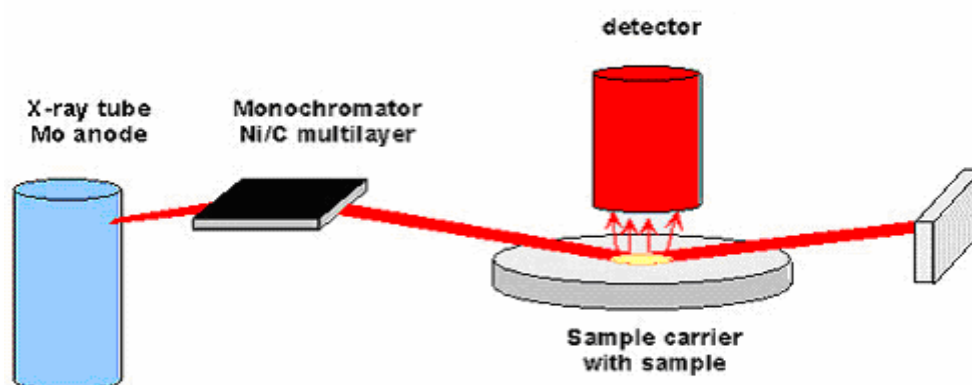


Figure 4 A TXRF spectrometer setup

TXRF technique is known to offer some significant advantages over conventional X-ray fluorescence spectrometry. These advantages are:

- Background reduction due to very little penetration or absorption into the reflector
- Double excitation of sample by both incident and reflected beam
- Small source-sample-detector distances (due to grazing incidence), thus providing large solid angle
- Small sample volume required
- Simpler quantification procedure owing to avoidance of correction for matrix effects
- Detection limits in the pg range

Further details on the principles of total reflection X-ray spectrometry and its applications can be found elsewhere (17 – 19).

5.3.2 Proton-Induced X-ray Emission (PIXE) analysis

The selected materials of Plexiglas and silicon wafer were also subjected to tests as to their suitability for PIXE analysis. In PIXE technique a beam of energetic protons are accelerated onto a target (sample) of interest. This causes ionization and atomic excitation, leading to the ejection of inner-shell electrons from atoms in the target. The inner vacancies created are filled by outer shell electrons resulting in the emission of X-rays which are characteristic of the target's elemental composition and concentration. The X-ray spectrum is usually recorded in an energy dispersive mode using a Si(li) detector. The energies of the emitted X-rays are used to identify the atoms or elements in the target, and the X-ray intensities used to determine the element concentration. Details on the principles of PIXE and its applications have been published elsewhere (20-22). The PIXE facility employed in this work is as shown in Figure 5 below:



Figure 5. (a) The Scattering Chamber (b) The IAEA PIXE beamline

5.3.2.1 PIXE analysis of candidate impactor substrates

Plexiglas material and silicon wafer were subjected to proton bombardment followed by PIXE analysis. Two types of Plexiglas material were used, and is described here as plain (for the transparent type) and blue (with slight tinge of pale blue reflection).

Figures 6 (a)-(c) shows the PIXE spectra of the candidate impactor substrates investigated

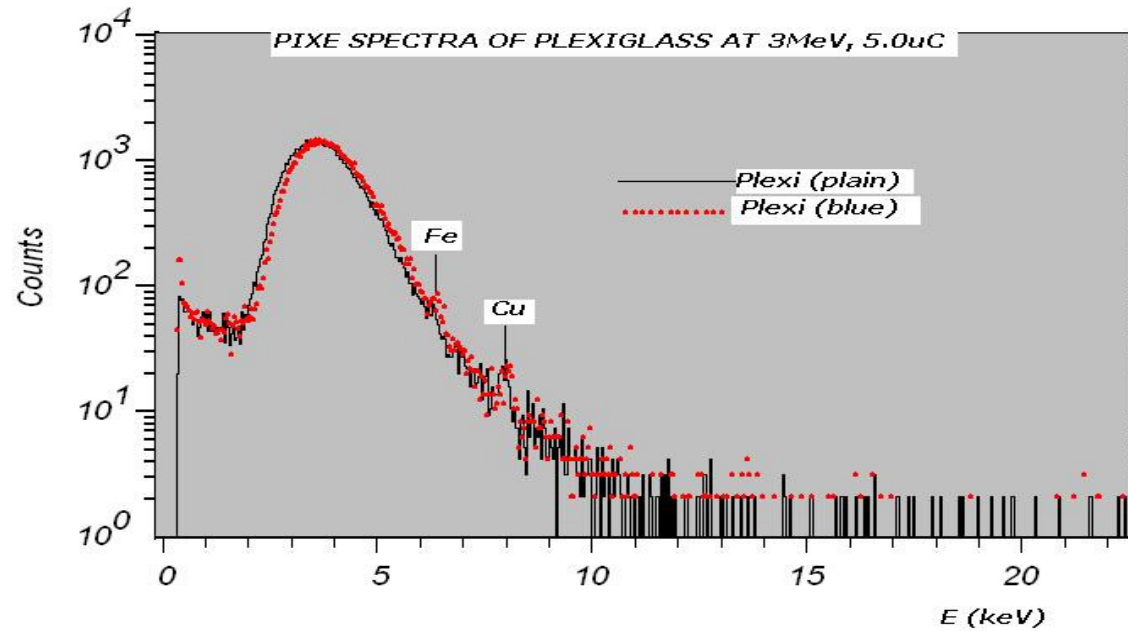


Figure 6a PIXE spectra of two different types of Plexiglas

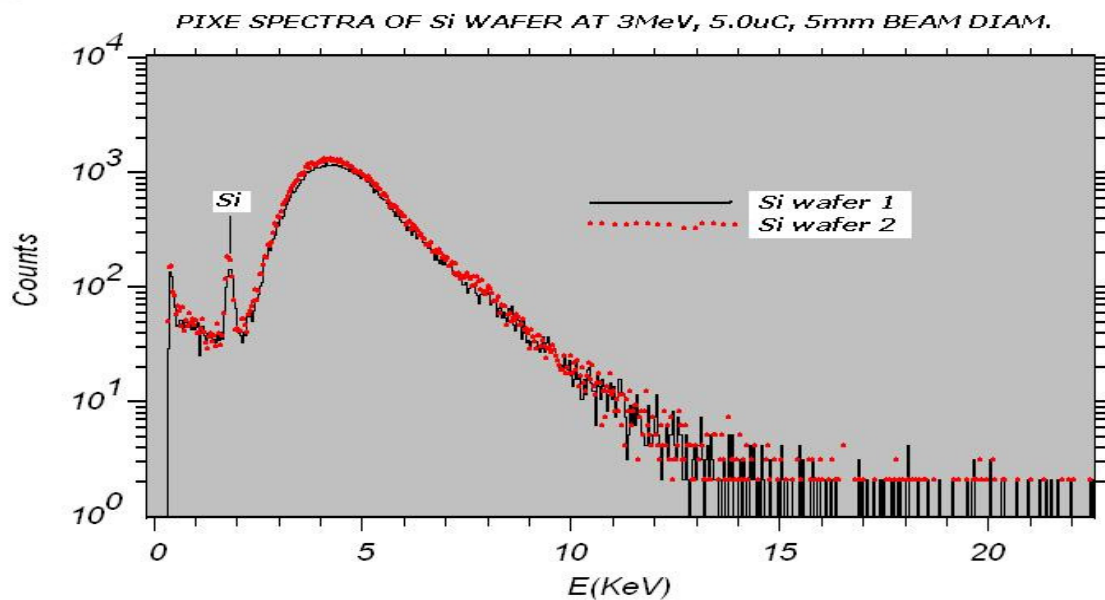


Figure 6b PIXE spectra of two replicate analysis of Si wafer material

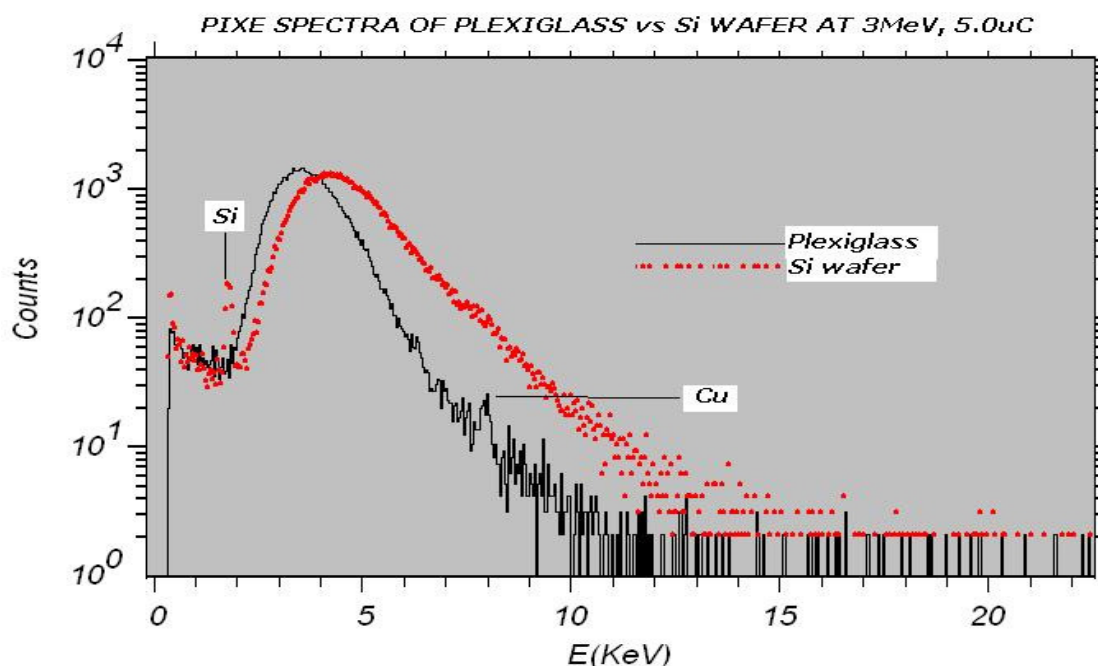


Figure 6c PIXE spectra of Plexiglas and Si wafer materials under same experimental conditions.

Figure 6a shows some small traces of Fe and Cu in the spectra for the Plexiglas material. These elements are instrumental blanks emanating from the setup within the scattering chamber, and are below the detection limits.. The elements Fe and Cu should also have been seen in the spectra of the silicon wafer sample. However, charging effects due to proton bombardment on the silicon wafer has swamped up the appearance of the said elements. Aside from the charging effect on the silicon wafer material, Figure 6b also shows its Si fluorescent peak. For air pollution studies, this will pose as a serious interference line for significant low Z elements needed in performing source profiling and pollution source apportionment. Consequently, the Plexiglas material was chosen as the preferred material for consideration as an impactor substrate.

A PIXE spectrum of a thick pelletized sample of the Prague Dust used in this work is shown in Figure 7 below. It shows the elements identified in this sample.

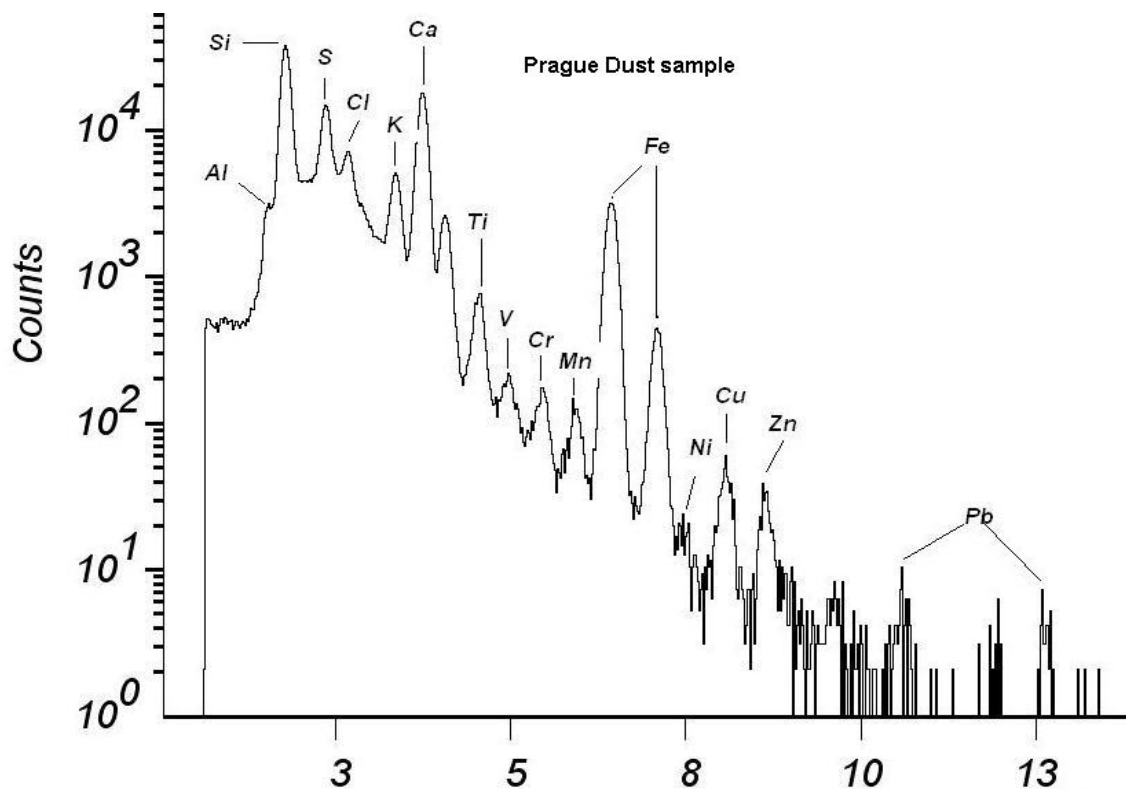


Figure 7. PIXE spectra of a thick pellet of Prague Dust

5.4. PLEXIGLAS AS AN IMPACTOR SUBSTRATE IN DEKATI-PM10 SAMPLER

The impaction substrate selected and used in the modified Dekati-PM10 sampler are commercially available Plexiglas carriers. These carriers have a diameter of 30 mm and a thickness of 4 mm. They fit directly into most of the TXRF spectrometers available on the market. To prevent particle bounce-off, different coating media were tried out. Trials with a coating media made from a mixture of Vaseline and Apiezon were found to be quite effective. After thin and uniform application of the above mixture on the Plexiglas surface, particles can be deposited without any bounce offs. The “Prague Dust” (22) was used in simulating particulate deposition through the air sampling system. The deposited particles on the coated carriers even resisted attempts to gently blow the particles off. Figure 8 shows examples of some of the samples collected in different size fractions on the Plexiglas impactor substrate.

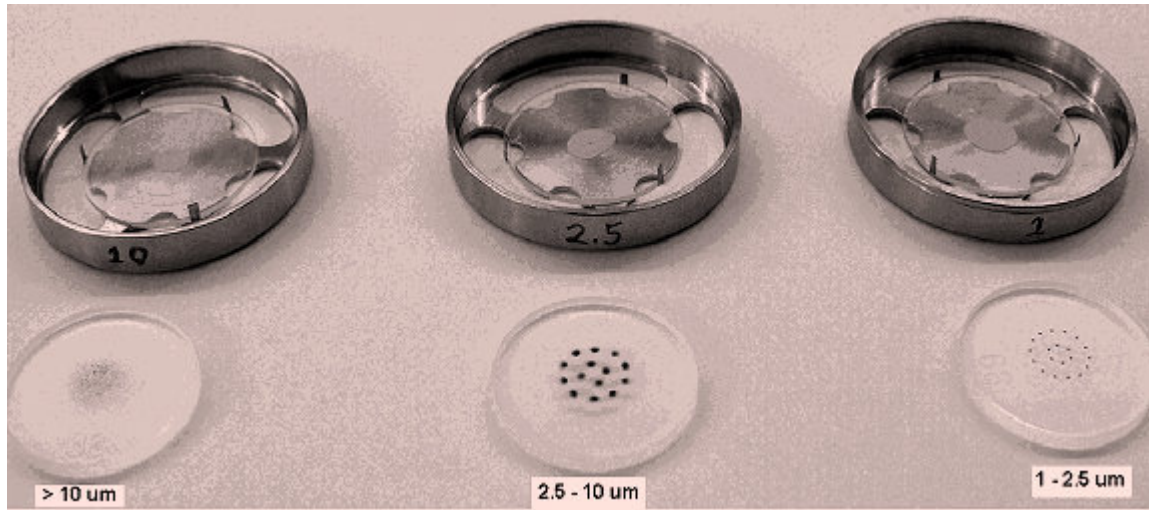


Figure 8. Dust particulates collected on coated Plexiglas impactor substrates

Also shown in Figures 9a and 9b are TXRF spectra of the deposited particulates on the Plexiglas reflectors/impactors.

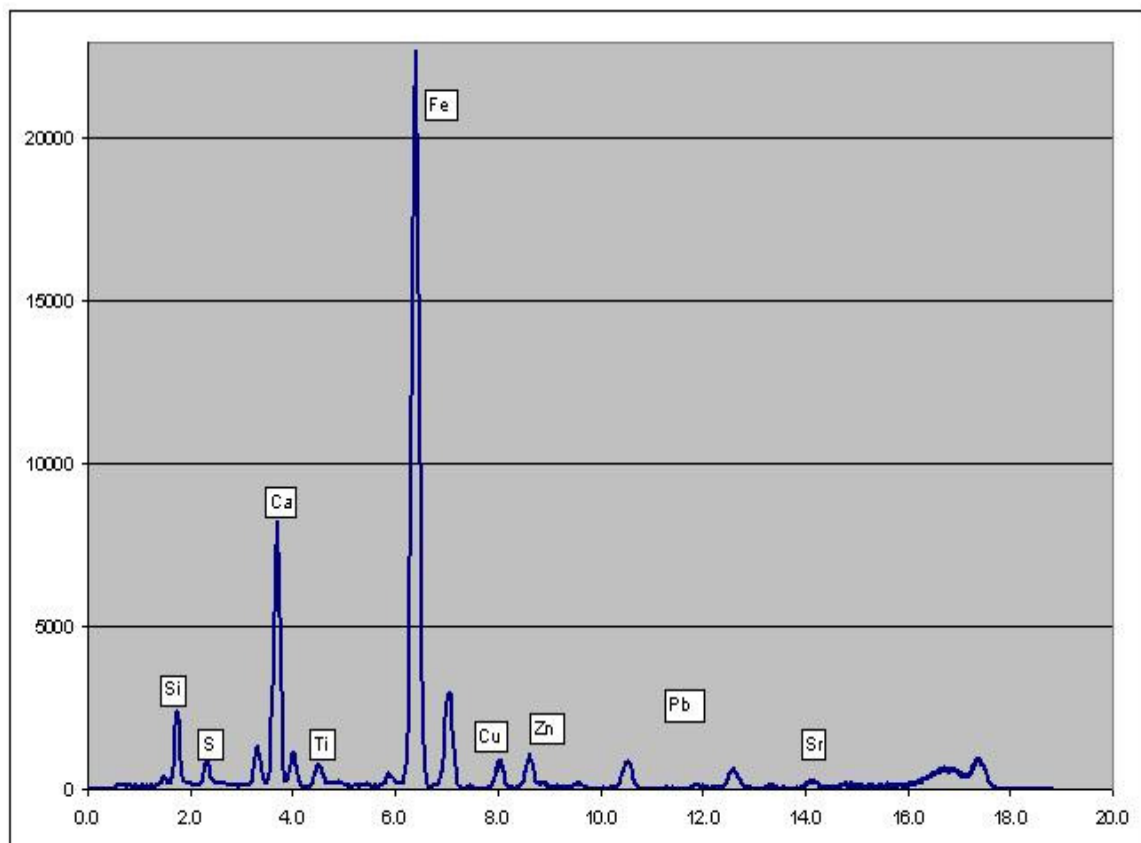


Figure 9a Typical TXRF spectrum of "Prague Dust" particulates deposited on Plexiglas impactor substrate.

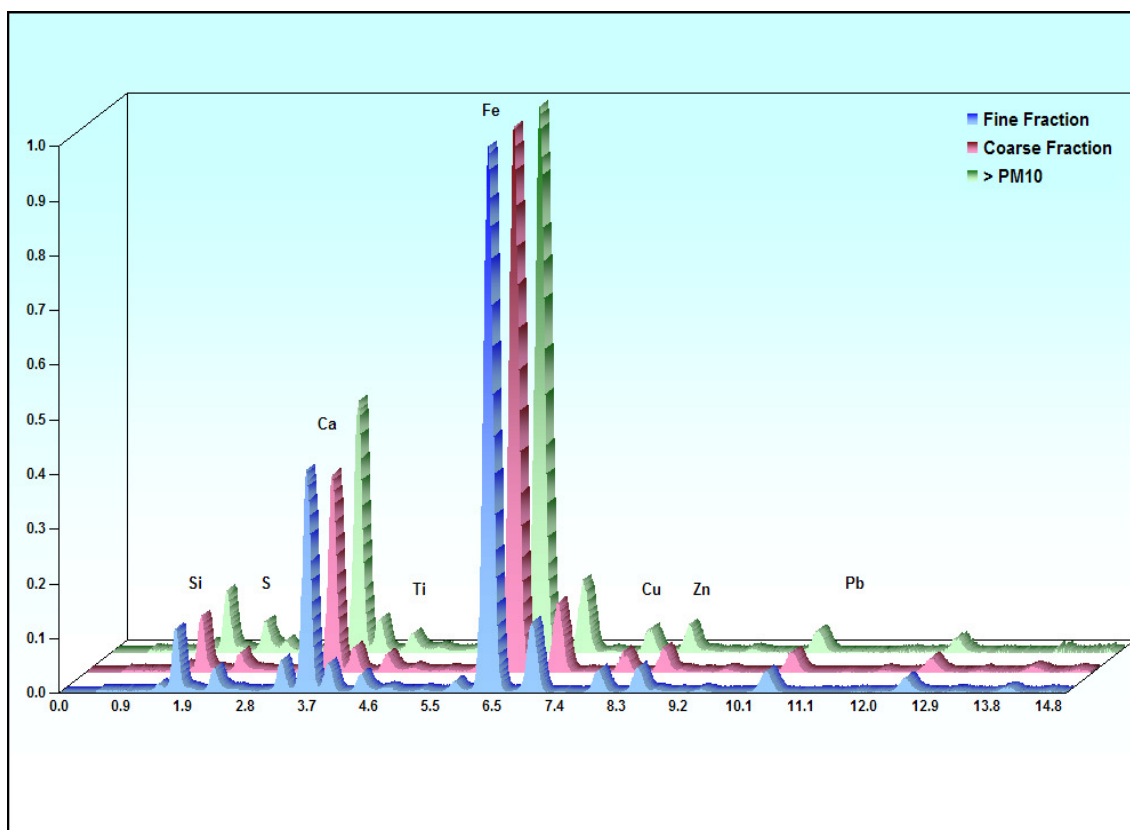


Figure 9b. 3D rendition of normalized TXRF spectra of “Prague Dust” deposited on Plexiglas impactors from the three stages in the Dekati-PM10 sampler

5.5. CONCLUSIONS

Modifications were carried out on a multi-orifice, Dekati-PM10 impactor air sampler in order to enable it use commercially available TXRF carriers as the impactor substrate. The modifications were done ensuring that the aerodynamic characteristics of the air sampler did not change. This was achieved essentially through maintaining the same Jet-to-Plate distance in the impaction system. The said modification enables direct deposition of airborne particulate matter on the impactor substrate for subsequent analysis by TXRF and PIXE. The potential impactor materials studied were Plexiglas and silicon wafer. They were selected considering their suitability for TXRF and PIXE analysis, their cost, and commercial availability. The silicon wafer was rejected because it showed charging effects with proton bombardment during PIXE analysis, and it also had an interfering fluorescent peak of silicon within a crucial energy range for air pollution studies (low Z elements). The Plexiglas (30 mm in diameter and 4 mm thick) was consequently selected as the preferred material for use as an impactor substrate in the air sampler. To reduce particle bounce-offs from the Plexiglas impactors, a special coating made from a mixture of Vaseline and Apiezon was thinly and uniformly applied to the impactor

surface prior to sampling. The coating media was effective, and samples collected by simulation with “Prague Dust” showed the expected deposition patterns in the different particle size fractions. A quantification procedure is being developed to enable quantitative determination by TXRF for the deposition pattern that the multi-orifice impactor produces.

5.6 REFERENCES

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CHAPTER 6 SUMMARY AND CONCLUSIONS

6.1 Summary

Gravimetric and elemental concentration analyses were carried out on airborne particulate matter in an urban residential area in the city of Zagreb, Croatia. The airborne particulates were collected on nuclepore filters using the Gent sampler and the EU reference air sampler LVS3 (KleinfILTERgerät). The samples were collected during summer and winter seasons in order to also study possible seasonal influences on the particulates. The sampler of interest was the Gent sampler. This is a sampler supplied by the International Atomic Energy Agency (IAEA), and has been given to many of the member state countries of the IAEA. The Gent sampler was field-tested in order to ascertain its equivalence to the reference sampler in accordance to the EU norm EN12341. The field testing was done throughout the sampling period of five months by collocation of the Gent Sampler with the reference sampler. The results obtained indicated that the Gent sampler does not meet the requirements of an equivalent sampler according to EU procedures. However, the Gent sampler showed good correlation with the reference sampler for its coarse particle fractions when mass concentrations were $\leq 25 \mu\text{g}/\text{m}^3$. Correlations were not so good for its fine particle fractions. Nevertheless, by establishing correlation equations between the two samplers for the various fractions, the Gent sampler measurements can be made comparable to the EU reference sampler LVS3.

Mass concentration determinations showed that airborne particulates during the summer period are generally much less than those of winter. Summer airborne particle mass concentrations were always below the PM₁₀ limit value of $50 \mu\text{g}/\text{m}^3$. In addition, coarse and fine particle fractions during summer were in similar proportions at an average value of $10 \mu\text{g}/\text{m}^3$. On the other hand, airborne particle mass concentrations in winter had over twenty exceedances above the PM₁₀ limit value during the two months sampling period. The winter particulates were predominantly in the fine particle fractions, at levels more than twice the levels of the coarse particle fractions.

Mass concentration determinations alone do not provide sufficient information when the limit values are exceeded. To provide a basis for the recommendation of abatement strategies, elemental concentration determinations in the collected samples are needed. Elemental concentration determinations were consequently done using

the energy dispersive X-ray fluorescence analysis, and proton-induced X-ray Emission analysis. The quantitative methods of the two techniques were optimized for air filter analysis, taking advantage of the inherent strengths and advantages of the respective techniques. The optimization also considered only elements that are necessary in air pollution studies, from the point of view of regulatory requirements and source apportionment. In this regard, the EDXRF analytical procedure was optimized through careful selection of the secondary/polarizing targets Ti, Co, Mo, Al₂O₃, and the fundamental parameters' evaluation model. The PIXE analytical procedure was optimized to achieve enhanced sensitivity in the determination of low Z elements. This was done by using 2 MeV protons, a 24 µm thick Mylar foil between sample and detector, and a 7 mm wide proton beam. The elements identified in the air filter samples using both techniques are Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, and Pb. The elemental concentration results obtained, showed distinguishing differences in the coarse and fine particle fractions, and also for the different seasons. The elements Al, Si, Cl, Ca, and Fe occurred predominantly in the coarse particle fractions, but Pb and S were predominantly in the fine fractions. Correlation tests performed between pairs of element concentrations revealed strong correlation for Al and Si, and Pb and S. Such correlations point to possible sources of the airborne particulates in the study area as including dust particulates and fossil fuel-based combustion sources. This information was combined with knowledge of the local area to identify the fossil fuel-based pollution sources as coming from vehicular traffic, and domestic heating during winter. Selected samples from the summer particulates were subjected to both PIXE and XRF analysis. The XRF results showed bias, and had the tendency to overestimate for some element concentrations. The source of this bias is the elemental interference from spurious lines due to the scattering of excitation radiation within the sample chamber (instrumental blank). Correction functions were therefore empirically derived from measurements of the standard filter SRM2783, and applied to the XRF results. This brought good agreement between the XRF and PIXE values.

In unpolluted and remote areas where air particulate mass loadings are very low, elemental concentration determinations with both techniques are severely limited. This can be attributed to low filter mass loadings at or below the detection limits of the said techniques. This constraint can be removed through the use of specialized samplers such as an impactor sampler. A multi-orifice and multi-stage

impactor sampler (Dekati-PM10) was consequently modified to enable the deposition of airborne particulates directly on the impactor substrate for subsequent analysis by Total Reflection X-ray Fluorescence (TXRF). Among the candidate impactor materials investigated, Plexiglas was selected for insertion into the modified sampler. The modification carried out ensured the maintenance of the original aerodynamic properties of the sampler, and enabled the placement of commercially available Plexiglas reflectors. To prevent particle bounce-off during sampling, a special thin film coating made from a combination of Vaseline and Apiezon was uniformly applied to the Plexiglas substrate. This enabled qualitative TXRF analysis of the coarse and fine particle fractions sampled.

6.2 Concluding Remarks

Atmospheric pollution studies revolve around ambient air monitoring. All the data and information generated are derived from the samples collected with the air sampler. Hence, the air sampler used in any studies is crucial if data generated can be compared to other data produced elsewhere. This has led to the prescription of reference and equivalent samplers in the USA and the European Community. Consequently, the Gent air sampler which was used in this thesis was assessed in terms of its equivalence to the EU sampler in accordance to EU norms. The results obtained indicate that the Gent air sampler, in its current form cannot be regarded as an EU equivalent sampler. It does not meet the requirements for equivalence as spelt out in the norm EN12341. The Gent sampler, however, showed good correlation to the reference sampler at particle mass loadings $\leq 25 \mu\text{g}/\text{m}^3$ for the coarse particle fractions. This observation indicates that the PM10 pre-impaction stage of the Gent sampler performs similarly to the reference sampler. The existing hindrance to comparability lies with the PM2.5 stage of the Gent sampler. This was reflected in its poor correlation particularly at mass concentrations $> 25 \mu\text{g}/\text{m}^3$. This observation with the fine fraction stage of the Gent sampler maybe attributed to the fact that other workers have found the actual cut-off point for the fine fractions of the Gent sampler to be at $2.2 \mu\text{m}$. In addition, the stacked filter arrangement seems to affect the performance of the PM2.5 stage at higher mass loadings of the coarse filter above it. In its existing form, data generated with the Gent sampler can only be made comparable after derivation of correlation equations. These equations have to be determined for each measurement site through collocation with a reference sampler.

Presently, the major advantage in using the Gent sampler lies in its ability to separate coarse and fine particle fractions directly. This facilitates pollution source profiling and apportionment.

Air quality management requires more than airborne particle mass concentration data. Additional information needed, includes elemental concentration determination of airborne particulates. PIXE and XRF techniques serve as effective tools for achieving this goal. They have the advantage of being non-destructive, and enabling rapid simultaneous, multi-element analysis. However, not all the elements that can be analysed by these techniques are needed or useful for air pollution studies. Consequently, the analytical procedures used in this thesis were optimized to cater for elements that are required by regulations and needed for pollution source apportionment. The optimization strategy also focused on the inherent strengths and advantages of the PIXE and XRF techniques. The PIXE analysis was optimized to enhance sensitivity for low Z elements which is usually a limitation with conventional XRF analysis. The elements identified in the air filter samples collected from the urban residential area in Zagreb, Croatia are Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, and Pb. The elemental concentrations results showed distinguishing influences of seasonal variations. The results also enabled the identification of some sources of pollution in the study area through simple correlation relationships, without use of sophisticated source apportionment models. The pollution sources identified are dust particulates, vehicular traffic, and fossil fuel-based domestic heating. The bias in XRF results compared to PIXE was due essentially to interfering elements from the instrument (instrumental blanks). The said bias was taken care of by deriving correction functions empirically, through repeated measurements of a standard air filter SRM2783. The correction functions when applied brought the XRF results into good agreement with PIXE results for most of the elements determined. Instrumental blank issues are a nagging problem in XRF analysis of thin film samples, including air filters. Hence, until a solution is provided from the instrumentation point of view, analyst will have to find ways of correcting the bias, as has been shown in this thesis.

PIXE and XRF techniques are severely limited when analysing air filters with very low mass loadings. In such cases the said techniques are inaccurate because they are operating either at or below their detection limits. Such constraints can be removed through deposition of particulates on impactor substrates in air impactor samplers. However, current practices in this approach usually deposit the particulates

on a thin film on the impactor stage. This film is then chemically digested prior to elemental analysis. Such an approach is time consuming, may introduce elemental contaminants, and is uneconomical when dealing with large number of samples, and for routine analysis. In this thesis, a multi-orifice, multi-stage air impactor sampler (Dekati-PM10) was appropriately modified to enable deposition of the particulates directly on an impactor substrate (Plexiglas). The deposited particulates on the Plexiglas substrate were analysed directly using Total X-ray Reflection technique. It was possible to carry out only qualitative analysis with the modified air impactor sampler. Future work required in this direction, is the development of a TXRF quantitative procedure which will take into consideration the pattern of deposition produced on the Plexiglas substrate by the multi-orifice air impactor sampler.

The determination of elemental concentrations in airborne particulates by a combination of X-ray emission techniques provided additional information needed for air quality management. It has also been shown that the existing constraints in the quantitative capabilities of the said techniques for air filters at or below detection limits, can be removed through appropriate modification of an air impactor sampler for direct deposition of airborne particulates.