

## Full Length Research Paper

# An assessment of common atmospheric particulate matter sampling and toxic metal analysis methods

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In this study, the atmospheric particulate matter (PM) was sampled using the tapered element oscillating microbalance, and the inductively coupled plasma mass spectroscopy (ICP-MS) and scanning electron microscopy coupled with energy dispersive spectrometry (SEM/EDS) were used for determination of elemental composition of the PM. The efficiency and relevance of the sampling method, ICP-MS and SEM/EDS in toxic metal analysis were assessed. Low flow rate yielded high accumulated mass of particulate matter. The efficiency of the filter media used was found to be, in decreasing order: teflon-coated glass fiber, ringed-teflon and quartz filters. The main elements identified from the SEM/EDS on ringed-teflon filters were Si, Fe, Mg, K, Na, C, S, F and O, and for ICP-MS, the following main elements were identified: Fe, Al, Ca, Mg, K, Na, Cr, Ni, Pb, Cu, Zn and Mn. The ICP-MS proved to be more relevant for the analysis of the toxic metals of interest. The standard deviations obtained from this method were less than 30% for most of the metals identified. The method detection limit was also low (0.2 to 1 µg/L) for most metals, and 50% and less standard deviation to mean ratios were obtained for Ni and Pb.

**Key words:** Toxic metals, inductively coupled plasma mass spectroscopy, scanning electron microscopy coupled with energy dispersive spectrometry, particulate matter, tapered element oscillating microbalance.

## INTRODUCTION

Particulate matter (PM) is linked with all sorts of health problems from a runny nose and coughing, to bronchitis, emphysema, asthma, and even death. Toxic (heavy) metals, chromium and nickel in particular, have been defined by the International Agency for Research on Cancer (IARC) as potential cancer causing agents (USEPA, 1996b).

A better understanding of the chemical constituents of ambient particles is fundamental in bridging the knowledge gap between the air quality and its health effects. There are several state-of-the-art technologies that are commercially available for automated continuous monitoring of PM. These include opacity monitors; light scattering technologies, beta gauge, acoustic-energy monitoring, triboelectric technology and tapered-element oscillating microbalance (TEOM) (Baron and Willeke, 2001). However, because of differences in properties of PM, particles that are larger and lighter than the reference sphere get through while some smaller, heavier particles may be settled out and lost.

The TEOM is the only device that measures the mass of PM directly, but it is sensitive to humidity and

temperature and requires periodic changes in down times of half an hour to two hours after each filter change. The existing technologies use inertial impactors or dichotomous samplers as particle size separators that only approximate PM size.

The type of filter media is important both for the efficiency of sampling as well as the selected analysis method. Filter media are judged for specific applications according to Chow (1995a) and Lippmann (2001) based on their mechanical stability, chemical stability, particle or gas sampling efficiency, flow resistance, loading capacity, blank values, artifact formation, and compatibility with analysis methods, cost, and availability. High and variable blank levels typically invalidate subsequent quantification of particle deposits using the particular batch of filters. The most commonly used filter media for atmospheric particle and gas sampling are teflon membrane, quartz fiber, nylon membrane, cellulose fiber, teflon-coated glass fiber, etched polycarbonate membrane, and glass fiber. None of these materials is suitable for all purposes.

Monitoring of both PM mass and chemical composition

is important for identification of the emission source, determination of compliance with the set air quality standards, bridging the knowledge gap between air quality and its health effects, and establishment of effective pollution control programs (Kgabi et al., 2008). Therefore a special technique is needed for the analysis of PM. Major components of PM include sulphate, nitrate, ammonium and hydrogen ions, trace elements (including toxic and transition metals), organic material, elemental carbon (or soot), and crustal components (Khlystov, 2001). PM can also consist of at least 160 organic compounds and 20 metals (Ag, As, Ba, Be, Dc, Ce, Cr, Co, Cu, Fe, Mn, Nd, Ni, Pb, Sb, Se, Sr, Ti, V and Zn) (Los Alamos national laboratory, 2003).

Ambient air quality has been monitored in South Africa for the last four decades using a variety of methods. There is however, no agreed method and system in function to monitor the levels of toxic/heavy metals in ambient air in South Africa. The objective of this study was to determine the efficiency and relevance of the inductively coupled plasma mass spectroscopy (ICP-MS) and scanning electron microscopy coupled with energy dispersive spectrometry (SEM/EDS) techniques in toxic metal analysis. The efficiency of the sampling method used was also assessed in terms of the sampling period, flow rate, site selection, and type of filter media.

## MATERIALS AND METHODS

The sampling equipment used for this study is the tapered element oscillating microbalance (TEOM Series 1400A), which is composed of a control unit and a sensor unit. The PM samples were collected with different filter media namely teflon-coated borosilicate fiberglass filters, ringed-teflon (teflon) filters and quartz filters. The teflon-coated borosilicate fiberglass filters were placed inside the mass transducer of the TEOM where the flow rate was measured as 3 L/min. The ringed teflon filters and the quartz filters were placed in the Automatic Cartridge Collection Unit (ACCU) of the TEOM, where the flow rate was measured as 13.67 L/min. The ambient sample stream was allowed to pass through the PM10 inlet at a flow rate of 16.7 L/min, which was then isokinetically split into a 3 L/min sample stream that was sent to the instrument's mass transducer and a 13.7 L/min exhaust stream.

The TEOM was successful in continuous determination of the concentrations of PM10 for every hour of the day. The difficult part of the sampling procedure was moving the TEOM from one site to another since it required total dismantling before transportation, and calibration before taking measurements at the new location. The TEOM device can calculate the mass concentration of the sample stream in real-time by maintaining a flow rate of 3 L/min through the instrument and measuring the total mass accumulation on the filter cartridge.

The sample stream in the TEOM is preheated to 50°C before entering the mass transducer so that the sample filter always collects the sample under the conditions of very low, and therefore relatively constant humidity. The TEOM series 1400a monitor was operated with a filter installed in the mass transducers.

The ESEM FEI QUANTA 200, coupled with the OXFID ENCA 200 EDS, was used during the analysis of samples. The requirements for sample analysis by SEM follows that the sample has to be stable under vacuum conditions, it has to be conductive to allow electron beam irradiation and lastly, the substrate of

sample should fit well into the sample stage. The samples were analysed at high vacuum, with a voltage of 15 kV and the working distance of 10 mm. A dead time of forty percent, which corresponds to a lifetime of 100 s, was used during the analysis of samples. The filters were fixed onto sample studs to ensure good electrical connection between the specimen and the microscope stage. The samples were not coated. The filters were scanned several (10) times (1 scan per 10 s) to ensure that a representative portion of the sample is covered. No extraction was performed.

Peaks were identified manually by entering the atomic symbol and then scrolling through the periodic table. The other way of identifying peaks is with auto ID, where the auto key is used to find peaks and label them. The quantifying function of the computer programme was used to determine the peak intensities and the resulting intensities were converted to percentage weight. The same samples analysed by SEM/EDS were subsequently analysed using the Agilent ICP-MS 7500c with the following operating conditions and measurement parameters: Rf power of 1.6 kW, Rf Matching of 1.64 V, Carrier gas flow rate of 1.09 L/min, Wash time = 5 s, Rinse time = 60 s, Sample uptake rate = 55 s, and Sample stabilization = 45 s; taking 3 replicates per sample. The procedure for ICP-MS analysis involved weighing of the filters, digestion, dilution, and measurements. Air particulates collected on filters were extracted into a dilute nitric acid solution by sonication with heating. The extraction solution was stored at room temperature until analysis by ICP-MS was carried out.

## DISCUSSION OF RESULTS

The sampling of PM was performed at three different sites identified as site A, B and C. The sampling period for seasonal variations lasted for 12 months that is from February 2004 to January 2005, during which three sampling sites within the Rustenburg area of the North West Province were covered. Sampling could not be performed simultaneously at the three sites since the TEOM had to be moved from one site to another.

### Accumulated mass of particulate matter

Table 1 gives a summary of the important parameters of the sampling procedure. A direct relationship between sampling period and the mass of PM accumulated on the filter was observed for site B and C. The PM10 mass of sample 5 accumulated over a continuous sampling period of 22 days at site C was obtained as 3100 µg, whilst an accumulated mass of 1309.4 µg was obtained from the sum of hourly average masses (sample 11 to 18) of PM10 over the same period. This suggests that the sampling period alone cannot determine the sampling efficiency, and that the sampling flow rate and the type of filter media need to be considered.

For most samples collected during this study, the elements identified by SEM/EDS and ICP-MS analysis comprise between 30 - 50% of the total mass accumulated on the filters. The fact that particulate matter can contain 30 - 50% of carbon (organic) species contributes to low masses of the inorganic species determined above and is a result of one limiting factor of the ICP-MS analysis, which is the difficulty in assessing the efficiency

**Table 1.** Sampling period, flow rate and filter media.

Site	Sample	Period (Days)	Flow rate (L/min)	Filter media	Mass of PM10 accumulated( $\mu\text{g}$ )	Concentration of PM10 ( $\mu\text{g}/\text{m}^3$ )
A	1	22	3	Teflon-coated borosilicate fiber glass	9479.3	99.74
	2	22			4631.3	48.73
B	3	23	3	Teflon-coated borosilicate fiber glass	4896.5	49.28
	4	23			4680.0	47.10
C	5	22	3	Teflon-coated borosilicate fiber glass	3100.0	32.62
	6	23			4310.0	43.38
D	11	22 (0:00 –3:00)	13.67	Ringed teflon	158.9	13.38
	12	22 (3:00 – 6:00)			174.6	14.70
	13	22 (6:00 – 9:00)			158.0	13.30
	14	22 (9:00 – 2:00)			158.3	13.32
	15	22 (12:00 –15:00)			173.7	14.62
	16	22 (15:00 – 8:00)			170.0	14.31
	17	22 (18:00– 21:00)			160.0	13.47
	18	22 (21:00– :00)			155.9	13.12

of extracting the PM from different filters. This has been reported before by Li et al. (1996) who estimated an efficiency of 20 - 50% of PM removed from filters, and Gilmour et al. (1996) who estimated an efficiency of 10 - 30%. Attempts were made to assess the extraction efficiency by measurement of the extracted mass. Some elements and their respective compounds like silicates and aluminium oxide are normally incompletely dissolved during extraction and dilution, or even escape the determination by evaporation. The mass concentration determined after digestion does not always represent the total mass concentration, instead only the portion that is determinable according to the distinct digestion for a given elemental composition is usually analyzed.

### Flow rate

The flow rate in any sampling procedure is important in determining the accumulation of material on the filters, as well as ensuring that all elements are kept on the filter. It was expected that low flow rates are suitable for longer sampling periods and high flow rates are more applicable for short sampling periods. In this study, sampling at a lower flow rate (3 L/min) yielded higher concentrations on the filters than the higher flow rate (13.67 L/min) over the same period of sampling. Table 1 also shows the sampling results at site C for the 22 day sampling period, which yielded an accumulated mass of 1309.4  $\mu\text{g}$  for the 13.67 L/min and 3100  $\mu\text{g}$  for the 3 L/min. It is worth noting that flow rate alone cannot be used to explain differences

in the accumulated mass and concentration on the filter media. The type of filter media used is also important.

### Filter media

Fibrous filters are the most economical means for achieving high-efficiency collection of submicrometer particles at low dust concentrations. The most important types of filters for aerosol sampling are fibrous and porous membrane filters (Hinds, 1999). Besides collection efficiency and pressure drop, the selection of a filter for aerosol sampling may depend strongly on the analytical method to be used. Glass fiber and cellulose ester filters are much less affected by moisture and age while polycarbonate, polyvinyl chloride, and Teflon filters are the least affected. If aerosol particles are to be analysed by chemical methods, the interferences caused by the filter material or contaminants in the filter should be taken into consideration. The filter media used in this study are ringed-teflon membrane, quartz fiber and teflon-coated borosilicate fiberglass. Table 2 shows the main elements identified using the different filter media. The results from quartz fiber filters for SEM/EDS had to be discarded since it just proved that quartz is not suited for determination of the selected elements. For site A, B and C, teflon-coated borosilicate fiberglass filters were used, but the hourly average concentrations at site C were also sampled onto the ringed teflon and quartz filters.

The main elements identified from the SEM/EDS

**Table 2.** Filter media and the main elements identified.

Site	Filter media	Elements identified
A	Teflon-coated borosilicate fiber glass	SEM/EDS: Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, C, Cl, S, F, O ICP-MS: Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, Ni, V, Pb, Cu, Zn, Mn
B	Teflon-coated borosilicate fiber glass	SEM/EDS: Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, C, Cl, S, F, P, V, Pb, Ni, O ICP-MS: Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, Ni, V, Pb, Cu, Zn, Mn
	Quartz	SEM/EDS: None ICP-MS: Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, Ni, V, Pb, Cu, Zn, Mn
C	Ringed teflon	SEM/EDS: Si, Fe, Mg, K, Na, C, S, F, O ICP-MS: Fe, Al, Ca, Mg, K, Na, Cr, Ni, Pb, Cu, Zn, Mn
	Teflon-coated borosilicate fiber glass	SEM/EDS: Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, C, Cl, S, F, V, Pb, Ni, O

analysis on ringed-teflon filters were Si, Fe, Mg, K, Na, C, S, F and O, and for ICP-MS, the following main elements were identified: Fe, Al, Ca, Mg, K, Na, Cr, Ni, Pb, Cu, Zn and Mn. Ringed-teflon membrane filters consist of a thin, porous polytetrafluoroethylene (PTFE) teflon sheet stretched across a polymethylpentane ring; the thin membrane collapses without the ring, and the filter cannot be accurately sectioned into smaller pieces. The white membrane is nearly transparent and according to Campbell et al. (1995), has been used to estimate light absorption.

PTFE teflon is very stable, absorbing negligible water or gases. It has inherently low contamination levels, but contamination has been found in some batches during acceptance testing. This filter type is commonly used for mass and elemental analyses. Although, aerosol carbon has been inferred from hydrogen measurements by Kusko et al. (1989), carbon cannot be measured on teflon membranes because of the high carbon content of the filters.

SEM/EDS analysis of the teflon-coated borosilicate fiberglass filters yielded Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, C, Cl, S, F, P, V, Pb, Ni and O while analysis using ICP-MS yielded Si, Fe, Al, Ca, Mg, K, Na, Ti, Cr, Ni, V, Pb, Cu, Zn and Mn. Teflon-coated glass fiber filters imbed teflon slurry onto a loosely woven glass fiber mat. These filters meet requirements in all categories except blank element and carbon levels. Though a small amount of nitric acid absorption has been observed by Mueller et al. (1983), it is tolerable in most situations. Teflon-coated glass fiber filters overcome some of the inherent inadequacies of glass fiber filters by being inert to catalyzing chemical transformations as well as by being less moisture sensitive.

Quartz filters are commonly used in high-volume air sampling applications involving subsequent chemical analyses such as atomic absorption, ion chromatography, and carbon analysis, due to their low trace contamination

levels as well as to their relative inertness and ability to be baked at high temperatures to remove trace organic contaminants. The main elements identified from ICP-MS analysis of these filters include Al, Cu, Pb, Ti, Zn, K, Fe, Cr, Ni, Mn, Ca, Mg, Na and V while for SEM/EDS analysis, the results had to be discarded because of poor quality.

For the two analysis methods, teflon-coated borosilicate fiberglass filters yielded better results since more metals could be detected compared to the quartz filters that yielded good results with one analysis (ICP-MS) method only. Fewer metals were determined from the analysis of ringed-teflon filters using both the SEM/EDS and ICP-MS. The efficiency of the filter media used in this study can thus be given in a decreasing order as teflon-coated glass fiber filters, ringed-teflon filters, and quartz filters.

### Site selection

Sampling of PM was done at three sites namely site A with latitude 25° 43' 03.0'' E and longitude 27° 23' 57.8'' S, site B with latitude 25° 40' 01.3'' E and longitude 27° 16' 38.5'' S, and site C with latitude 25° 30' 15'' E and longitude 27° 5' 45'' S. These sites are representative of well-defined environments, exposure situations or source activities like remote areas, urban background, traffic and industry.

The map in Figure 1 shows the exact location of sites A, B and C within the Rustenburg district. It is evident from the results obtained that Site A and B were the most suitable sites for this study. The location of Site C relative to the natural and anthropogenic sources and the prevailing meteorological conditions, did not give a true reflection of the levels in the area. This may be because the site has always been used by a certain industry for compliance monitoring and is thus positioned to suit the

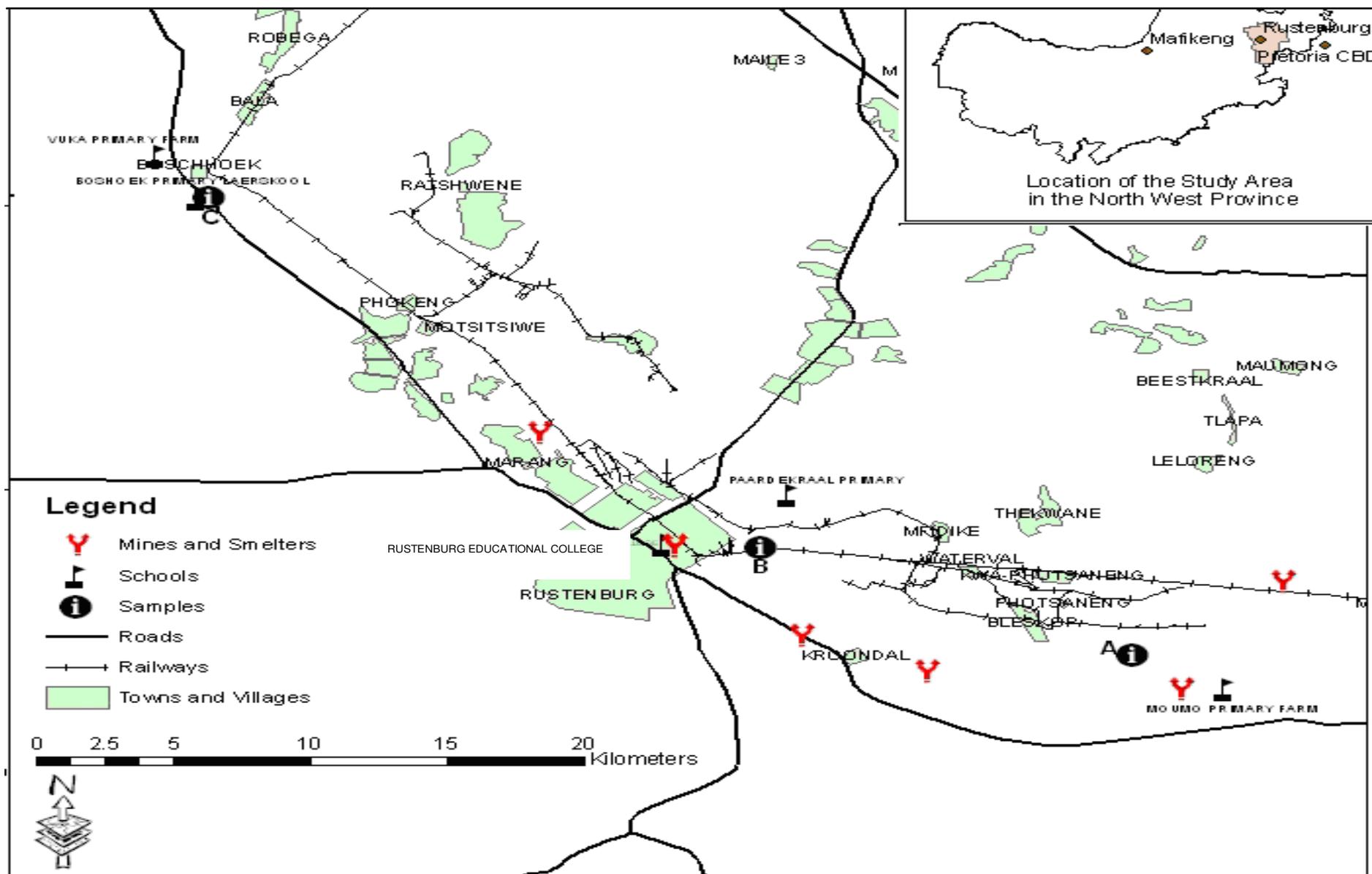


Figure 1. A map showing sampling sites A, B and C in the Rustenburg district.

**Table 3.** The mean, standard deviation and method detection limit (MDL) for the main metals identified during the study

Metal	Method (MDL)	Site A mean (SD)( $\mu\text{g}/\text{m}^3$ )	Site B Mean (SD) ( $\mu\text{g}/\text{m}^3$ )	Site C mean (SD)( $\mu\text{g}/\text{m}^3$ )	
				Monthly	Hourly
Cr	ICP-MS (1 $\mu\text{g}/\text{L}$ )	2.55 (1.42)	0.18 (0.08)	-	0.2 (0.005)
	SEM/EDS	2.28 (0.64)	0.14 (0.04)	0.08 (0.06)	-
Ni	ICP-MS (0.3 $\mu\text{g}/\text{L}$ )	1.41 (0.73)	0.13 (0.07)	-	0.003(0.003)
	SEM/EDS	-	-	0.01 (0.00)	-
V	ICP-MS (0.2 $\mu\text{g}/\text{L}$ )	0.28 (0.12)	0.03 (0.01)	-	-
	SEM/EDS	-	0.00 (0.00)	0.01 (0.00)	-
Pb	ICP-MS (0.1 $\mu\text{g}/\text{L}$ )	0.35 (0.15)	0.48 (0.28)	-	0.02 (0.019)
	SEM/EDS	-	0.03 (0.03)	0.09 (0.02)	-
Cu	ICP-MS (0.2 $\mu\text{g}/\text{L}$ )	0.22 (0.02)	0.20 (0.08)	-	1.11 (0.31)
	SEM/EDS	-	-	-	-
Zn	ICP-MS (0.2 $\mu\text{g}/\text{L}$ )	0.34 (0.04)	0.33 (0.06)	-	0.58 (0.14)
	SEM/EDS	-	-	-	-
Mn	ICP-MS (0.1 $\mu\text{g}/\text{L}$ )	8.47 (8.26)	0.31 (0.08)	-	0.03 (0.015)
	SEM/EDS	-	-	-	-
Ti	ICP-MS (0.2 $\mu\text{g}/\text{L}$ )	0.17 (0.07)	0.19 (0.10)	-	-
	SEM/EDS	0.23 (0.12)	0.04 (0.01)	0.03 (0.01)	-
Ca	ICP-MS (100 $\mu\text{g}/\text{L}$ )	4.91 (1.63)	3.39 (0.69)	-	0.11 (0.03)
	SEM/EDS	3.00 (0.79)	0.34 (0.05)	0.13 (0.02)	-
Fe	ICP-MS (50 $\mu\text{g}/\text{L}$ )	12.83 (6.16)	6.69 (1.75)	-	0.017 (0.04)
	SEM/EDS	4.11 (0.73)	0.59 (0.15)	0.46 (0.18)	0.01 (0.01)
Si	ICP-MS (100 $\mu\text{g}/\text{L}$ )	2.05 (0.28)	4.22 (1.77)	-	-
	SEM/EDS	11.89 (2.41)	2.64 (0.29)	2.02 (0.27)	0.05 (0.02)
Al	ICP-MS (0.7 $\mu\text{g}/\text{L}$ )	3.85 (0.99)	3.46 (0.64)	-	0.09 (0.05)
	SEM/EDS	5.17 (0.56)	0.88 (0.15)	0.81 (0.12)	-
S	ICP-MS	-	-	-	-
	SEM/EDS	4.10 (1.39)	1.06 (0.18)	0.46 (0.22)	0.07 (0.03)

needs of a particular industry. The scale of transportation of pollutants within a specific area depends, according to Carslaw and Beevers (2002) and Pacyna (1995), on the effective height of the emission source and the meteorological conditions, as well as on the size and chemical composition of particles. Site C used in this study is situated close to trees that may affect the concentration levels of the pollutants in the vicinity of the sampler. The site was also upwind of industrial sources for most of the time.

### Efficiency of the elemental analysis methods

The analysis methods used are SEM/EDS and ICP-MS. In general, the ICP-MS method proved to be more relevant for the analysis of the metals of interest in this study. The standard deviations obtained from this method were less than 30% for most of the metals identified. The method detection limit (MDL) was also low (0.2 to 1  $\mu\text{g}/\text{L}$ ) for most metals. This suggests that the method is suited for trace elemental determinations. Table 3 gives the

**Table 4.** Summary of the concentrations of the potentially toxic trace metals in the Rustenburg area.

Metal ( $\mu\text{g}/\text{m}^3$ )		Site A (Monthly)	Site B (Monthly)	Site C (Hourly)	Standard or limit	
Cr	ICP-MS	Range	0.36 – 5.2	0.03 – 0.5	0.01 – 0.03	
		Mean	2.55	0.18	0.02	
		SD	1.42	0.08	0.00	
	SEM/EDS	Range	1.1 – 3.8	0.1 – 0.28	0.03 – 0.32	1 $\mu\text{g}/\text{m}^3$ – NIOSH 1.5 $\mu\text{g}/\text{m}^3$ - APCEL
		Mean	2.28	0.14	0.08	
		SD	0.64	0.04	0.06	
Ni	ICP-MS	Range	0.34 – 2.8	0.03 – 0.46	0 – 0.02	
		Mean	1.41	0.13	0.01	
		SD	0.73	0.07	0.00	
	SEM/EDS	Range	-----	-----	0.01 – 0.03	No safe level -WHO
		Mean			0.01	
		SD			0.00	
V	ICP-MS	Range	0.04 – 0.4	0.01 – 0.05	-----	
		Mean	0.28	0.03		
		SD	0.12	0.01		
	SEM/EDS	Range	-----	0.00 – 0.02	0.00 – 0.01	1 $\mu\text{g}/\text{m}^3$ – WHO
		Mean		0.00	0.01	
		SD		0.00	0.00	
Pb	ICP-MS	Range	0.06 – 0.5	0.02 – 1.4	0 – 0.007	
		Mean	0.35	0.48	0.02	
		SD	0.15	0.28	0.01	
	SEM/EDS	Range	-----	0.00 - 0.24	0.03 – 0.21	0.5 $\mu\text{g}/\text{m}^3$ - WHO
		Mean		0.03	0.09	
		SD		0.03	0.02	

standard deviations and method detection limits for the main elements measured during this study. Detection limits and analytical precision vary widely with analytical protocol, instrumental response, blank contamination, interferences, matrix composition, and isotope abundance, but range from <100 ppb to <1 ppt in aqueous solution. Analytical precision is typically ~2%, of one standard deviation. The method detection limits for SEM/EDS are not easy to determine since they depend on different factors such as size and density of the sample, resolution of the detector and the working voltage. In this study, the spectrum range of 0 - 20 keV was maintained throughout, and quant-optimisation of the system was done with Ni to standardise the system. On each filter, the fault boundaries (weight % sigma) were observed in the range of  $\pm 0.05$  to 0.3.

It is also evident from Table 2 that more metals were identified using ICP-MS. The SEM/EDS however, cannot

be considered irrelevant since it enables one to determine the oxides of the carbon-containing compounds. A summary of the results obtained for the toxic metals of concern in this study is given in Table 4. The efficiency of the methods in determining the potential toxic metals (Cr, Ni, V and Pb) of PM can be assessed based on the mean and standard deviations given in Table 5 obtained for each metal. ICP-MS generally has a high SD to mean ratios for Ni and Pb. The lower (50% or less) ratio may imply better results or concentrations obtained using a particular method.

#### Relevance of the analysis methods to source apportionment studies

The efficiency and relevance of any air pollution analytical method to the identification and apportionment

**Table 5.** Percentage of the ratio of the standard deviation to the mean for the ICP-MS and SEM/EDS methods.

Site	Cr	Ni	V	Pb
<b>ICP-MS</b>				
A	55.7	51.8	42.9	42.9
B	44.4	53.9	33.3	58.3
C	0	0	-	50.0
<b>SEM/EDS</b>				
A	28.1	-	-	-
B	28.6	-	-	100
C	75.0	0.0	0.0	22.2

of pollutant sources is crucial to any air monitoring study. The hourly elemental concentrations (Sample 11 to 18) obtained using ICP-MS and SEM/EDS methods were further analysed using regression analysis and principal component analysis (PCA) to identify and apportion the possible sources. The sources in this study were expected to be mainly due to anthropogenic activities like traffic, soil dust from scraping of the earth crust, and anthropogenic smelting, mainly due to the type of mining and industrial activities in the Rustenburg area. The correlation coefficients obtained from the site C ICP-MS hourly concentrations showed a negative and very small ( $r = 0.154$  to  $0.299$ ) correlation with PM<sub>10</sub> concentrations. The correlations between the crustal and trace metals and between the toxic metals themselves were very small. The highest correlation coefficients in this matrix were obtained as  $r = 0.99$  for Ca and Mg,  $r = 0.71$  for Al and K, and  $r = 0.69$  for Cr and Fe. Principal component analysis has been used by several researchers (Sun et al., 2004) for apportionment of pollutant sources. Figure 2 gives the PCA results for the hourly concentrations at site C. The results yielded four factors making up 89.3% of the PM<sub>10</sub> analyzed. The remaining 10.7% of PM<sub>10</sub> is labelled as unknown in Figure 2.

The first factor, which accounts for 40% of the variance contained Al, Mg, K, Na and Pb, with high loadings of Mg and K. The composition of this factor suggests road or soil dust and biomass burning as the sources of PM<sub>10</sub>. The second factor contained Mn, Zn and Ni, which suggests metal smelting as a source at site C. The occurrence of Fe in this factor is not unusual since there are various ferrochrome smelting activities in the Rustenburg area. The third factor contained Ca only. This may be indicative of building material and activities in the area. The fourth factor contained Cr and Cu, which suggests anthropogenic activities related to mining of ferrochrome in the area. It was not possible to use the regression analysis and the principal component analysis methods to apportion sources of the hourly concentration obtained from SEM/EDS method (Sample 11 to 18) mainly due to the number of variables (elements) identified as shown in Table 6.

The site C SEM/EDS monthly concentrations however, showed a strong correlation between Al and the toxic metals of concern (Cr, Ni, V and Pb). According to Al-Momani (2003), crustal material is the only source of Al. The Al was therefore used as a tracer for crustal material source, and a high correlation between any element and Al was considered to suggest crustal material as a major source of that particular element. The percentage  $r^2$  values obtained from the regression analysis ranged from 0.8 to 1% for Al and V, 0.8 to 32% for Al and Pb, and 62 to 63% for Al and Cr, 0 and 1.4% for Al and Ni at site C. The values rule out the possibility of the same source for Al and the trace metals of concern, except for Al and Cr. The high  $r^2$  value for Al and Cr at site C presents the possibility of Cr being from a crustal source. This, however, does not rule out anthropogenic activities since they may cause re-suspension of particulate matter. It can be observed that the ICP-MS yields sufficient data for further analysis using the common source apportionment methods, while for the SEM/EDS it is not always possible to detect the number of variables needed.

#### Relevance to health and environmental impact studies

The primary goal of air pollution research is identifying culprit agents of air pollution to understand and prevent adverse health outcomes. The ICP-MS and SEM/EDS techniques in this study revealed the presence of atmospheric particles of complex composition including S, Si, Al, Mg, Ca, Pb, Fe, Cr, Ni, V, and Pb among other elements. These particles can be harmful not only to human health, but also to the cultural heritage and the ecosystem as a whole. The main trace metals of concern in this study were Cr, Ni, V and Pb. Nickel and chromium (VI) compounds have been classified as human carcinogens by IARC (Group 1), manganese is neurotoxic (WHO, 2000), and iron has recently been linked to cardiovascular outcomes of PM exposures. The WHO has given guideline values of 0.25 and 25  $\text{ng}\cdot\text{m}^{-3}$  for  $10^{-5}$  excess cancer risk for Cr (VI) and Ni, respectively. Information on the speciation of chromium in ambient air is essential since, when inhaled, only hexavalent chromium is carcinogenic to humans. The trace metals (Cr, Ni, Pb and V) form 6.3% of the metals determined in this study. This may seem comparatively small but has health implications for the exposed community since the limit of 1  $\mu\text{g}\cdot\text{m}^{-3}$  set for Cr by NIOSH and the World Health Organisation (WHO), was exceeded at site A (Table 4). According to Gatari et al. (2005), the WHO does not recommend any concentration level as safe for Ni. The Pb limit of 0.5  $\mu\text{g}\cdot\text{m}^{-3}$  was exceeded only at site B during this study.

The (WHO, 2003) suggests that besides physical aspects such as particle number, size, or surface, the chemical composition of particles is likely to play a crucial role in assessing the health implications of particulate

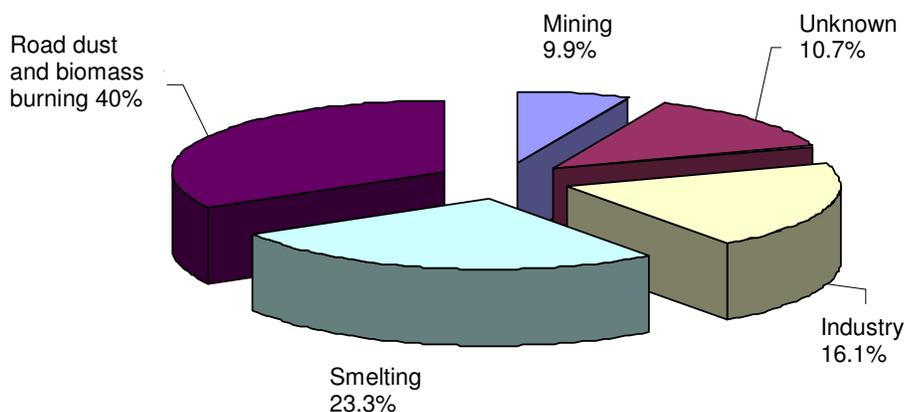


Figure 2. PCA for 19 April to 10 May (sample 11 – 18) using ICP-MS concentrations.

Table 6. Average hourly concentrations from Site C using ICP-MS and SEM/EDS.

19 April – 10 May 2005 : SEM-EDS										
Sample	PM10	Si	Fe	Mg	K	Na	C	S	F	O
11	13.38	0.05	0.02	-	-	-	1.44	0.07	7.79	4.01
12	14.7	-	-	-	-	-	1.45	-	9.38	3.87
13	13.3	0.02	-	-	-	-	1.36	-	8.28	3.64
14	13.32	-	-	-	-	-	1.33	0.01	8.42	3.56
15	14.62	0.06	-	-	-	-	1.63	0.08	8.32	4.53
16	14.31	0.05	-	-	-	-	1.55	0.08	8.32	4.29
17	13.47	0.05	-	-	-	-	1.39	0.06	8.13	3.84
18	13.12	-	-	-	-	-	1.33	-	8.26	3.53
Mean	13.78	0.03	0.00				1.44	0.04	8.36	3.91
SD	0.61	0.01	0.00				0.04	0.01	0.16	0.13

19 April – 10 May 2005: ICP-MS													
Sample	PM10	Fe	Al	Ca	Mg	K	Na	Cr	Ni	Pb	Cu	Zn	Mn
11	13.38	0.26	0.11	0.10	0.13	0.40	0.35	0.02	0.01	0.07	1.00	0.58	0.02
12	14.70	0.15	0.05	0.17	0.13	0.30	0.87	0.02	0.00	0.01	1.00	0.52	0.02
13	13.30	0.17	0.05	0.09	0.06	0.22	0.53	0.02	0.01	0.01	0.90	0.50	0.02
14	13.32	0.12	0.03	0.10	0.02	0.20	0.14	0.01	0.00	0.00	0.90	0.46	0.01
15	14.62	0.16	0.12	0.12	0.12	0.41	0.82	0.01	0.00	0.02	1.00	0.94	0.06
16	14.31	0.18	0.07	0.08	0.05	0.35	0.24	0.02	0.00	0.01	1.20	0.55	0.02
17	13.47	0.19	0.20	0.14	0.11	0.41	0.73	0.02	0.00	0.02	1.00	0.52	0.02
18	13.12	0.13	0.05	0.05	0.02	0.18	0.14	0.02	0.00	0.00	1.90	0.58	0.04
Mean	13.78	0.17	0.09	0.11	0.08	0.31	0.48	0.02	0.003	0.02	1.11	0.58	0.03
SD	0.61	0.04	0.05	0.03	0.04	0.09	0.28	0.005	0.003	0.019	0.31	0.14	0.015

matter. Various health effects of PM, from less serious to very serious ones, are associated with its specific chemical and physical (but mostly chemical) components (Sharma and Maloo, 2005). Schneider and Hill (2005) explain typical composition of particles from traffic or fuel combustion sources. Most of these particles contain carbon at their core, with toxics and carcinogenic substances attached to their surfaces. Tables 2 to 6

presented in this study suggest that one can be able to identify more elements even in trace concentrations using the ICP-MS compared to SEM/EDS and thus be able to determine attainment of air quality standards and the possible health impacts. The SEM/EDS however, is still relevant to health impact studies since it can give an indication of the toxics attached to the surface of the pollutant particle.

## Conclusion

The study was successful in assessing the efficiency of ICP-MS and SEM/EDS techniques in elemental analysis of atmospheric particulate matter. The efficiency of the sampling method used was also assessed in terms of the sampling period, flow rate, site selection, and type of filter media. The low flow rate yielded high accumulated mass of particulate matter. The efficiency of the filter media used was measured in a decreasing order as teflon-coated glass fiber filters, ringed-teflon filters and quartz filters. A direct relation between sampling period and an accumulated mass of particulate matter was also observed. Selection of the analytical method for air particulate matter is very important because it dictates the type of filter media and the compatible sampling system to be used. The specific filter used depends upon the desired physical and chemical characteristics of the filter and the analytical methods used.

Determination of the elemental composition of the collected samples was successfully achieved using ICP-MS. The monthly concentrations of the potentially toxic trace metals of particulate matter were measured in the range of 0.03 - 5.2  $\mu\text{g}/\text{m}^3$  for Cr, 0.03 - 2.8  $\mu\text{g}/\text{m}^3$  for Ni, 0.01 - 0.05  $\mu\text{g}/\text{m}^3$  for V and 0.02 - 0.5  $\mu\text{g}/\text{m}^3$  for Pb. ICP-MS was shown to be a relevant characterization tool for particulate aerosols. The technique provides valuable information which, when properly analysed, contributes significantly to studies on seasonal variations and source apportionment, and ultimately to exposure assessment studies. More metals were identified using ICP-MS. The ICP-MS proved to be more relevant for the analysis of the metals of interest in this study. The standard deviations obtained from this method were less than 30% for most of the metals identified. The MDL was also low (0.2 to 1  $\mu\text{g}/\text{L}$ ) for most metals. It is however, suggested that determination of elemental composition of PM using ICP-MS for the purpose of identifying and quantifying major source contributions, be coupled with chemical speciation of ammonium, sulfate, nitrate, organic carbon, and elemental carbon. This is necessary because atmospheric particulate aerosols, in general, consist of sulphates, nitrates, sea-salt, mineral dust, organics and carbonaceous components. The ICP-MS was also proved to be more relevant both to source apportionment and health impact studies. The physical and chemical composition of the samples collected was determined using SEM-EDS. The concentrations of the trace metals of concern were in the range of 0.03 - 3.8  $\mu\text{g}/\text{m}^3$  for Cr, 0.01 - 0.03  $\mu\text{g}/\text{m}^3$  for Ni, 0.00 - 0.02  $\mu\text{g}/\text{m}^3$  for V and 0.00 - 0.24  $\mu\text{g}/\text{m}^3$  for Pb. The study has shown that SEM-EDS can be used as a tool to characterise particulate matter. A lower number of metals were determined using the SEM/EDS. The MDL could not be determined for this technique. The technique however, cannot be considered irrelevant since it enables one to determine the oxides of the carbon-containing compounds. The ability to perform non-destructive analysis of individual particles by SEM/EDS is

indispensable in the characterisation of PM samples because it allows the same sample to be chemically speciated by other spectroscopic methods. In some cases, the SEM/EDS analysis may not provide conclusive analysis as in the distinction between sulfate and sulfite or Cr (III) and Cr (VI) in the particles; however, the ambiguity of the chemical composition can be resolved using other analytical techniques such as inductively coupled plasma mass spectroscopy and atomic absorption spectroscopy.

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