Comparative evaluation of the performance of aerosol samplers for the assessment of soluble platinum exposure

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Preface

The work is presented in article format as prescribed by the guidelines of Annals of Occupational Hygiene. The guidelines are presented before the article in Chapter 3. The reference style of the journal is used throughout the dissertation for uniformity.

The study was intended to investigate the performance of samplers in the collection of dust and soluble platinum salts. The findings from this study will have to be substantiated by rolling out similar research projects in different primary and secondary platinum refining and handling workplaces.

Authors' contributions

The planning an execution of this study was a team effort involving the following individuals:

Name	Role
Ms MC Ramotsehoa	✓ Planning ✓ Sampling ✓ Literature review ✓ Results interpretation ✓ Writing up of articles
Mr PJ Laubscher	✓ Supervision ✓ Planning of the study, ✓ Approval of methods, ✓ Feedback and recommendations: regarding interpretation of results ✓ review of mini-dissertation
Prof FC Eloff	✓ Co-supervision ✓ Feedback and recommendations regarding interpretation of results ✓ review of mini-dissertation

The following is a statement from the supervisors confirming each individual's role in the study:

I declare that I have approved the article and that my role in the study as indicated above is representative of my actual role. I hereby give consent that it may be published as part of Cynthia Ramotsehoa's M.Sc (Occupational Hygiene) mini-dissertation.

_____ _____

Mr PJ Laubscher — Supervisor

Prof FC Eloff — Co-supervisor

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Summary

Introduction

The primary focus of this study was to compare the efficiency of six filter samplers in the collection of inhalable soluble platinum (Pt) salts at a South African base metal refinery. Inhalation remains the major route of occupational exposure to platinum groups metals (PGMs). South Africa would benefit from the study since it's amongst the major countries where PGMs are produced and hence, monitoring of worker exposure with the most efficient sampler is of utmost importance. The IOM is currently being used in routine exposure monitoring although no studies have been carried out to compare its performance to that of the other samplers under the actual base metal refinery conditions.

Method: The button, closed face cassette (CFC), Gesamtsstaubprobenhome (GSP), (Institute of Medicine) IOM, PAS-6 and seven hole (SH-sampler) samplers were randomly allocated to six different positions in presumably high exposure areas. The samplers were moved around in the subsequent sampling days and the process repeated 3 times. The average dust mass and Pt concentrations were used as a basis of sampler performance and comparisons from which sampler hierarchies were determined.

Results: The average relative humidity ranged between 37% and 43% and the average dry bulb temperature of 22.4°C was measured. Comparison of the dust mass concentrations revealed no statistically significant differences amongst the six filter samplers tested. The SH-sampler and CFC however collected the highest and lowest dust mass and Pt concentrations respectively.

Discussion: The SH-sampler was found to be a sampler with more reliability than the the IOM for the collection of dust mass and soluble Pt. The IOM collected 98% of the SH-sampler dust mass and Pt concentrations. This was in spite of the larger variations indicated by the highest relative standard deviations and confidence intervals shown by the IOM than the other samplers. The GSP sampler, however, showed better precision than all the other samplers in the collection of platinum. The seven 4 mm orifices of the SH-sampler sampler allow for uniform distribution of sampled particles onto the filter supporting its better precision than the IOM which has only one 4 mm opening. The worst performing sampler was the CFC sampler since it collected the

lowest dust mass and Pt concentrations. The CFC and the PAS samplers have downward facing inlets that are affected by gravity especially in lower wind speeds which, therefore, influences their efficiency. The GSP sampler concentrations placed it as 4th and 3rd best in Pt and dust mass hierarchies respectively even though it showed better precision than SHS in the sampling of Pt. The button sampler did not perform as well as would have been expected considering that its many evenly spaced orifices and the stainless steel are meant to reduce sample losses.

Conclusion: The sampler hierarchy according to dust mass concentrations was in the following order: SH-sampler, IOM, PAS, GSP, button and CFC. The hierarchy obtained from Pt concentrations gave the order as SH-sampler, IOM, GSP, button, PAS and CFC. Similar studies have to be undertaken in primary and secondary platinum workplaces to validate the study results. Such studies should compare better performing samplers (SHS, IOM, Button and GSP) as well as incorporate particle size determination and distribution in those areas.

Keywords: Inhalable aerosol sampler, sampler comparison, soluble platinum.

Opsomming

Inleiding:

Die primêre fokus van hierdie studie was om die doeltreffendheid van ses filter monsternemers in die versameling van inasembare oplosbare soute platinum teen 'n Suid-Afrikaanse basis metaal raffinadery te vergelyk. Inaseming bly belangrikste roete van blootstelling aan PGM'e. Suid-Afrika sal bevoordeel word uit die studie aangesien dit een van die hoof lande is waar PGM'e vervaardig word en dus, die monitering van werker blootstelling met die mees doeltreffendste monsternemer is van uiterste belang. Die Instituut van Medisyne (IVM) monsternemer word tans gebruik in roetine blootstelling monitering hoewel geen studies uitgevoer is om sy prestasie onder die werklike basis metaal raffinadery kondisies met dié van die ander monsternemers te vergelyk nie.

Metode:

Die knoppie, geslote gesig kassette (GGK), Gesamtsstaubprobenhome (GSP), IVM, PAS-6 en sewe opening (SO) monsternemers is lukraak aan ses verskillende posisies in 'n vermoedelik hoë blootstellingsarea toegeken. Die monsternemers is rondgeskuif in die gevolglike monsternemingsdae en die proses was 3 keer herhaal. Die gemiddelde stof massa en Pt konsentrasies was gebruik as 'n basis van monsternemer vergelykings waaruit ‘n monsternemers hiërargie bepaal was.

Resultate:

Die gemiddelde relatiewe humiditeit het tussen 37% en 43% gewissel en die gemiddelde droëbal temperatuur van 22.4°C is gemeet. Vergelyking van die stof massa konsentrasies het geen statisties betekenisvolle verskille tussen die monsternemers wat getoets is onthul nie hoewel die SO-monsternemer hoogste (1.609 mg/m^3) en GGK die laagste (0.423 mg/m^3) konsentrasies gegee het. Die hoogste Pt konsentrasies is met SO-monsternemer (0.29 µg/m^3) gemeet terwyl die GGK die laagste (0.04 µg/m^3) konsentrasies van alle monsternemers versamel het.

Bespreking: Die SO-monsternemer is as die meer betroubaar monsterneme as die IVM vir die meting van die stof massa en oplosbare Pt gevind. Die IVM het 98% van die SO-monsternemer stof massa en Pt konsentrasies gemeet. Dit was ten spyte van die groter variasies aangedui deur die hoogste relatiewe standaardafwykings en vertrouensintervalle deur die IVM getoon as die ander monsternemers. Die GSP

monsternemer het egter beter akkuraatheid as al die ander monsternemers in die versameling van platinum getoon. Die sewe 4 mm openinge van die SO-monsternemer maak vir eenvormige verspreiding van monster deeltjies op die filter wat sy beter akkuraatheid ondersteun as die IVM wat slegs een 4 mm opening het. Die swakste presterende monsternemer was die GGK monsternemer aangesien dit die laagste stof massa en Pt konsentrasies versamel het. Die GGK en PAS monsternemers het afwaartse openinge wat deur die swaartekrag beinvloed word veral in laer windsnelhede wat dus hul doeltreffendheid beïnvloed. Die GSP monsternemer konsentrasies het dit as 4de en 3de beste in Pt en stof massa hiërargieë onderskeidelik geplaas, selfs al het dit beter akkuraatheid as die SO-monsternemer in die meting van platinum. Die knoppie monsternemer het nie so goed soos verwag presteer nie tenspyte van die eweredig openinge en die vlekvrye staal wat bedoel is om monster verliese te verminder.

Gevolgtrekking:

Die monsternemer hiërargie volgens stof massa konsentrasies was in die volgorde: SO-monsternemer, IVM, PAS, GSP, die knoppie en GGK. Die hiërargie verkry vanaf Pt konsentrasies is as vol: SO-monsternemer, IVM, GSP, die knoppie, PAS en GGK gegee. Soortgelyke studies moet in primêre en sekondêre platinum werksplekke onderneem word om die studieresultate te bevestig. Sulke studies moet beter presterende monsternemers (SO-monsternemer, IVM, knoppie en GSP) vergelyk sowel as deeltjiegrootte bepaling en verspreiding in dié gebiede te inkorporeer.

Sleutel woorde: Inasembare aërosol monsternemer, monsternemer vergelykings, oplosbare platinum.

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List of abbreviations

µg/m^3 - micrograms per cubic metre

CFC - Closed face cassette

Cu - Copper

FIC - Final concentrator

g/cm^3 - grams per cubic centimetre

GSP - Gesamtsstaubprobenhome

HCl - hydrochloric acid

Ir - Iridium

l/min – litres per minute

m/s - metres per second

MCE - mixed cellulose ester

mg/m^3 - milligrams per cubic metre

ml - millilitre

mm – millimetre

Ni - Nickel

ºC - degrees Celsius

OEL - Occupational Exposure Limit

PAS - PAS-6 sampler

Pd - Palladium

PGM - Platinum group metals

Rh - Rhodium

ROS - reactive oxygen species

RSD - relative standard deviation

Ru - Ruthenium

SH-sampler - Seven hole sampler

SPSS - Statistical Package for Social Sciences

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CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

Aerosol sampling is motivated by the need for quantitative and qualitative characterisation of airborne particles in ambient and occupational environments. Of major importance is the assessment of people's exposure to aerosols for purposes of epidemiology, risk assessment and evaluation of compliance with regulatory standards (Vincent, 2007). This can be achieved through personal and area sampling. Personal sampling is carried out by placing the sampler in the person's breathing zone, which is the area around the nose or mouth. Area sampling on the other hand, involves collecting the sample in the general environment by use of one or more sampling devices placed in fixed locations and aerosol levels are only representative of the location (Li *et al.,* 2000; Bisesi 2004; Vincent, 2007). Area sampling, however, is more practical since the imposition on workers is avoided especially when many samplers are to be tested as in this study. Furthermore, since worker involvement is required in personal sampling, the particles collected on the filter may be easily affected by body movement. All this makes routine personal measurements of aerosols very difficult and unreliable (Vincent, 2007).

The efficiency of sampler performance is affected by wind speeds and direction, particle size distribution and concentration, humidity, sampler orientation, body, orifice shape and size, sampling flow rate and sample handling. Some of these factors can be controlled in laboratory settings and may vary greatly in field sampling thereby influencing sampler performance (Tatum *et al., 2*001; Vincent, 2007; Zugasti *et al.,* 2012). Workplaces produce particles of different sizes and varying wind speeds, making the evaluation of sampler performance under the actual work conditions of critical importance (Zugasti *et al.,* 2012).

Different methods can be explored in the testing of samplers for area sampling. The first option involves exposing samplers to the same environment side by side or close enough together so that aerosol concentration is the same upstream of each sampler, and yet far enough apart to ensure that no mechanical interference occurs. The second option is where samplers are sequentially placed at the same test location through which several cycles and sampler interchanges take place. The

problem of sampler interference is cancelled out and the method works well in environments where the aerosol concentration remains the same throughout the sampling periods such as when test aerosol is generated over time. The real world, however, is variable and complex and the variability applies to changes in contaminant emissions and other external factors mentioned above (Vincent, 2007).

Sampler performance is based on the concentrations that a sampler would measure and not necessarily on how it compares to the sampling convention (Kenny *et al*., 1997). A more technical look at this concept brought to the fore the factors that have to be taken into account when an assessment of performance is made. The air flow near the sampler inlet, bearing in mind that there are different inlet shapes as well as the manner in which the sampler is orientated in relation to the moving air are amongst those factors (Vincent, 2007) Various studies were carried out over the years in laboratory settings mainly to evaluate the performance of various groups of inhalable aerosol samplers (Kenny *et al.* 1997; Maynard *et al.,* 1997; Davies *et al.,* 1999; Kenny *et al.,* 1999; Aizenberg *et al.,* 2000; Li *et al.,* 2000; Koch *et al.,* 2002; Witschger, 2002; Zugasti *et al.,* 2012). There is, however, a gap that has been identified in the literature on performance evaluation testing carried out under the actual workplace environments, especially, base metal refinery conditions, hence the study was performed.

1.1.1 Importance of the study

Platinum group metals (PGMs) which include platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os); are sourced from ores bearing sulphur in South Africa. These metals occur together naturally or in combination with other metals such as iron, tin copper, lead, mercury and silver (Hunter *et al*., 1945; European Union, 2012). South Africa, being the major producer of platinum group metals, requires an extensive understanding of the levels of worker exposure to these metals in refineries. Furthermore, the demand for platinum group metals has increased over the years due to its applications in a wide range of industries and technology sectors. Platinum is used in auto-catalysts, jewellery and industries such as chemical, electrical, medical, glass and petroleum (Chamber of Mines, 2010). Considering that there are 3 major routes of exposure namely; inhalation, ingestion

and skin; inhalation received more attention since the focus of the study is on the most efficient inhalable aerosol sampler whilst the latter two are beyond the scope of the study.

Complex soluble platinum salts (ammonium chloroplatinate, sodium chloroplatinate or platinum tetrachloride) are formed during the refinery process irrespective of the method used. Those complex salts are transferred into the air atmosphere as either a dust when a dry form is handled or as small droplets that result during parts of the wet process. Refinery workers were found to suffer from a variety of symptoms caused by humoral immune response accompanied by higher levels of IgE that last for as long as they are exposed. These start with sneezing and runny nose followed by chest tightness, shortness of breath, cyanosis and wheezing; all caused by inhalation of the complex platinum salts and exacerbated by smoking (Hunter *et al.,* 1945; OSHA, 1978; Calverley and Murray, 2005; Cristaudo *et al.,* 2005; Gad, 2005; Linnet, 2005; HCN, 2008; Nordberg and Nordberg, 2009). Platinum salts are more potent than other PGM salts (Merget *et al*., 2001) and it is, therefore, beneficial for the workers to be transferred from areas of high exposure as soon as asthma is detected (Merget *et al*., 1999).

1.2 Research aim and objectives

The aim of the study was to compare the dust mass and soluble platinum salts (as platinum) concentrations collected by six commercially available personal inhalable aerosol samplers in a base metal refinery.

1.2.1 General objectives

The following objectives were set for the study:

- Measurement of environmental conditions namely; air velocity, temperature and humidity.
- Collection of dust mass and analysis for soluble platinum salts collected by each sampler.
- Determine the hierarchy of samplers on the basis of dust mass and Pt concentrations.

1.3 Hypothesis

The comparison of samplers such as this one, within a base metal refinery has not been carried out thus far. Studies carried out in other industries such as wood and nickel refineries have shown the Institute of Medicine (IOM) sampler to be the most efficient inhalable aerosol sampler and it is currently used at the base metal refinery for routine monitoring. The IOM is also recommended in the general method for sampling and gravimetric analysis of respirable and inhalable dust (HSE, 2000). It was, therefore, hypothesised, that the IOM would produce better results when compared with other inhalable aerosol samplers.

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CHAPTER 2: LITERATURE REVIEW

2.1 Workplace aerosols

Aerosol is a term used to refer to a collection of particles, solid or liquid, suspended in the air. It may be made up of particles that are either mineral or metals, released from different production and industrial processes (Harrington and Gardiner, 1995). Aerosols found in occupational hygiene and environmental settings vary widely in terms of chemical and biological make-up and behaviour which together, have an influence on the toxicological effects (Vincent, 2007). These aerosols encountered in workplaces, have the potential to produce adverse health effects through ingestion, inhalation and/or dermal contact. Inhalation, however, is taken to be of major importance when aerosol measurement is considered (Volkwein *et al.,* 2011). The behaviour of airborne particles is determined by physical characteristics that involve density, shape and aerodynamic properties (Vincent, 2007). Furthermore, these characteristics determine the region of the respiratory system in which particles will be deposited. The resultant health effects will be influenced by a combination of mass, chemical composition, morphology, particle size, surface area and surface chemistry. Aspiration, on the other hand is determined by parameters such as, particle size, external air speed, orientation to prevailing air direction, breathing rate and volume (Volkwein *et al.,* 2011).

In general, it would seem that the aerodynamic diameter of the aerosol carries more weight when it comes to whether the particle becomes airborne, the distance over which it will be carried from the source, its effective capturing by the control system in use and if the worker will be exposed or not (Harrington and Gardiner, 1995). There is a 100% chance of particles with aerodynamic diameters of few micrometres entering the mouth and nose at low wind speeds. This is reduced to 50% at aerodynamic diameters of 100 µm (Davies *et al.,* 1999; Sleeth and Vincent, 2011; Volkwein *et al.*, 2011).

2.1.1 Aerosol exposure measurement

The level of exposure in indoor work environments is influenced by characteristics of air such as wind speed and ventilation parameters, aerosol source and type which include particle size and initial velocity. Such environments are characterised by generally low wind speeds which are not easily achieved in tunnels commonly used to test samplers. When air is calm, air movement is solely driven by the aspiration action of the sampler (Witschger *et al.,* 2004).

The sampling of aerosols is motivated by the need to practically understand the qualitative and quantitative properties of the particles occurring in occupational environments. This involves the monitoring of how those particles are emitted from different work processes into the atmosphere, epidemiological findings or risk assessment in which people's exposure to aerosols is assessed, as well as, determining whether regulatory standards are adhered to or not (Vincent, 2007). Volkwein *et al*. (2011) have a different view in which they state that the main aim of sampling is to determine or evaluate human exposure and not necessarily to characterise aerosol or the physical process through which it is produced. Additionally, aerosols are measured as a way of monitoring and controlling specific work procedures or processes (Vincent, 2007).

The strategy to be followed in aerosol measurements is determined by the objectives for which sampling is to be carried out. However, irrespective of what the objectives are, the quantity and quality of data gathered, is of prime importance. Sampling for health based objective, can be done either through area or personal sampling. Area sampling measures the amount of aerosols in the environment, through the use of one or more samplers placed in fixed locations. The main aim of area sampling is to provide measurements of aerosol concentration that are a representation of that location and to a certain extent, people close-by. In personal sampling on the other hand, measurements are carried out much closer to the individuals, in their breathing zone, ± 30 cm around the mouth, with the use of mounted personal samplers (Vincent, 2007). Personal sampling although desirable, relies on people participation and may be seen as an imposition for many workers at a time, and the collected sample may be affected by body movements. Area measurements have been found

to produce concentrations that are 3 to 5 times lower than personal sampling, a factor that can be accounted for by the fact that the sampler may be much closer to the source of the aerosol in personal sampling as well as each worker's capacity of generating their own personal dust cloud (Harrington and Gardiner, 1995; Li *et al.,* 2000; Vincent, 2007; Gorner *et al.,* 2010; Sleeth and Vincent, 2011). A study by Kenny *et al.* (1997), however, found no differences in the sampling performance of the eight samplers tested between area and personal sampling at wind speeds less than 0.1 m/s.

To assess exposure to inhalable dust accurately, sampling methods that can be relied upon for measuring concentrations of inhalable airborne particles are required (Tsai *et al.,* 1996a*;* Gorner *et al.,* 2010), and the performance of an ideal sampler must match the inhalability convention (Li *et al.,* 2000). Generally, aerosol samplers, both personal and static (area), have important and widespread use in monitoring airborne particulates in workplaces and, therefore, play a major role in ensuring that workers are well protected (Aizenberg *et al.,* 2000b).

Currently, methods used in sampling and analysis begin at the aerodynamic sizing of aerosols, followed by use of filters as media of collection. The analysis of mass either by gravimetric or chemical analysis for specific elements or compounds form part of the last step. The accuracy and being amenable to automations and instrumental analysis for gravimetric and chemical analysis add weight to the use of mass concentrations (Volkwein *et al*., 2011).

2.1.2 Sources of error in sampling

Harrington and Gardiner (1995) stated that errors associated with different steps of the sampling process may have an overall effect on the accuracy of measured concentration. Those that have to do with sampling head performance, flow rate and sample analysis can be controlled. Random errors on the other hand, including sample selection and place, as well as changes in exposure concentrations, cannot be controlled. It is of utmost importance that a sampler chosen for the collection of inhalable aerosols is suitable for that purpose and its functioning is in agreement with the inhalable convention. The flow rate of a particular sampler must be properly determined so that the final mass concentration can be calculated correctly. This is

especially important when more than one sampler is being used or tested. Furthermore, the pump flow rate must be verified using a suitable standard before and after use and the built in rotameter cannot be relied upon for that purpose. Gravimetric analysis of samples is usually the main method of analysis and to avoid errors during this process, temperature and humidity must be controlled in the room where the weighing is carried out. This is also important for the conditioning of filters before each weighing. In cases where chemical analysis is necessary, the correct method is utilised and the entire sample is scraped off or digested from the filter to determine the concentration. Variations in worker exposure may occur from one day to the next, as well as between workers performing the same or different functions. These will, therefore, constitute sources of random error that must be taken into account when deciding on the sample selection, how long, how often and where to sample.

2.1.3 Factors influencing sampler efficiency

Gravitational settling of particles has an effect on how aerosols are transported, more so for larger particles. This means that measuring particle size distribution at a distance from the source will produce different results when compared to original powder or dust closer to the source (Witschger *et al.,* 2004). Wind conditions closer to the sampler have to be taken into account because of the influence they have on aspiration of particles, especially large particles (Gorner *et al.,* 2010). In addition to that, wind speeds also have a further effect on the inhalable convention (Baldwin and Maynard, 1998). When sampler efficiency is dependent on sampler orientation, the measurements are affected if the worker movement remains the same throughout the sampling period in relation to the aerosol source (Aizenberg *et al.,* 2000b). Efficiency of the aerosol sampler is also determined by ratio of sampled and reference aerosol concentration with reference to the aerodynamic diameter of particles (Gorner *et al.,* 2010).

2.2 Methods for testing sampler performance

According to Vincent (2007), the assessment of sampler performance can be done in one of two ways namely, the direct or trajectory and indirect or comparison method. The indirect method has received widespread application through many experiments

in which sampler comparisons were carried out. It involves exposure of the test and reference samplers to the same aerosol concentration within a stream. The samplers are either placed side by side or close together so that the upstream aerosol concentration is the same for each and enough distance being allowed between the two to prevent mechanical interference. Alternatively, samplers are sequentially rotated through the same test location over a number of cycles, the advantage of which is that interference of samplers is cancelled out (Lidén, 1994; Vincent, 2007).

Generally, the indirect method more straightforward and may be used in different types of experimental settings. However, the fact that all particles entering the sampling orifice are used in the determination of aspiration efficiency, presents a disadvantage inherent in the indirect method since, some of those particles may have been introduced from bouncing off from external surfaces of the sampler and not due to true aspiration (Vincent, 2007).

2.3 Inhalable aerosol samplers

2.3.1 Inhalable aerosol sampler design

Physical principles such as filtration, inertia, gravitational collection, passive diffusion, thermophoresis and electrostatic effects are determined by sampler design (Aizenberg *et al.,* 2000b). The choice and development of inhalable samplers is influenced by how aspiration is affected by complex external factors such as wind speed and direction (Volkwein *et al.*, 2011). Differences in sampler inlet design and operational parameters such as sampling flow rate result in differing performance characteristics. The sampling efficiency on the other hand, is dependent on particle size and ambient air velocity (Witschger *et al.,* 2004).

2.3.2 Characteristic of the different inhalable aerosol samplers

2.3.2.1 The IOM sampler

The IOM sampler has a plastic cylindrical body that is 37 mm in diameter and 27 mm in length, in which an internal cassette is incorporated. According to recommended use, the cassette and filter are weighed as one unit for gravimetric analysis, which means the particles deposited on the internal surfaces of the cassette are also

measured. The sampler uses a 25mm filter and works at a flow rate of 2 l/min (Kenny *et al.,* 1997; Vincent, 2007).

2.3.2.2 The button sampler

The button sampler has a curved, multi orifice (381 µm) surface inlet made of conductive stainless steel. It is designed to eliminate electrostatic effects and sensitivity to wind direction and speed. Losses in transmission are reduced by having a small distance between the filter and the inlet. This also provides for even distribution of particles loaded onto the filter and to avoid oversampling. It is used with a 25 mm filter and a flow rate of 4 l/min (Aizenberg *et al.,* 2000b; Witschger, 2002; Lee *et al.,* 2011).

2.3.2.3 The seven hole sampler (SH-sampler)

The sampler is either made of non-conducting plastic (SKC) or aluminium (Casella) and has seven 4 mm diameter outward facing holes in the face plate. It is intended to provide a uniform distribution of particulate matter onto the filter. The sample is collected onto a 25 mm filter at a flow rate of 2 l/min (Kenny *et al.,* 1997; Vincent, 2007).

2.3.2.4 GSP and the PAS-6 samplers

The GSP sampler is a German (Germany Strohlein) version of the conical inhalable sampler (CIS). It was originally manufactured from metal with its conical inlet made of aluminium. It has an 8 mm inlet through which the aerosol is aspirated on to a 37 mm filter at a flow rate of 3.5 l/min (Kenny *et al.,* 1997). The PAS-6 sampler on the other hand is a dutch version of the CIS manufactured by University of Wageningen. It is an all metal sampler with a 6 mm inlet. The aerosol sample is collected at a flow rate of 2 l/min onto a 25 mm filter. Like the closed face cassette, the PAS-6 sampler orifice must face downwards at a 45º angle to the horizontal plane (Kenny *et al.,* 1997).

2.3.2.6 The closed face cassette sampler

This sampler is made up of a three part system moulded from non-conducting plastic material and is commonly used in the United States. It has a three part cassette that

is assembled together once the filter is put in place and then sealed with masking tape. The pump must be calibrated to a flow rate of 2 l/min and the sampler orifice has to face downwards during use. The substances collected onto the filter are analysed to determine the sampling efficiency (Vincent, 2007). The disadvantage of this sampler is that the sample is not spread evenly throughout the filter because of high aspiration velocity through the 4 mm opening and the small distance between the opening and the filter, making microscopic work difficult (Witschger, 2002).

2.4 Inhalable aerosol sampler efficiency studies

Inhalable aerosol samplers were compared in different laboratories, using tunnel experiments, and field studies.

2.4.1 The IOM sampler

A study that compared six inhalable aerosol samplers by Li *et al.* (2000), using three orientations, 0, 90 and 180º to the wind, at wind speeds of 0.55 and 1.0 m/s, showed that the efficiency of the IOM sampler increased with an increase in particle diameter from 10 to 68 µm at 0º orientation. A change in the orientation to 90 and 180º resulted in a reduction in measured efficiency from 100% to 0% when particle sizes were increased. This means that the IOM sampler oversampled larger particles greater than 20 µm at 0º and under-sampled when the orientation was at 90 and 180º. The same result was observed in other studies (Aitken and Donaldson, 1996; Kenny *et al*., 1997; Aizenberg *et al.,* 2000a; Witschger *et al.,* 2004; Gorner *et al.,* 2010). Similar oversampling findings were reported in a nickel refinery (Koch *et al.,* 2002), nickel alloy production (Tsai *et al.,* 1996b), as well as in collection of welding fumes (Zugasti *et al*., 2012).

2.4.2 The button sampler

In the Li *et al.* (2000) study, the efficiency of the button sampler was found to be relatively stable (87 to 98%) at particle diameters less than 10 µm. Furthermore, a significant decrease was observed when the particle diameters increased to between 41 and 68 µm. Additionally, the sampler also oversampled inhalable aerosols with diameters greater than 20 µm at 0º wind orientation. However, the button sampler efficiency is reported to be independent of the wind orientations (0 - 180º) and its

precision was found to be the best or second best in comparison to GSP, IOM and closed face cassette sampler (Aizenberg *et al*., 2000b; Witschger *et al*., 2004). The button sampler is also described as a sampler that should not suffer from any transmission losses since the filter is located directly behind the inlet, and the steel from which the sampler is made, eliminates electrostatic wall losses. Furthermore, the fact that the many 381 µm orifices are uniformly distributed on the inlet that is curved, not only provides for an even distribution of sample on the filter, but it also reduces the power of air turbulence around the inlet (Kalatoor *et al*., 1995; Aizenberg *et al*., 2000b; Witschger *et al.*, 2004). In contrast, a study carried out in the collection of agricultural dust showed the button sampler to under-sample to an extent where it was more comparable to the 37 mm closed face cassette sampler than to the IOM (Reynolds *et al.,* 2009).

2.4.3 The SH-sampler

The SH-sampler is intended to provide a uniform distribution of particulate matter onto the filter. This is made possible by the seven 4 mm orifices through which the sample is collected and should, therefore, have had better precision (Kenny *et al*., 1997; Vincent, 2007). It was found to behave in a similar way to the IOM under the same orientations and wind speed except at 0.55 m/s in which the efficiency decreased gradually as particle diameters increased (Li *et al*., 2000). Variable results were found when the sampler was tested in different wood facilities (Tatum *et al.,* 2001).

2.4.4 The GSP sampler

The GSP sampler, referred to as one of the conical inhalable sampler (CIS) in this study, was found to under-sample when particle diameters were greater than 50 µm and this applied to all wind conditions tested. The sampler produced inside losses that increased with an increase in particle diameter at 0º orientation to the wind. These are said to be due to bouncing off of particles and settling due to gravity (Li *et al*., 2000). According to Davies *et al*. (1999), Aizenberg *et al.,* (2000a) and Tatum *et al.,* (2001), the GSP sampler tends to suffer from oversampling due to its larger orifice that is likely to collect larger projectile particles, similar to what was observed with the IOM sampler due to its inlet that extends from the torso. In contrast, Kenny

et al. (1999) reported the efficiencies of the GSP sampler and IOM sampler to be similar only at lower particle diameters and that of the GSP sampler to be lower than that of the IOM sampler when particle diameters are increased.

2.4.5 The PAS sampler

The PAS sampler in comparison to an open face cassette in the collection of metalworking fluid aerosols was found to sample twice the concentration collected by the open face cassette sampler (Lillienberg *et al.,* 2008). An earlier study in a wind tunnel (Kenny *et al*., 1997), showed the sampler to perform in agreement with the inhalable convention for particles with aerodynamic diameter of 30 µm. From the literature studied, it would seem that more testing of the PAS-6 sampler is necessary. The smaller 6 mm inlet of the PAS-6 sampler as well as the 45° angle at which it works reduces its sampling efficiency as noted for the CFC sampler as well (Gorner *et al*., 2010).

2.4.6 The CFC sampler

The aerosol measurement efficiency of the closed face cassette was found to decrease from 100% with an increase in particle diameter. This was due to the increase in internal losses that occurred when particles increased above 40 µm, and would, therefore, result in under-sampling (Davies *et al.,* 1999; Kenny *et a*l., 1999; Li *et al.,* 2000; Gorner *et al.,* 2010). In addition to that, aspiration efficiency of the CFC is influenced by the downward angle at which the sampler faces during sampling. At 45º, the opening is shielded by the cassette structure thus having a negative effect on the sampler efficiency which adds to the effect of gravity even under calm air conditions (Gorner *et al*., 2010). Furthermore, the CFC sampler tends to suffer from leakage of external air even in the presence of the tape used to seal it. Additional losses occur when the filter is removed from the cassette (Baron, 2003).

2.5 Platinum

2.5.1 Chemical properties

Platinum group metals are noble metals that do not combine or react with other elements or compounds, accounting for their widespread uses. The primary use of

platinum is as catalysts, such as its use in production of automobile catalytic converters that help with the complete burning of petrol. It has a melting point of 1.7 ºC, boiling point of 3.8 ºC and a density of 21.45 g/cm^3. It does not tarnish or corrode when exposed to air (Rillema, 2004).

2.5.2 Extraction of platinum

The first step in the recovery of platinum group metals involves a metallurgical flotation process in which sulphide minerals are recovered. The ore that is ground to a fine powder is reacted with different chemical reagents, pumped into agitated tanks through which volumes of air are introduced. A concentrate with PGM content higher than the original ore and quantities of silicate minerals is produced. The concentrate then goes through the smelting process which further separates the sulphides from the silicates with the use of furnaces. The product is now referred to as a matte, containing PGM and copper nickel sulphide, which is fed into the refinery. The base metals are removed through a metallurgical process, leaving a PGM concentrate. The refining process involves precipitation of platinum into one of its complex salts, either ammonium chloroplatinate which is then ignited to produce the platinum sponge, or sodium chloroplatinate (Hunter *et al*., 1945; Gouldsmith and Wilson, 1963; Randolph, 1993; Linnett, 2005).

The process of handling the complex salts is either in a dry form which produces dust when released into the atmosphere or in a wet process where droplets may be suspended into a fine spray (Hunter *et al*., 1945).

2.5.3 Health effects of platinum exposure

Occupational exposure to PGMs in dust or droplets generated in refinery as stated above, however, brings with it serious challenges to human health. Platinum refinery processes produce various complex halide salts to which workers are exposed. These salts are potent sensitisers and the sensitisation occurs mainly from occupational exposure. The symptoms following sensitisation include; watering of the eyes, rhinitis, coughing, wheezing, dyspnoea, and cyanosis characteristic of severe asthma, itching, contact dermatitis and urticaria. The condition, previously known as platinosis, is now commonly referred to as platinum salt hypersensitivity.

This is likely to occur even at levels below the occupational exposure limit (OEL) of 0.002 mg/m^3 which may also worsen pre-existing asthma due to the presence of additional irritants such as chlorine. hydrochloric acid and ammonia (Maynard *et al.,* 1997; WHO, 2000; Petrucci *et al.,* 2004; Linnet, 2005). The period from initial contact with platinum salts to appearance of symptoms varies from a few weeks to several years, with symptoms becoming worse as the length and intensity of exposure increases. Initial clearing of the symptoms occurs upon removal from exposure although they may persist in longer exposure periods (WHO, 2000).

Allergy to platinum is induced by a group of charged compounds with reactive ligand systems with the most potent being: hexachloplatinic acid and chlorinated salts ammonium hexachloroplatinate, potassium tetrachloroplatinate, potassium hexachloroplatinate and sodium tetrachloroplatinate. The allergy is a Type I, IgE mediated allergic responses in which low molecular weight platinum salts act as haptens which form complete antigens when combined with serum proteins (WHO, 2000). Sensitisation occurs when the Pt salts are absorbed through the mucosa or epithelial linings in which conjugates are formed with proteins in the area (Murdoch and Pepys, 1984). The compounds combine with proteins by binding to the sulfhydryl groups which results in the formation of immunogenic complexes (Murdoch *et al*., 1985).

Sensitisation was found to occur in 0.73 to 6.8 cases for every 100 person months worked and symptoms are likely to occur in 0.59 to 2.4 of those cases and is more common in cigarette smokers. The symptoms will be suppressed by medical treatment, however, the only effective solution to this problem is to remove the individuals from exposure permanently (Calverley and Murray, 2005).

Many more hazardous chemicals that act as respiratory irritants such as chlorine, hydrochloric acid and ammonia are used in the work environment. These may worsen pre-existing conditions such as asthma even when exposure is maintained at levels below the OEL (Linnet, 2005; HCN, 2008).

Furthermore, Waters *et al*. (1975) observed the occurrence of reduced viability of alveolar macrophages under the influence of moderately high concentrations of platinum tetrachloride in rabbits as well as toxicity to lung fibroblasts in humans.

Exposure of mice to platinum salt (sodium hexachloroplatinate) produced an influx of inflammatory cells into the lungs and areas around the airways and blood vessels. Consequently, higher hyperplasia scores were found in correlation to the number of exposures (Ban *et al*., 2010). The same platinum complex was found to have higher toxicity in terms of inducing the formation of reactive oxygen species (ROS) in human bronchial epithelial cells when compared to $Pt(NO_3)_2$ (Schmid *et al*., 2007). An *in vitro* investigation into the toxic effect of platinum salt on human ciliated nasal epithelial cells was carried out using hydrogen hexachloroplatinate. The movement of cilia was seen to have been slowed down, associated with damage to the structural architecture of the epithelial cells, an effect which seemed to be mediated by neutrophils (Feldman *et al*., 2005).

2.6 Summary

The demand for platinum group metals has increased over the years due to its applications in a wide range of industries and technology sectors. Platinum is used in auto-catalysts, jewellery and industries such as chemical, electrical, medical, glass and petroleum (Hochreiter *et al.,* 1985; Chamber of Mines, 2010). South Africa requires an extensive understanding of the level of worker exposure to soluble platinum salts in the refinery is needed since it is one of the major producers of platinum group metals. This can only be achieved when the most efficient sampler is identified and used. Workers in base metal refineries are not only exposed to a variety of metals, but chemicals as well. The aim of the study was to evaluate the efficiency of six commercially available inhalable aerosol samplers in the measurement of soluble platinum compounds from which the best sampler would be identified under the specific workplace conditions. Since the performance characteristics of a sampler are influenced by different factors that include environmental temperature, humidity, air velocity, particle size distribution, sampler orientation and wind direction it was deemed important to perform sampler comparison that is specific to the base metal refinery (Reynolds *et al.,* 2009).

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CHAPTER 3: ARTICLE

The article is presented in the format prescribed by Annals of Occupational Hygiene.

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***Language*:** Manuscripts must be in English and authors should try to write in a way which is simple and clear. British or American styles and spelling may be used, but should be used consistently, and words or phrases which might be unclear in other parts of the world should be avoided or clearly explained.

Brevity: The necessary length of a paper depends on the subject, but any submission must be as brief as possible consistent with clarity. The number of words, excluding the abstract, references, tables and figs, must be stated as a message to the Editor at the time of submission. If this length is more than 5000 words, a statement must be included justifying the extra length, and papers without this information may be returned unread. Suitable extra material can be included in the online edition only.

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***Authorship**:* Persons should only be named as authors if they have made significant identifiable intellectual contributions to the work; other contributions may be recognised by acknowledgement at the end of the submission. All names and affiliations of authors should be clearly stated at the beginning of the paper.

Structure of paper: Papers should generally conform to the pattern: Introduction, Methods, Results, Discussion, and Conclusions, unless these are clearly inappropriate. A paper must be prefaced by an abstract of the argument and findings, which may also be arranged under the same headings. As with many other journals, we are unable to publish footnotes to the text. Please therefore incorporate this sort of material into the body of the paper, in brackets if appropriate.

Design and analysis: The quality of the data and analysis must always be good enough to justify the inferences and conclusions drawn. Particular attention should be given to design of sampling surveys, which should be planned using modern statistical principles, and to the treatment of results below the limit of detection.

Units and symbols: SI units must be used, though their equivalent in other systems may be given as well.

Figures**:** These include photographs, diagrams and charts. The first submission should include good quality low resolution copies of Figures, and may be incorporated into the text or at the end of the manuscript.

Tables**:** Tables should be numbered consecutively and given a suitable caption. As with Figures, it is helpful to incorporate them into the text of the first submission, but in the revised version each table should be presented on a separate page. Footnotes to tables should be provided below the table and should be referred to by superscript lowercase letters.

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Jones and Brown (1995) and Hospath *et al.* (2006) observed total breakdown of control..., or

Total breakdown of control has sometimes been observed (Jones and Brown, 1995; Hospath *et al*., 2006).

Papers whose references are not properly arranged may be returned for revision without review.

At the end of the paper, references should be listed in alphabetical order by name of first author, using the Vancouver Style of abbreviation and punctuation. ISBNs should be given for books and other publications where appropriate. Material unobtainable by readers should not be cited. Personal Communications, if essential, should be cited in the text (e.g., Professor O.H. Poobah, Institute for Dusty Sciences). Internet material can be referred to if it is likely to be permanently available; the date on which it was last accessed should be given. References will not be checked editorially, and their accuracy is the responsibility of authors.

Examples:

Simpson AT, Groves JA, Unwin J, Piney M. (2000) Mineral oil metal working fluids (MWFs)—Development of practical criteria for mist sampling. Ann Occup Hyg; 44: 165–72.

Swift DL, Cheng Y-S, Su Y-F, Yeh H-C. (1994) Ultrafine aerosol deposition in the human nasal and oral passages. In Dodgson J, McCallum RI, editors. Inhaled Particles VII. Oxford: Elsevier Science. p. 77–81. ISBN 0 08 040841 9 H.

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Comparative evaluation of the performance of aerosol samplers for the assessment of soluble platinum exposure

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Keywords: Sampler precision evaluation, soluble platinum, inhalable sampler.

Abstract

Background: The study was carried out in a base metal refinery in South Africa. South Africa is amongst the major countries where platinum and platinum group metals (PGMs) are produced. Considering that inhalation remains the major route of occupational exposure, having an efficient sampler to monitor exposure is in the best interest of worker health since soluble platinum salts are more toxic than the metal itself and occur at higher concentrations than other PGMs. Different samplers are used in different parts of the world by occupational hygienists for the measurement of inhalable aerosols.

Aims and Objectives: The IOM sampler is currently used for routine exposure measurements at this specific base metal refinery. The performance of the Institute of Medicine (IOM) sampler for the sampling of soluble platinum salts, however, has not been compared to that of other samplers in the base metal refinery setting. The primary focus of this study was to compare the performance of filter aerosol samplers namely; Button, Closed Face Cassette (CFC), Gesamtsstaubprobenhome (GSP), IOM, PAS and seven hole (SH-sampler) with each other in the sampling of inhalable soluble platinum salts (as platinum) in a base metal refinery.

Methods: Samplers were randomly allocated to six positions identified as high exposure areas from previous measurements and rotated with subsequent sampling runs. A total of 3 cycles, each with 6 sampling runs with duration of 240 minutes for each run, were carried out. The gravimetric mass and soluble Pt concentrations collected by each sampler was used in the hierarchical comparison of the samplers.

Results and Discussion: No statistically significant differences were found between samplers in both dust mass and Pt hierarchies. The seven 4 mm orifices of the SH-sampler as opposed to only one for IOM sampler provides for uniform distribution of particulate matter onto the filter. This also gives better precision in dust collection as indicated by the lower average relative standard deviation (RSD) obtained with the SH-sampler. The IOM sampler collected 98% of SH-sampler averages albeit with greater variations. The button sampler was found to have higher precision than IOM although it under-sampled the SHS dust mass and Pt averages by 24.25% and 33% respectively. The GSP demonstrated better precision than PAS, button and CFC in the collection of platinum.

Conclusion: The use of the IOM in routine monitoring has to be reviewed. More data is required to support the findings obtained from this study.

3.1 Introduction

3.1.1 Platinum occupational exposure and health effects

South Africa is amongst the major countries where platinum and platinum group metals (PGMs) are mined. Overall, the production of PGMs including Pt, has increased over the years due to their important use as industrial and vehicle exhaust catalysts, brought about by the international drive to reduce gaseous emissions of pollutants such as carbon monoxide, nitrogen oxide and hydrocarbons (LeRoy, 1975; Hochreiter *et al*., 1985; Ravindra *et al*., 2004; Bencs *et al*., 2011; Iavicoli *et al*., 2012; EU, 2012). The major route of occupational exposure to PGMs remains inhalation hence it forms the focus of this study. Dermal route through jewellery is important for the general population whilst the oral route has not received much attention due to the poor absorption that occurs from it. The clearance of inhaled platinum is very slow and it is mainly excreted through the faeces. The platinum metal salts, especially the soluble types, such as chloroplatinates (Na_2PtCl_4, $(NH_4)_2PtCl_4$, Na_2PtCl_6, $(NH_4)_2PtCl_6$); formed as precipitates during the refining process, are more toxic than the metal itself. The absorption of those salts through the epithelial or mucosal layers leads to formation of conjugates with proteins. This results in the induction of type I allergic symptoms, a risk aggravated by smoking (Calverley *et al*., 1995; Merget *et al*., 2000). New platinum refinery workers remain at high risk for platinum induced sensitisation. The symptoms include coughing, wheezing, shortness of breath, and an asthma-like manifestation collectively known as platinosis (Hunter *et al*., 1945; Gouldsmith, 1963; Murdoch and Pepys, 1984; Linnet and Hughes, 1999; Cristaudo *et al*., 2004; Gad, 2005; Linnet, 2005; HCN, 2008; Puls *et al.*, 2012). These symptoms were found to persist for as long as workers remained within the refinery and for up to an hour after they had left the workplace (Hunter *et al*., 1945). Exposure to PGM levels below the occupational exposure limit tend to worsen pre-existing asthma due to presence of additional irritants of the respiratory system such as chlorine, hydrochloric acid and ammonia (Linnet, 2005). Furthermore, reduced viability of alveolar macrophages was observed under the influence of moderately high concentrations of platinum tetrachloride in rabbits as well as toxicity to lung fibroblasts in humans (Waters *et al*., 1975). Exposure of mice to platinum salt (sodium hexachloroplatinate) produced an

influx of inflammatory cells into the lungs and areas around the airways and blood vessels. Consequently, higher hyperplasia scores were found in correlation to the number of exposures (Ban *et al*., 2010). The same platinum complex was found to have higher toxicity in terms of inducing the formation of reactive oxygen species (ROS) in human bronchial epithelial cells when compared to $Pt(NO_3)$ (Schmid *et al*., 2007).

3.1.2 Sampler comparison studies

Evaluation of personal exposure in the workplace is widely done through sampling of airborne contaminants. The task can be achieved effectively provided that the performance characteristics of the instruments used in sampling are properly understood and the best is selected (Sleeth and Vincent, 2011). A study carried out in platinum production is one of the few identified to have come close to the current study even though only two samplers were compared (Maynard *et al.,* 1997). The bulk of studies were performed in the laboratory and measurements from such studies will be different from those carried out at the workplace since, in a laboratory, conditions are controlled whilst the same cannot be said for the workplace (Tsai *et al*., 1995; Kenny *et al*., 1997; Tatum *et al*., 2001; Gorner *et al*., 2010). The need for site specific research was brought to the fore by Reynolds *et al*. (2009), hence the

3.1.3 The aim and importance of the study

The primary focus of this study was therefore to compare the concentrations of aerosol samplers in the collection of inhalable soluble platinum salts. The samplers evaluated in this study are used in different parts of the world by occupational hygienists for the measurement of inhalable aerosols (Sleeth and Vincent, 2011). Inhalable aerosols are defined as those particles that can enter into the mouth or nose during breathing and have aerodynamic diameters of up to 100 µm. (BSI, 1998; Davies *et al*., 1999; Sleeth and Vincent, 2011). Although the aerodynamic diameter of particles containing soluble Pt salts in the base metal refinery is unknown, the effects they have on the lungs and the rest of the body warrants the sampling of inhalable dust with the most effective sampler.

3.2 Materials and methods

3.2.1 Study area and design

The study was carried out at the final concentrator of a South African base metal refinery. Dust generating activities involved in the drying and milling processes made this an ideal test area. Six different positions, identified as high exposure areas from occupational exposure results were chosen to which samplers were randomly allocated. The samplers were then rotated in following sampling runs as shown in Table 1 and the process was repeated 3 times. The samplers were positioned on stands at a height of 1.7 m clear of any obstruction (HSE, 2000; Hickey *et al*., 2002).

Table 1: One cycle of sampler positions and rotation sequences used during the study period

Position	**Day 1**	**Day 2**	**Day 3**	**Day 4**	**Day 5**	**Day 6**
1 (*Up ball mill)*	IOM	SHS	GSP	CFC	Button	PAS
2 (*RH of ball mill*)	Button	CFC	SHS	PAS	GSP	IOM
3 (*LH of ball mill*)	SHS	PAS	Button	GSP	IOM	CFC
4 (*Drier 2*)	GSP	Button	CFC	IOM	PAS	SHS
5 (*Drier 1*)	PAS	GSP	IOM	SHS	CFC	Button
6 (*Baghouse)*	CFC	IOM	PAS	Button	SHS	GSP

3.2.2 Sampling equipment

3.2.2.1 Samplers used

Six different samplers were tested. The IOM sampler uses a cassette system and operates at a flow rate of 2 l/min (Kenny *et al*., 1997). The button sampler uses a filter that is placed directly behind the inlet. and functions at a flow rate of 4 l/min (Aizenberg, 2000). The seven hole sampler (SH-sampler) aspirates particles at a flow rate of 2 l/min through seven evenly spaced 4 mm orifices that face outwards with the filter placed on a supporting plastic grid (Kenny *et al*., 1997). Two conical inhalable samplers namely; (Gesamtsstaubprobenhome) GSP and the Dutch PAS-6 (PAS) were also included. The GSP sampler has a single 8 mm inlet through which the aerosol is collected at a flow rate of 3.5 l/min. The PAS sampler on the other hand, has a smaller 6 mm orifice that faces downwards and its pump flow rate is 2 l/min. The CFC sampler is made from non-conductive plastic, has a 4 mm opening and operates at a flow rate of 2 l/min (Kenny *et al*., 1997). All samplers with the exception of the disposable CFC cassette, were washed with soap and water,

assembled in a dust free, environmentally controlled environment and reused for subsequent sampling sessions (HSE, 2000; Sleeth and Vincent, 2011).

3.2.2.2 Filters

Soluble mixed cellulose ester (MCE) filters with a 0.8 µm mean pore diameter recommended for collection and analysis of soluble platinum salts were used for all samplers (37 mm for GSP and CFC-sampler, and 25 mm for the rest of the samplers) (HSE, 1996; OSHA, 2002; NIOSH, 2003). Blanks were included with every set of 10 filters weighed using either a five decimal OHAUS Analytical Plus or Mettler AT 250 chemical balance. All filters were handled as specified in the different methods and published works (HSE, 1996; Kenny *et al*., 1997; HSE, 2000; Vincent, 2007).

3.2.3 Environmental conditions

Barometric pressure was measured with a Greisinger Digital Barometer GDH 11. The Dräger smoke tube was used to determine the direction of air flow before its velocity was measured with the aid of a Pacer Vane Anemometer. Temperature and relative humidity were measured with a QuestTemp 34 Thermal Environment Monitor. These measurements were taken at each sampling area with every sampling run.

3.2.4 Sampling method

The study followed the area sampling method to allow for all the test samplers to be used with each event and be exposed to relatively similar conditions at the same time (Zugasti *et al*., 2012). The Gilair Plus pumps were calibrated with a Gillibrator 2 before and after sampling. A cutoff deviation of 5% was not exceeded by any of the samples (Sleeth and Vincent, 2011).

3.2.5 Analysis of samples

3.2.5.1 Gravimetric analysis

The difference between the final corrected filter masses (post and pre weight) and the volume of air corrected to normal temperature and pressure (NTP), were used to

calculate concentration of dust collected from each sampler (HSE, 2000; NIOSH, 2003).

3.2.5.2 Chemical analysis

The filters were leached in 5-10 ml of 0.07 M HCl for 30 minutes in an ultra-sonic bath (40Hz). The solution was filtered through a 0.22 µm filter membrane using Buchner apparatus and made up to 25 mL with 10 ppb of rhenium. The amount of soluble Pt (as metal) was then determined using the Element XR High Resolution Magnetic Sector Mass Spectrometer. The method follows the MDHS 42/6 (HSE, 1996).

3.2.5.3 Data processing

The estimates for Pt concentrations below the detection limit were calculated using the β- substitution method (Ganser and Hewett, 2010). Statistical calculations were done using the SPSS version 21.0. The Sidak Adjusted pair-wise comparison method was used to compare samplers according to dust mass and platinum concentrations; as well as to determine the effect of positions on the sampler performance. The differences were considered to be significant when the p value was less than or equal to 0.05. The graphs were drawn using Statistica 12 (StatSoft Inc). The variations in sampler measurements were analysed by calculating the relative standard deviations (% RSD) (Witschger *et al.*, 2004). The results of overall sampler performance were presented in the form of hierarchies (descending order) based on dust mass and soluble platinum concentrations collected by each sampler. The concentrations collected by various samplers relative to best performing sampler were calculated as follows:

$(sampler\ concentration \div best\ sampler\ concentration)$ x 100%.

3.3 Results

A total of 108 samples were collected over three cycles of six sampling runs each with an average running time of 240 minutes. The average environmental air velocity was generally below the anemometer detection limit of 0.1 m/s. The average relative humidity ranged between 37 and 43%.

3.3.1 Gravimetric analysis

3.3.1.1 Descriptive statistics (Figure 1)

The average dust concentrations were log transformed to achieve normality. Extremely large values obtained with the button (2 values) and the IOM (1 value) were treated as outliers and removed before statistical analysis. The basic statistical results showed no statistically significant differences amongst the six filter samplers. However, SH-sampler collected higher average concentration (1.609 mg/m^3) than the IOM sampler (1.587 mg/m^3) whilst the lowest average of 0.423 mg/m^3 collected by the CFC sampler The button sampler collected an average concentration of 1.218 mg/m^3, whilst the PAS collected a slightly higher average concentration of 1.453 mg/m^3 than the 1.378 mg/m^3 collected by the GSP. All the sampler averages had large standard deviations as depicted in Figure 1.

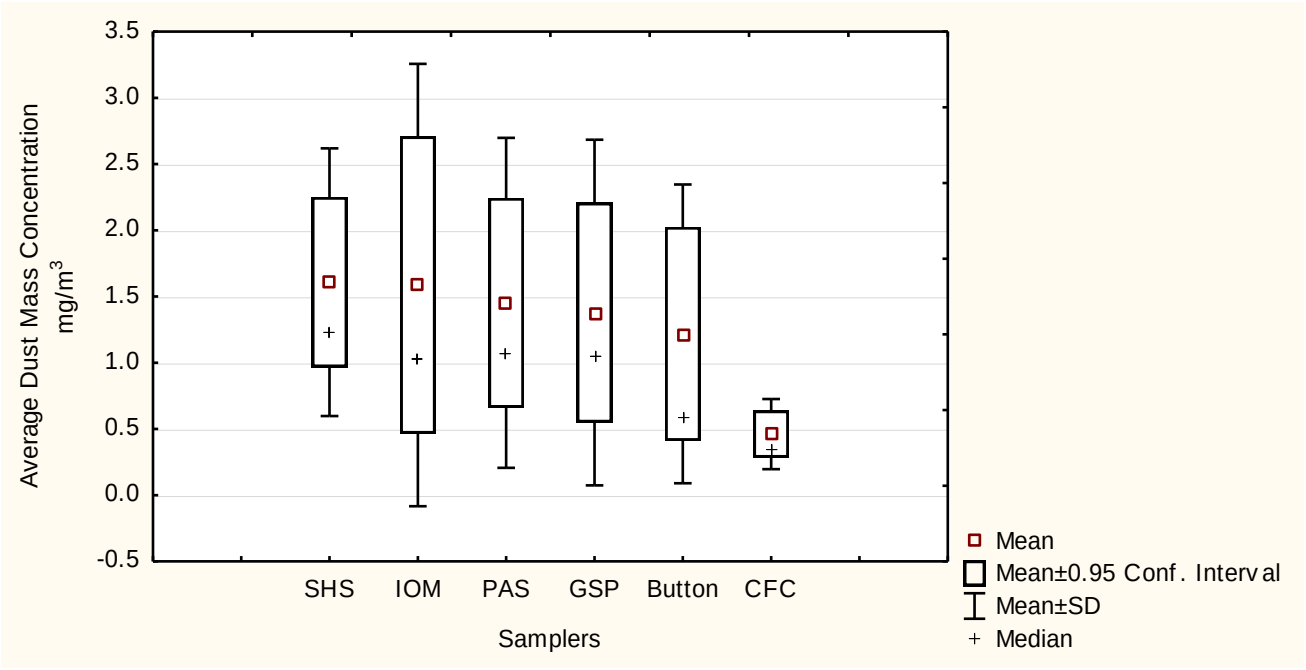

Figure 1: Box & Whisker plots showing dust mass concentrations collected by various samplers in the hierarchy.

3.3.1.2 The hierarchy of samplers: dust mass concentrations (Table 2)

The SH-sampler collected the highest dust mass concentrations with the IOM and the CFC samplers collecting 98.7 and 26.3% of the SH-sampler average respectively, equivalent to 1.33% and 73.7% under-sampling. The average concentration collected by the button sampler placed it as the second last sampler in

the hierarchy with its average being equivalent to 75.74% of the SHS concentration. The two conical inhalable samplers collected concentrations that were lower than that of the IOM with the PAS (1.453 mg/m^3) sampler giving slightly higher measurements than the GSP (1.378 mg/m^3).

Table 2: Sampler hierarchy based on dust mass concentrations collected by various samplers

Sampler	**Average dust mass (mg/m^3)**	**SD**	**RSD (%)**	**% sampled relative to the SHS**
SHS	1.609	1.01	62.82	--------
IOM	1.587	1.67	105.23	98.66
PAS	1.453	1.25	85.75	90.31
GSP	1.378	1.30	94.66	85.70
Button	1.218	1.13	92.58	75.75
CFC	0.423	0.29	67.49	26.30

3.3.1.3 Variations in sampler measurements: dust mass concentrations (Table 2)

The highest RSD was obtained with the IOM sampler of 105.23% as opposed to SH-sampler (62.82%), the PAS (85.75%), Button (92.58%), GSP (94.66%) as well as that of the worst performing sampler the CFC (67.49%). The IOM sampler results also produced the widest confidence interval than that of all other samplers as depicted in Figure 1.

3.3.2 Platinum

3.3.2.1 Descriptive statistics (Figure 2)

The SH-sampler and the IOM collected 0.287 µg/m^3 and 0.284 µg/m^3 respectively whilst the lowest average of 0.04 µg/m^3 was obtained with the CFC sampler. The conical inhalable aerosol samplers collected average concentrations of 0.214 µg/m^3 and 0.113 µg/m^3 for the GSP and the PAS respectively. These differences however were not statistically significant ($p \geq 0.05$). The standard deviations of the different sampler averages were generally high whilst the confidence intervals were higher for the IOM than those obtained with the other samplers.

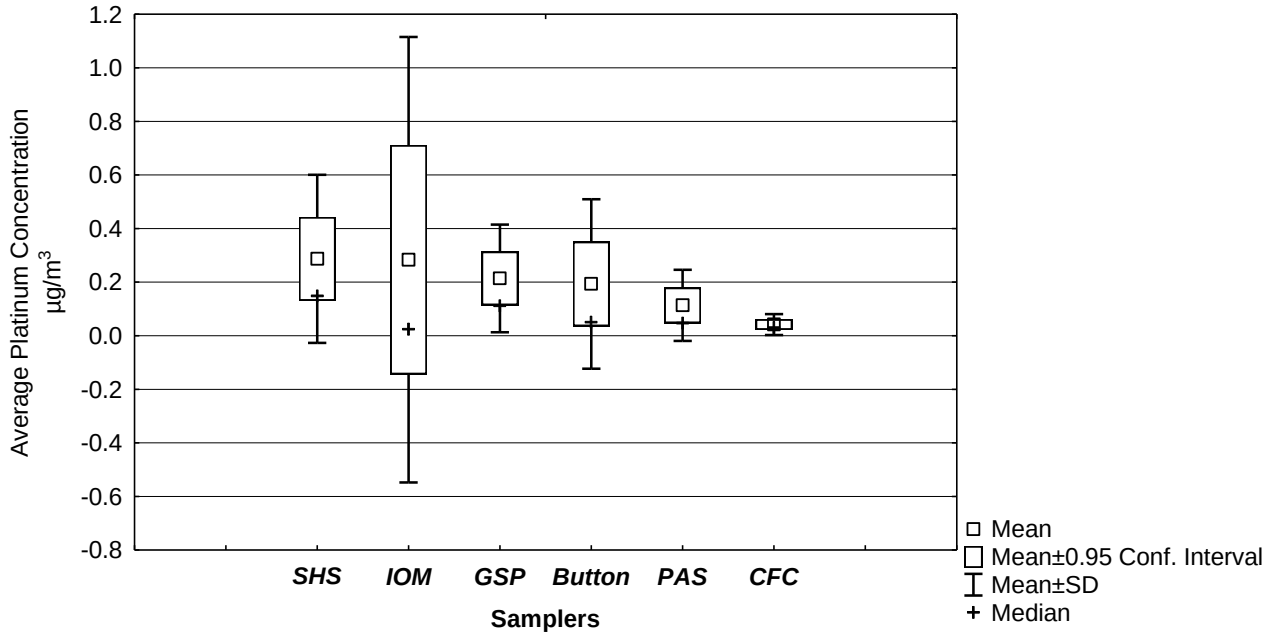

Figure 2: Box Plots showing average Pt concentrations collected by various samplers in the hierarchy.

3.3.2.2 Sampler hierarchy according to soluble platinum concentrations (Table 2)

The highest platinum concentrations were collected by the SH-sampler and IOM averages placing them in 1st and 2nd hierarchical positions respectively. The difference between the IOM sampler and SH-sampler concentrations was negligible with the IOM concentration being equivalent to 98.88% of the SH-sampler average concentration. The gap between the SH-sampler and the rest of the samplers widens with GSP collecting 74.56%, the button sampler 67.34%, 39.46% for the PAS and 14.53% for the CFC sampler relative to SH-sampler concentration.

Table 3: Sampler hierarchy based on platinum concentrations collected by various samplers.

Samplers	Mean (mg/m^3)	SD	RSD (%)	% sampled relative to SHS
SHS	0.29	0.31	109.29	--------
IOM	0.28	0.83	293.08	98.88
GSP	0.21	0.19	87.79	74.56
Button	0.19	0.32	163.76	67.34
PAS	0.11	0.13	117.32	39.46
CFC	0.04	0.04	93.59	14.53

3.3.2.3 Variations in sampler measurements: platinum concentrations (Table 3)

The highest relative standard deviation was observed with the IOM sampler 293.1% and the second highest obtained with the button sampler (163.76%) whilst that of the SH-sampler was 109.3%. The lowest RSD of 87.79% was obtained with the GSP sampler. The lowest concentrations in the study collected by the PAS and the CFC samplers produced RSD values of 117.32 and 93.59% respectively.

3.4. Discussion

The main aim of the study was to determine the most effective sampler for the collection of inhalable soluble platinum. The occurrence of very low environmental air velocities in this study (below 0.3 m/s) were also found in different workplaces in a survey carried out by Baldwin and Maynard (1998). This kind of environment is referred to as having slowly moving air when the air velocity is below the detection limit of the anemometer (Witschger *et al*., 2004). In such environments, the most important factor will, therefore, be sedimentation controlled by gravitational force and the degree to which falling particles will be captured by the sampler and not wind speeds (Lidén and Harper, 2006). Comparison revealed no statistically significant differences amongst the filter samplers tested.

3.4.1 Gravimetric results

The good performance shown by the SH-sampler in collecting higher concentration was further strengthened by higher precision with which it sampled as indicated by RSD of 62.82% as opposed to IOM with 105.23%, 92.58% for the button and 94.66% for the GSP sampler. The button sampler was found to have higher precision than IOM in slowly moving air (Witschger *et al*., 2004) and that is in agreement with current findings. This is notwthistanding that the button sampler only collected 75.75% of the SH-sampler concentration, and the IOM 98.66%, which translated to a 24.25% of under-sampling by the button sampler when compared to SH-sampler. The CFC sampler collected the lowest concentrations which showed an under-sampling of the SH-sampler average by 73.7% albeit with lowest variations than all other samplers.

3.4.2 Sampler specific discussions

3.4.2.1 The SH-sampler

The SHS is designed to provide uniform distribution of particulate matter onto the filter, made possible by the seven 4 mm orifices through which the sample is collected (Kenny *et al*., 1997; Vincent, 2007), hence the better precision in the collection of dust mass and second highest concentrations of soluble Pt in this study. The RSD obtained for Pt collection (109.29%) was comparatively lower than that of IOM (293.08%) and button sampler (163.76%). The results obtained with dust mass concentrations were even better since an even lower RSD of 62.82%. The under-sampling detected in a study by Li *et al*. (2000) was mainly associated with particles larger than 20 µm when its orientations to the wind were at 90 and 180°. This, therefore, implies that the SH-sampler would not have performed as well as it did if soluble platinum particles were of large aerodynamic diameters.

3.4.2.2 The IOM sampler

The importance of the results obtained with the IOM sampler in this study are 3 fold; the IOM is currently being used in this base metal refinery for routine measurements of worker exposure, it has been found to satisfy the inhalable convention (BSI, 1993), and is also recommended together with the SH-sampler in MSDH 14/3 (HSE, 2000). The sampler, however, is affected by particle sizes, wind speeds and orientation to the wind as observed in a study by Li *et al*. (2000). In that study, the IOM was found to under-sample when particles were smaller than 20 µm and that was dependent on the wind orientation. The collection of higher concentrations by the IOM sampler found in previous laboratory and field studies when compared to the CFC sampler was also evident in this study (Kenny *et al*., 1997; Spear *et al*., 1997; Skaugest *et al.*, 2013). There was good agreement between the IOM sampler and the SH-sampler sampler concentrations in both hierarchies as well as the amounts collected by the IOM (98%) of the SH-sampler concentrations. The greater variations obtained with the IOM sampler of 105% and 293% RSD for dust mass and Pt concentrations respectively than even the comparatively worst performing sampler the CFC sampler which produced 67% and 93% in this study have to be pointed out. This finding is important since it a direct indication of the unreliability or lower precision of the IOM sampler in this study.

3.4.2.3 The GSP and PAS samplers

The GSP sampler inlet that is extended from the torso or attachment was found to contribute to oversampling that is similar to that of the IOM sampler (Aizenberg *et al*., 2000) was not evident in this study since the average Pt concentration collected by the GSP sampler was only slightly higher that of the PAS sampler whilst the opposite result was observed in the average dust mass concentration. The smaller 6 mm inlet of the PAS sampler as well as the 45° angle at which it operates reduces its sampling efficiency similar to that noted for the CFC sampler even though it collected slightly higher average than the GSP sampler (Gorner *et al*., 2010). A lower RSD of 87.79% demonstrated higher precision for the GSP sampler when compared to SH-sampler (109.29% RSD) even though it under-sampled the SH-sampler dust mass and Pt average by 25%. Tatum *et al*. (2001) also found the GSP sampler to have higher efficiency than IOM and SH-sampler in collection of wood dust. The lower wind speed measured in this study worked in favour of the GSP sampler as was also observed in a study by Sleeth and Vincent (2011) in ultra-low wind speeds.

3.4.2.4 The button sampler

The precision of the button sampler was much lower (RSD 92.58%) than that of SH-sampler (RSD 62.82%) although higher than that of the IOM sampler (293%). This is similar to observations made in slowly moving air by Witschger *et al*. (2004). Furthermore, Kalatoor *et al*. (1995); Aizenberg (2000) and Witschger *et al*. (2004) described the button sampler as a sampler that should not suffer from any transmission losses since the filter is located directly behind the inlet. The steel from which the sampler is made eliminates electrostatic wall losses. In spite of all these inherent advantages, the button sampler performed poorly in both hierarchies. Reynolds *et al*. (2009) also found the button sampler to under-sample to an extent where it was more comparable to the CFC sampler than to the IOM sampler.

3.4.2.5 The CFC sampler

The lowest average relative to the SH-sampler dust mass and Pt concentrations of 26.3% and 14.53% respectively were obtained with the CFC sampler. This is similar to findings from laboratory and field studies that compared different sampler combinations (Reynolds *et al*., 2009; Lee *et al*., 2011). Particles bounce off after

hitting the filter with resultant losses to the walls, thereby lowering efficiency of the CFC sampler (Li *et al.,* 2000). In addition to that, aspiration efficiency of the CFC sampler is influenced by the downward angle at which the sampler is facing. At 45º, the opening is shielded by the cassette structure thereby having a negative effect on the sampler efficiency which adds to the effect of gravity even under calm air conditions, as would be the case in this study (Gorner *et al*., 2010).

3.4.3 Effect of workplace variations on results

Daily variations in workplace activities such as the number of batches dried and milled or floor cleaning on some of the sampling days would have resulted in non-uniform distribution of particles as well as possible variations in aerosol concentrations (Li *et al*., 2000). This could have contributed to large standard deviations obtained from the data. The IOM sampler however, gave the largest variations, the CFC sampler the lowest, and the second lowest was obtained with the SH-sampler.

3.4.4 Comparison between dust mass and platinum sampler hierarchies

There was agreement between the dust mass and platinum sampler hierarchies in so far as the SH-sampler and the IOM sampler being identified as the top 2 samplers the CFC sampler as the poorest sampler of all on the basis of average concentrations alone. This is in spite of the IOM sampler having shown the highest variations in both hierarchies than all samplers. The positions of the GSP, PAS and button samplers varied between the hierarchies as well as in terms of the RSD.

3.5 Conclusion

The best performing filter sampler was found to be the SH-sampler. The IOM sampler which is in current use at this particular base metal refinery collected 98% of the SH-sampler dust mass and Pt concentrations. The greater confidence interval (Figure 2) and highest RSD (Tables 3 and 4), gave a strong indication of the IOM being an unreliable sampler in the collection of both dust mass and soluble Pt salts, thus its use has to be reevaluated. This was also observed in a sampler comparison study carried out by Tatum *et al*. (2001) in wood products industry facilities. Poor

performances of the CFC sampler and the PAS sampler reported by other authors were confirmed in this study. Follow up studies must include particle sizes and distribution within a base metal refinery for the best sampler to be identified. The higher precision shown by GSP sampler requires further investigation. There is a need for more sampler comparison studies to be carried out in similar workplace environments since the lack of information was found to be evident as well as for the validation of results obtained in this study. The measurements of particle sizes should be incorporated in future studies since the likelihood of the presence of sub-micron particles was found in a study carried out at by (Badenhorst, 2011 Unpublished MSc results)

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Chapter 4: Limitations, conclusion and recommendations

4.1 Study limitations

4.1.1 Particle sizes and distribution

The lack of data on particle sizes and distributions makes the data all the more inconclusive since it has a bearing on the concentrations collected at each sampling position.

4.1.2 The lack of a reference sampler

It would have been ideal to compare the concentrations collected by the different samplers to a concentration collected by a reference sampler or a golden standard. In the absence of such, issues pertaining to over or under-sampling are used with caution.

4.2 Conclusions

4.2.1 The method used in the study

The randomisation and rotation of samplers in this study allowed for a proper sampler comparison to be achieved. Biases that could have been brought about by the non-homogeneity of particle distribution, ambient factors as well as variations in dust concentrations caused by production activities were reduced.

4.2.2 The sampler that collected the highest concentrations: SH-sampler

The SH-sampler proved to be more reliable sampler of the six tested in this study. Its performance (highest dust mass and platinum concentrations) was supported by a lowest variations indicated by % RSD than the IOM sampler in both hierarchies. The design of the sampler provides for an even distribution of the sample onto the filter which gives its better precision.

4.2.3 The performance of the IOM sampler

The IOM sampler which is in current use at this particular base metal refinery collected 98% of the SH-sampler dust mass and Pt concentrations albeit with greater

variations and a wider confidence interval. These gave a strong indication of the IOM being an unreliable sampler as confirmed by the highest relative standard deviation from the measurements obtained at the different positions used in this study.

4.2.4 Other samplers

No statistical significant differences were found between the best performing filter sampler, SH-sampler and the other top two samplers; the GSP and button samplers. The IOM, of interest in this study since it is currently used at this base metal refinery, collected 2% less than the SH-sampler. Nonetheless, the measurements obtained with the IOM were shown to have greater variations that all other samplers in this study which, therefore, renders it an unreliable sampler. The use of the IOM sampler in routine monitoring of worker exposure in the base metal refinery has to be reviewed. The samplers with downward facing inlets, the CFC and PAS samplers were described by other authors as displaying poor performances due to the effect of gravity on the particle mobility and capture, and this was confirmed in this study. The inlets (4 and 6 mm) of these samplers are also smaller than those of other samplers. The CFC sampler tends to suffer from sample losses due to leakage on sides and electrostatic forces on walls of the cassette. The only positive aspect of the PAS is that it is made from metal and can avoid losses due to electrostatic forces hence it was the better of the two.

4.3 Recommendations

4.3.1 The best sampler

The SH-sampler is recommended for routine monitoring of worker exposure on the basis of performance shown in the study as well as a cost saving of 61% per unit item when compared to the IOM sampler.

4.3.2 Samples

More samples have to be taken with the top performing samplers namely, SH-sampler, GSP, button and the IOM to investigate issues of wide confidence interval and large RSD.

4.3.3 General confirmation of study results

Similar studies have to be undertaken in more workplaces with similar environmental conditions and operations in which platinum is handled.

4.3.4 Determination of particle sizes and distribution

Future studies should include the characterisation of particles to determine aerodynamic diameters and distribution.