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Evaluation of thermal desorption as an alternative technique for the measurement of coal tar pitch volatiles

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(B.Sc; B.Sc. Hons)

Mini-dissertation submitted in partial fulfilment of the requirements for the degree *Master of Science in Occupational Hygiene* at the Potchefstroom Campus of the North-West University

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Preface

This mini-dissertation is presented for the partial fulfilment of the degree *Master of Science in Occupational Hygiene* at the School of Physiology, Nutrition, and Consumer Sciences of the North-West University, Potchefstroom Campus. It was decided to use the article format for the purpose of this study. Throughout, references are for uniformity purposes presented according to the guidelines of an accredited journal, *Annals of Occupational Hygiene.* Therefore, Chapter 3 is a manuscript in the form of an article. Although the appropriate and relevant literature background is discussed in the manuscript, Chapter 2 serves as a literature study and gives an additional, more elaborate literature background. Chapter 4, the concluding chapter, provides a summary of the main findings, confounders are discussed, conclusions are drawn and recommendations are made.

Author's contribution

This study was planned and executed by a team of researchers. The contribution of each is reflected in Table 1.

Table 1: Research Team

NAME	CONTRIBUTION
Mr. CJ Van der Merwe	• Literature research, statistical analysis and writing of the mini-dissertation including article.
Dr. JL Du Plessis	• Assisted with the planning and design of the study, statistical interpretation, reviewing of the mini-dissertation and administration associated with research projects.
Mr. PJ Laubscher	• Assisted with the planning and design of the project.
Mr. M De Beer	• Assisted with the planning and financial administration of the project.

The following is a statement from the co-authors regarding the role they played in the study:

I declare that I have approved the mini-dissertation and article and that my contribution as reflected in the above table is a true reflection of my actual contribution and that I hereby give my informed consent that it may be published as part of CJ Van der Merwe's *M.Sc (Occupational Hygiene)* mini-dissertation.

Dr. JL Du Plessis

Mr. PJ Laubscher

Mr. M De Beer

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- My wife Alicia van der Merwe for her love, friendship and support.

Soli Deo Gloria

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Chapter 3

List of abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists, USA
ATSDR	Agency for Toxic Substances and Disease Registry
BSF	Benzene Soluble Fraction
CTPVs	Coal Tar Pitch Volatiles
EPA	Environmental Protection Agency, USA
GC	Gas Chromatography
GFF	Glass Fibre Filters
HCS	Hazardous Chemical Substances
HPLC	High Pressure Liquid Chromatography
IARC	International Agency for Research on Cancer
MHSA	Mine Health and Safety Act, South Africa
MHSR	Mine Health and Safety Regulations
NIOSH	National Institute for Occupational Safety and Health, USA
OEL – CL	Occupational Exposure Limit – Control Limit
OEL – RL	Occupational Exposure Limit – Recommended Limit
OHSA	Occupational Health and Safety Act, South Africa
OSHA	Occupational Safety and Health Administration, USA
PACs	Poly-cyclic aromatic compounds
PAH	Poly-aromatic hydrocarbons
PEL	Permissible Exposure Limit
PGMs	Platinum Group Metals
PNAs	Poly-nuclear aromatics
PPE	Personal Protective Equipment
RHCS	Regulations for Hazardous Chemical Substances
SAIOH	Southern African Institute of Occupational Hygiene
SANAS	South African National Accreditation System
TD	Thermal Desorption
TWA	Time Weighted Average
VOCs	Volatile Organic Compounds

Summary

English title: Evaluation of thermal desorption as an alternative technique for the measurement of coal tar pitch volatiles.

Motivation: The accurate and reliable measurement of the concentration of coal tar pitch volatiles (CTPVs) in ambient air has proved to be a challenge for occupational hygienists. The challenge must however be confronted due to, amongst others, the carcinogenic properties of some poly-aromatic hydrocarbons (PAHs) contained in CTPVs.

Aim: To determine the feasibility of a thermal desorption (TD) technique based method as an alternative method to be used for the measurement of the concentration of CTPVs in ambient air by assessing it along criteria such as ease of use, cost, accuracy and precision by comparing it to NIOSH's Method 5515 and OSHA's Method 58 and to determine the level of exposure to CTPVs on the anode paste floor of an electric furnace, used for the smelting of platinum group metals (PGMs) concentrate.

Methodology: To satisfy the research objective, two accepted methods – the National Institute of Occupational Safety and Health's (NIOSH) method 5515 and the Occupational Safety and Health Administration's (OSHA) method 58 – were used for the measurement of the concentration of CTPVs with a TD technique based method used as a third, alternative method. All three methods were used concurrently to measure the concentration of CTPVs in ambient air, at the anode paste floor of a platinum group metals (PGMs) concentrate smelter.

Results and conclusions: The NIOSH method proved to be the most precise method while the TD technique based method proved to be the most accurate. The TD technique based method proved to measure the widest range of individual CTPVs and were able to measure the highest concentration of Benzo(a)pyrene, an individual CTPV that is classified as a Group 1 (carcinogenic to humans) chemical substance by the International Agency for Research on Cancer (IARC). The OSHA method measured on average almost four times less total CTPVs than either the NIOSH or the TD technique based method and failed to readily measure individual CTPVs with a molecular weight lower than that of Phenanthrene.

Keywords: coal tar pitch volatiles, polycyclic aromatic hydrocarbons, smelter, furnace, NIOSH 5515, OSHA 58, thermal desorption.

Opsomming

Afrikaanse titel: Evaluering van termiese desorpsie as ‘n alternatiewe tegniek vir die meet van vlugtige koolteerwaterstowwe.

Motivering: Die akkurate en betroubare meting van vlugtige koolteerwaterstowwe se konsentrasie in lug is ‘n uitdaging vir beroepshigiëniste. Hierdie uitdaging moet egter aanvaar word weens die karsinogeniese eienskappe van sekere poli-aromatiese koolwaterstowwe in vlugtige koolteerwaterstowwe.

Doel: Ten einde vas te stel of dit uitvoerbaar is om ‘n termiese desorpsie (TD) tegniek gebasseerde metode te gebruik om die konsentrasie van vlugtige koolteerwaterstowwe in lug te bepaal deur dit te meet aan maatstawwe soos gebruikersvriendelikheid, koste, akkuraatheid, presisie en dit te vergelyk met NIOSH se Metode 5515 en OSHA se Metode 58 en deur die blootstelling aan vlugtige koolteerwaterstowwe op die anode-pasta vloer van ‘n elektriese hoogoond, wat gebruik word vir die smelt van platinum groep metaal konsentraat, te bepaal.

Metodologie: Ten einde die navorsingsvraag te beantwoord is twee aanvaarde metodes naamlik die “National Institute of Occupational Safety and Health” (NIOSH) se Metode 5515 en die “Occupational Safety and Health Administration” (OSHA) se Metode 58 gebruik om die konsentrasie van vlugtige koolteerwaterstowwe te bepaal terwyl ‘n TD tegniek gebasseerde metode as ‘n derde metode gebruik is. Al drie die metodes is gelyktydig gebruik om die konsentrasie vlakke van vlugtige koolteerwaterstowwe te bepaal in die lug van die anode-pasta vloer van ‘n platinum groep metale smelter.

Resultate en gevolgtrekkings: Die NIOSH metode se presisie was die beste van die drie metodes, terwyl die TD tegniek gebaseerde metode die akkuraatste was. Die TD tegniek gebasseerde metode het die grootste verskeidenheid van vlugtige koolteerwaterstowwe gemeet en was in staat om die hoogste konsentrasie van Benzo(a)pyrene, ‘n spesifieke vlugtige koolteerwaterstof wat geklassifiseer is as ‘n Groep I substans (karsinogenies vir mense) deur die “International Agency for Research on Cancer” (IARC), te meet. Die OSHA metode het gemiddeld vier keer minder vlugtige koolteerwaterstowwe gemeet as die NIOSH of TD tegniek gebasseerde metode en het gefaal om vlugtige koolteerwaterstowwe te meet met ‘n molekulêre massa wat minder is as die van Phenanthrene.

Sleutelwoorde: vlugtige koolteerwaterstowwe, poli-sikliese aromatiese waterstowwe, smelter, hoogoond, NIOSH 5515, OSHA 58, termiese desorpsie.

Chapter 1

General Introduction

1.1 Introduction

Platinum is both a commercial and a precious metal and is part of the six member family of platinum group metals (PGMs) which also include palladium, rhodium, iridium, osmium and ruthenium. More than 80% of the global platinum production originates from South Africa with PGMs being geographically concentrated in the Bushveld Complex (Nell, 2004). PGMs are used in various industries ranging from the automotive to the medical industry (Xiao and Laplante, 2004; Jones, 2005; Wilburn and Bleiwas, 2005; Ndabezitha *et al.*, 2011).

The beneficiation process of PGMs, the process during which PGMs is separated from the ore containing them, is complex, with each step designed to increase the concentration of PGMs until the individual metals is refined into their pure form. The process may be summarised in three steps namely extraction, concentrating and refining. During the concentration process, the concentrate containing PGMs is smelted in order to separate the oxide and silicate minerals (gangue) from the sulphide minerals associated with the PGMs. In Southern Africa the smelting of concentrate takes place solely in electric furnaces (Jones, 2005).

Most producers of PGMs in South Africa utilize furnaces equipped with vertically submerged Söderberg electrodes. Söderberg electrodes are continuously formed by adding coke and coal tar pitch, usually as anode paste, to steel casings. The steel casing together with the anode paste is fed continuously into the furnace. The anode paste is baked by the heat generated by the electric current flowing through the electrode as well as the heat from the furnace itself. During the baking process the soft, non-conductive paste at the top of the electrode becomes a solid carbon conductor that is continuously consumed (Jones, 2005; Schreiter *et al.*, 2006).

During the baking process of the anode paste, coal tar pitch volatiles (CTPVs) are released into the work environment (Bentsen *et al.*, 1998; Priest and O'Donnell, 1999). CTPVs is a term denoted specific to the emissions of organic compounds from coal tar pitch. These emissions may however include poly-cyclic aromatic compounds (PACs), also known as poly-nuclear aromatics (PNAs) and poly-cyclic aromatic hydrocarbons (PAHs) according to the Agency for Toxic Substances and Disease Registry (ATSDR), (ATSDR, 1995, 2002). According to the International agency for research on cancer (IARC) some of the PAHs contained in CTPVs are carcinogenic such as benzo(a)pyrene while others such as naphthalene, benzanthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluorathene, indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene are either probably or possibly carcinogenic to humans (Waterman, *et al.*, 2000; Friesen, 2003; IARC, 2010; 2011*)*.

CTPVs released into the work environment may be inhaled by workers (Waterman, *et al.*, 2000). The respiratory system is the most common route of entry for hazardous chemical substances (HCS) in the occupational and industrial environment. The accurate and reliable measurement of CTPVs' concentration in ambient air is critical to enable the occupational hygienist to assess exposure to CTPVs (Scobbie, 1998; Thorne, 2003).

The measurement of CTPVs' concentration in ambient air has proved to be a challenge for occupational hygienists (Balya *et al.*, 1984). Various techniques or methods are available for the measurement of CTPVs' concentration in ambient air. The Pocket Guide to Chemical Hazards published by the National Institute for Occupational Safety and Health (NIOSH) subscribes to the use of the Occupational Safety and Health Administration's (OSHA) Method 58 (NIOSH, 2005). The Manual of Analytical Methods, also published by NIOSH, on its part subscribes to NIOSH Method 5042 (NIOSH, 2003). In the South African industrial context Method 5042 is not widely used (Van Rensburg, 2011). The measurement of CTPVs' concentration in ambient air is done mainly with the use of Method 5515 and Method 58. Unfortunately both methods are renowned for problems regarding ease of use, validity and reliability due to their inherent solvent extraction based approach (Sai Hang Ho, 2008; Van Rensburg, 2011). More recently thermal desorption (TD) as a direct analysis technique has been effectively used for the analysis of trace levels of VOCs. Samples collected are adsorped onto charcoal contained in stainless steel tubes and thereafter desorbed in a flow of inert gas to extract the compounds of interest into the vapour stream. The sample is then transferred to an analyzer for analysis (Bates, 2009). In this context a thermal desorption based method, using a direct analysis technique, may prove to be a feasible alternative method that can be used for the measurement of CTPVs' concentration in ambient air.

1.2 General aim and objectives

The general aim of this study is to explore the feasibility of a TD technique based method as an alternative method to be used for the measurement of CTPVs' concentration in the work environment.

The specific objectives of the study are to:

a) Assess a TD technique based method, as an alternative method for the measurement of CTPVs' concentration in ambient air, according to criteria such as ease of use, cost, accuracy and precision.

b) Compare three methods, namely OSHA's Method 58, NIOSH's Method 5515 and a TD technique based method that can be used for the measurement of CTPVs, with each other and to establish which method is best suited for use in the smelting industry.

c) Determine the levels of exposure to CTPVs on the paste floor of an electric furnace used for the smelting of concentrate containing PGMs.

1.3 Hypothesis

A TD technique based method is a superior alternative method to other traditionally used methods, such as OSHA's Method 58 and NIOSH's Method 5515, for the measurement of the concentration level of CTPVs in the work environment.

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Chapter 2

Literature Study

2 Literature overview

This literature overview will draw from current information available and make brief reference to the platinum group metal (PGM) industry in South Africa in order to establish the context of this study. The physical and chemical nature of coal tar pitch volatiles (CTPVs) will be discussed as well as the relevant health hazards posed due to exposure to them. Current methods available and used to measure CTPVs' concentration in the work environment will be put forth and paralleled with a thermal desorption (TD) based technique as an alternative method.

2.1 Mining in South Africa

The South African mining sector contributed roughly 10% to the country's gross domestic product (GDP) in 2009 and is the primary earner of foreign exchange (Ndabezitha *et al.*, 2011). Mineral sales has traditionally been dominated by gold, that position has, however, been usurped by PGMs followed by coal (Chamber of Mines, 2010). The world's largest deposit of PGMs is located in the Bushveld Complex, a geological formation located in South Africa (Nell, 2004). It is, therefore, not surprising that South Africa boasts as the largest producer of PGMs. South Africa was responsible for 76% of the platinum, 35% of palladium and 86% of rhodium produced globally in 2010 (Johnson Matthey, 2011a).

2.2 Platinum group metals

During the 16th century, in the Chocó District of Columbia, platinum was considered as a poor-quality by-product of silver mining operations. The name platinum indeed originated from the Spanish phrase "Platina del Pinto", which means "little silver" – as it was regarded as inferior to silver-, from the Pinto River (Xiao and Laplante, 2004).

Platinum is part of the six member family of PGMs which also includes palladium, rhodium, iridium, osmium and ruthenium. Due to the scarcity of platinum and the other PGMs as well as that of silver and gold, these metals are considered as precious metals. Platinum, in addition to having value as a precious metal, is also valued because of its use in a vast array of commercial applications. Platinum is used as a precious metal in jewellery making and as a commercial metal in the manufacturing of, amongst others, catalysts. Platinum is furthermore used commercially for the manufacturing of dentistry equipment, automobile catalytic convertors, superior electrical contacts, electrodes and glass (Johnson Matthey, 2011a).

2.3 Beneficiation process of PGMs

The beneficiation process of PGMs, the process during which PGMs is separated from the ore containing them, is complex with each step designed to increase the concentration of PGMs until the individual metal is refined into their pure form. The process may be summarized in three steps namely ore extraction, concentrating and refining. During the extraction process, PGM containing ore is mined from either underground mines or opencast mines. In both instances holes are drilled after which they are charged with explosives. After blasting, the ore is transported to concentrators where the concentrating process begins. Ore is crushed utilizing either jaw crushers or gyratory crushers or a combination of both. After crushing the ore is milled to reduce the particle size further. The fine particles are then transferred together with water and reagents to float cells where air is pumped through the liquid to create froth. The PGM containing particles adhere to the air bubbles and float to the top where it is skimmed from the top as PGM containing concentrate (Jones, 2005; Johnson Matthey, 2011b).

During the final stage, the PGM containing concentrate is dried in flash driers and then smelted in electric furnaces. During the smelting process, the valuable metals settles at the bottom of the furnace while the oxide and silicate containing minerals or gangue settles at the top. The PGM containing matte is tapped from the furnace and sent to the convertors where it enters the second part of the refining process namely the converting process. During the converting process air is blown through the molten matte in order to remove iron and sulphur. Finally the PGMs are separated from the base metals at the base metals refinery while the final stage is performed at the precious metals refinery where the six PGMs are extracted (Johnson Matthey, 2011b).

In Southern Africa, the smelting of PGM containing concentrate takes place solely in electric furnaces (Jones, 2005). Most producers of PGMs in South Africa utilize furnaces equipped with vertically submerged Söderberg electrodes. Söderberg electrodes are continuously formed by adding coke and coal tar pitch, usually as an anode paste, to steel casings. The steel casing together with the anode paste is fed continuously through the roof of the furnace into the furnace. The anode paste is baked by the heat generated by the electric current flowing through the electrode, as well as from the heat from the furnace itself (Jones, 1999). During the baking process the soft, non-conductive paste at the top of the electrode becomes a solid carbon conductor that is continuously consumed (Bermúdez, 2002).

2.4 Coal tar pitch volatiles

Hazardous chemical substances (HCS) in ambient air can be classified into different categories according to their chemical and physical characteristics. CTPVs is a term that refers to the emission of organic compounds from coal tar pitch. These emissions may, however, include poly-cyclic aromatic compounds (PACs), also known as poly-nuclear aromatics (PNAs) and poly-cyclic aromatic hydrocarbons (PAHs) according to the Agency for Toxic Substance and Disease Registry (ATSDR), (ATSDR, 1995, 2002).

CTPVs are found in industry wherever coal tar or coal tar pitch is heated. Coal tar pitch is used in several industrial settings which include processes such as smelting operations where coal tar pitch is used as an anode paste in Söderberg electrodes (Jones, 2005). The Environmental Protection Agency (EPA) of the United States has listed 16 PAHs as priority pollutants (Sun, *et al.*, 1998; United States, 2011). The 16 priority PAHs are listed together with their chemical and physical properties in Table 1.

2.4.1 Human health effects of CTPVs and routes of exposure

According to the International Agency for Research on Cancer (IARC), some of the PAHs contained in CTPVs are carcinogenic, such as benzo(a)pyrene, while others such as naphthalene, benzanthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluorathene, indeno(1,2,3-cd)pyrene and dibenz(a,h)-anthracene are either probably (Group IIA) or possibly (Group IIB) carcinogenic to humans (Waterman *et al.*, 2000; Friesen, 2003; IARC, 2010; 2011).

The history of CTPVs and the association thereof with occupational cancers are well documented and are indeed intertwined with some of the earliest documented cases of occupational induced cancers. Chimney sweeps of the 17th century was exposed to soot which penetrated their clothing and resulted in scrotal cancers. Only during the 19th century was it determined that chimney soot contains high levels of PAHs (Di Corleto, 2010). Epidemiological research has indicated that exposure to CTPVs may result in an increased risk of cancer of the lungs, skin, kidneys and bladder. Exposure can occur through dermal, oral or inhalation exposure or a combination of more than one route of exposure. Various sources such as ATSDR (1995, 2002), Priest and O'Donnell (1999), Carlsten *et al.* (2005), Bosetti *et al*. (2007), OSHA (2007) and Di Coleto (2010) may be consulted for extended information regarding the human health effects of CTPVs.

While South African national legislation does not provide for Occupational Exposure Limits (OELs) for individual CTPVs an OEL for exposure to total CTPVs is provided for by both the Mine Health and Safety Regulations (MHSR) of the Mine Health and Safety Act (MHSA) (South Africa, 1996) and the Regulations for Hazardous Chemical Substances (RHCS) of the Occupational Health and Safety Act (OHSA) (South Africa, 1993). For exposure limits to individual CTPVs, limits provided by the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) as well as the American Conference of Governmental Industrial Hygienists (ACGIH) were consulted.

These OELs are listed in Table 2 together with the 16 priority PAHs as listed by the Environmental Protection Agency of the United States (EPA, 2011).

Table 1: 16 Priority PAHs as listed by the EPA US (EPA, 2011).

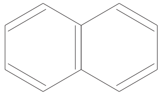
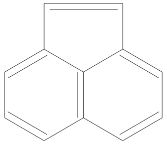
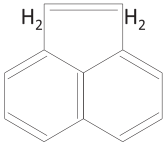
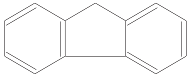
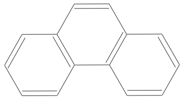
No.	Compound	Structure[2]	Formula[2]	Molecular weight[2]	Melting point (°C)[3]	Boiling point (°C)[3]	OEL – TWA*			IARC classification[7]
							OSHA[4]	NIOSH[5]	ACGIH[6]	
1.	Naphthalene		$C_{10}H_8$	128.17	80.2	218	10 ppm	10 ppm (15 ppm STEL)	10 ppm (15 ppm STEL)	II B
2.	Acenaphthylene		$C_{12}H_8$	152.20	92 – 93	265 – 275	–	–	–	Not classified
3.	Acenaphthene		$C_{12}H_{10}$	154.21	96.2	279	–	–	–	III
4.	Fluorene		$C_{13}H_{10}$	166.22	116	293 – 295	–	–	–	III
5.	Phenanthrene		$C_{14}H_{10}$	178.23	100	340	0.2 mg/m^3	–	–	III

Table 1: 16 Priority PAHs as listed by the EPA US (continues)

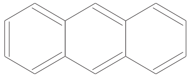
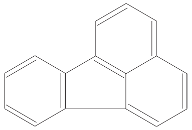
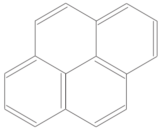
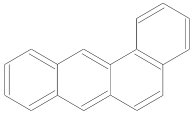
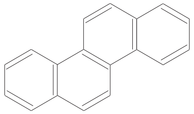
No.	Compound	Structure[2]	Formula[2]	Molecular Weight[2]	Melting Point (°C)[3]	Boiling Point (°C)[3]	OEL – TWA*			IARC Classification[7]
							OSHA[4]	NIOSH[5]	ACGIH[6]	
6.	Anthracene		$C_{14}H_{10}$	178.23	218	340	0.2 mg/m³	–	–	III
7.	Fluoranthene		$C_{16}H_{10}$	202.26	110	384 (sub)	–	–	–	III
8.	Pyrene		$C_{16}H_{10}$	202.26	156	393	0.2 mg/m³	–	–	III
9.	Benz(a)anthracene		$C_{18}H_{12}$	228.29	162 – 167	435	0.2 mg/m³	–	–	II B
10.	Chrysene		$C_{18}H_{12}$	228.29	255 – 256	448	0.2 mg/m³	–	–	II B

Table 1: 16 Priority PAHs as listed by the EPA US (continues)

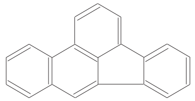
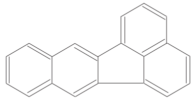
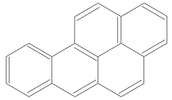
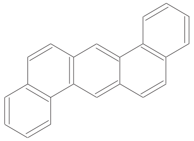
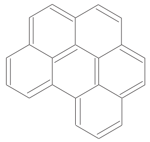
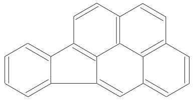
No.	Compound	Structure[2]	Formula[2]	Molecular Weight[2]	Melting Point (°C)[3]	Boiling Point (°C)[3]	OEL – TWA*			IARC Classification[7]
							OSHA[4]	NIOSH[5]	ACGIH[6]	
11.	Benzo(b)fluoranthene		$C_{20}H_{12}$	252.32	168	-	0.2 mg/m^3	0.1 mg/m^3	–	II B
12.	Benzo(k)fluoranthene		$C_{20}H_{12}$	252.32	217	480	0.2 mg/m^3	0.1 mg/m^3	–	II B
13.	Benzo(a)pyrene		$C_{20}H_{12}$	252.32	179	495	0.2 mg/m^3	0.1 mg/m^3	–	I
14.	Dibenz(a,h)anthracene		$C_{22}H_{14}$	278.35	267	524	–	–	–	II A
15.	Benzo(ghi)perylene		$C_{22}H_{12}$	276.34	273	–	–	–	–	III

Table 1: 16 Priority PAHs as listed by the EPA US (continues)

No.	Compound	Structure[2]	Formula[2]	Molecular Weight[2]	Melting Point (°C)[3]	Boiling Point (°C)[3]	OEL – TWA*			IARC Classification[7]
							OSHA[4]	NIOSH[5]	ACGIH[6]	
16.	Indeno(1,2,3-cd)pyrene		$C_{22}H_{12}$	276.34	161.5 – 163	530	–	–	–	II B

Legend to Table 1.

I	Carcinogenic to humans.
IIA	Probably carcinogenic to humans.
IIB	Possibly carcinogenic to humans.
III	Not classifiable as to its carcinogenicity to humans.
IV	Probably not carcinogenic to humans.
sub	Undergoes sublimation
*	Occupational Exposure Limit – Time Weighted Average over 8 hrs
–	No current OEL

References in Table 1.

1 EPA, 2011.
2 United States, 2011.
3 PubChem, 2011
4 United States, 2005.
5 United States, 2007.
6 ACGIH, 2011.
7 IARC, 2006; 2010; 2011.

2.5 Methods available for the measurement of the concentration of CTPVs in ambient air

Various methods, based on different techniques, are available for the measurement of CTPVs' concentration in ambient air. The Pocket Guide to Chemical Hazards published by NIOSH subscribes to the use of OSHA's Method 58 (NIOSH, 2005). The Manual of Analytical Methods, also published by NIOSH, on its part subscribes to NIOSH's Method 5042 (NIOSH, 2003). In addition to the two methods mentioned above, NIOSH's Method 5515 is also extensively used in the South African Industry (Van Rensburg, 2011).

Both Method 5515 (NIOSH, 2003) and Method 5042 has been partially evaluated whereas Method 58 has been subjected to the established procedures of the Organic Methods Evaluation Branch of OSHA (NIOSH, 2003; NIOSH, 2005).

In the South African industrial context Method 5042 is not widely used. The measurement of CTPVs' concentration in ambient air is done mainly with the use of Method 5515 and Method 58. Unfortunately both methods are renowned for problems regarding replicate area sample sizes required, lengthy and labour intense preparation, contamination, validity and reliability due to their inherent solvent extraction based approach (Sai Hang Ho, 2008; Van Rensburg, 2011).

More recently TD as a direct analysis technique has been effectively used for the analysis of trace levels of VOCs (Bates, 2009). In this context thermal desorption as a direct analysis technique may prove to be a feasible alternative method that can be used for the measurement of CTPVs' concentration in ambient air. Three methods available for the determination of the concentration of CTPVs in ambient air namely NIOSH's Method 5515, OSHA's Method 58 and a TD technique based method will be discussed. A concise comparison of the three methods is provided in Table 2.

2.5.1 NIOSH's Method 5515

NIOSH's method 5515 has been developed for the measurement of PAHs. The selection of target compounds include benzo(e)pyrene in addition to the 16 PAHs targeted by the US EPA. The method was first published on 15 May 1985 after which it was revised and published again on 15 August 1994. The method has been partially evaluated against numerous field filters and sorbent tubes but no statistical studies have been initiated. A sample is collected by using a vacuum pump to draw a known amount of air through a polytetrafluoroethylene (PTFE) filter connected to a sorbent tube (XAD-2) via a flexible polyvinyl chloride tube.

As both a PTFE filter and a XAD-2 sorbent tube is used during the sampling process, CTPVs, both in the particulate phase as well as the vapour phase, are captured in order for their presence and concentration to be determined.

The method mainly relies on eight area samples to be taken in addition to the amount of required samples to be taken whether they are area or personal samples. The eight area samples are then used to determine the best solvent to extract the compound of interest. After sampling has been conducted and the solvent of choice has been determined the samples of interest are extracted using the solvent of choice.

The filters are transferred to scintillation vials and the solvent of choice is added. The front and back portions of the sorbent tube are transferred to two separate culture tubes. After extraction has completed the sample is injected into a gas chromatograph. Using the peaks generated by the gas chromatograph and the retention times supplied, the compounds and their concentrations are identified.

The range studied, accuracy, bias and overall precision of NIOSH's method 5515 has not been determined. Known interferences include heat, ozone, nitrogen oxide and ultraviolet light. There is some carcinogenic risk involved when using the method as some of the PAHs to be measured are known carcinogens in addition to benzene which is one of the solvents used (NIOSH, 2008).

2.5.2 OSHA's Method 58

OSHA's Method 58 has been developed for the measurement of CTPVs, coke oven emissions (COE) and selected PAHs. The method has been evaluated as it has been subjected to the evaluation procedures of the Organic Methods Evaluation Branch. Target compounds used during the evaluation process include phenanthrene, anthracene, pyrene, chrysene and benzo(a)pyrene. Samples are collected using a vacuum pump attached with flexible tubing to polystyrene cassettes containing glass fibre filters (GFF). After having sampled a known amount of air the filter is removed and placed in a scintillation vial with benzene. The contents of the scintillation vial are filtered and the filtrate is taken to dryness after which it is weighed.
The method mainly relies on the gravimetrically determination of the benzene-soluble fraction (BSF). Should the BSF exceed the permissible exposure limit (PEL) the sample is analyzed using high performance liquid chromatography (HPLC) combined with a fluorescence or ultraviolet detector in order to determine the presence of selected PAHs (United States, 1986).

2.5.3 TD technique based method

The low volatility of PAHs has historically been the reason why solvent extraction combined with liquid injection into gas chromatography mass-spectrometry (GC-MS) has been the analysis technique of choice. Recent developments in TD techniques have however provided an alternative analysis technique. TD as a direct analysis technique has been effectively used for the analysis of trace levels of VOCs. The TD technique mainly relies on samples which are adsorbed onto charcoal contained in stainless steel tubes after which they are desorbed in a flow of inert gas to extract the compounds of interest into the vapour stream. The sample is then transferred to an analyzer for analysis (Bates, 2009). Samples are collected by drawing known amounts of ambient air through the stainless steel tube containing the adsorbent material by a vacuum pump which is connected to the stainless steel tube with flexible tubing. The TD technique provide some useful advantages over solvent extraction which includes the following: increase in sensitivity, no need for manual sample preparation, no analytical interference from solvent, close to 100% desorption efficiency, selective focusing on compounds of interest, no solvent disposal concerns, cost efficiency as the sampling tubes may be re-used up to a hundred times and time savings as the process can be automated. Due to the design of the thermal desorption tube, CTPVs in both the particulate phase, as well as the vapour phase, is collected during sampling after which their presence and concentration is determined (Di Corleto, 2010).

Table 2: Concise comparison of NIOSH’s Method 5515, OSHA’s Method 58 and a TD technique based method.

Method	Advantages	Disadvantages	Limit of detection	Reference
NIOSH’s Method 5515	• Method has been partially evaluated.	• Extensive, labour intensive preparation required before the sample can be taken. • Protection from sunlight or UV light is required. • Sampling train can only be used once.	0.3 µg per sample	NIOSH, 2008
OSHA’s Method 58	• Method has been fully evaluated.	• Solvent extraction is required, implicating additional exposure to carcinogens such as benzene. • Sample can only be analyzed once. • Eight field samples required for determination of correct solvent to be used.	0.6 µg per sample	United States, 1986
TD based method	• Sample preparation is minimal. • Sorbent tubes can be used more than once. • Sample can be analyzed more than once. • Individual compounds may be focused on.	• Initial cost of sorbent tubes. • Method has not been evaluated.	0.1 µg per sample	Bates, 2009

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Chapter 3

Manuscript: Evaluation of thermal desorption as an alternative technique for the measurement of coal tar pitch volatiles.

This article is to be submitted to *The Annals of Occupational Hygiene. The Annals of Occupational Hygiene* published by Oxford University Press on behalf of the British Occupational Hygiene Society is regarded as one of the world's top research journals on matters involving work related hazards and risks. Some of the topics covered by *The Annals of Occupational Hygiene* include the recognition, quantification, management, communication and control of risks associated with the occupational environment.

Although the instructions for authors state that illustrations, tables and graphs are to be submitted as separate pages, for the purpose of this mini-dissertation the tables and figures will be inserted within the results section of Chapter 3 in order to improve readability. It is acknowledged that the article exceeds the limit for the number of words used due to the comprehensive nature thereof and for examination purposes. The article will be shortened before submission.

Summary of instructions for authors: *The Annals of Occupational Hygiene*

- Only original work, not published elsewhere, should be submitted.
- The corresponding author should be indentified in the submission. Full postal addresses must be given for all co-authors. The preferred practice is that persons should only be named as authors if they have made significant identifiable intellectual contributions to the work, and other contributions may be recognized by acknowledgement at the end of the submission.
- If requested, authors must produce original data for inspection by the editor. The ethics committee which gave approval must be named in the paper.
- The source of financial support for the work must be stated in the acknowledgements, unless it is clear from the authors' affiliations.
- Manuscripts must be in English, British or American styles and spelling may be used, but should be used consistently.
- The number of words, excluding the abstract, references, tables and figures, must be stated as a message to the editor at the time of submission.
- Manuscripts should conform to a pattern of introduction, methods, results, discussion and conclusions. The abstract may be arranged under the headings of objectives, methods, results and conclusions. The list of keywords should be given after the list of authors.
- References in the text should be in the form of Jones (1995), or Jones and Brown (1995), or Jones et al. (1995) if there are more than two authors.
- At the end of the manuscript, references should be listed in alphabetical order by name of first author, using the Vancouver Style of abbreviation and punctuation.

Evaluation of thermal desorption as an alternative technique for the measurement of coal tar pitch volatiles

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Abstract

The measurement of coal tar pitch volatiles' (CTPVs) concentration in ambient air has proved to be a challenge for occupational hygienists. Various techniques or methods are available for the measurement of CTPVs' concentration in ambient air but with apprehension due to questions regarding accuracy and reliability. The rationale for this study was to compare two accepted methods, The National Institute for Occupational Safety and Health's (NIOSH) method 5515 and the Occupational Safety and Health's (OSHA) method 58 with a thermal desorption (TD) technique based method as the third, alternative method. The concentration of CTPVs in the ambient air at the paste floor of a platinum group metals (PGMs) concentrate smelter was measured concurrently using all three methods where after the methods were assessed according to criteria such as ease of use, cost efficiency, practical application, accuracy and precision. Results were compared to determine variance in results within any single method in addition to variance between methods (intra-, and inter-variance) while the results of the average concentration level of total CTPVs were compared to national Occupational Exposure Limits (OELs). Total CTPV concentration levels measured with the TD technique based method (0.039 mg/m^3) and the NIOSH method (0.038 mg/m^3) was significantly higher when compared to results obtained by the use of OSHA method 58 (0.010 mg/m^3) while average total CTPVs concentration levels complied with national OELs. The NIOSH method measured the concentration of CTPVs with the highest precision while the TD technique based method, followed closely by the NIOSH method revealed the highest accuracy. The OSHA method under-measured the concentration of total CTPVs by a factor of four. The TD technique based method proved to be the least expensive method of choice for sample sizes up to 14. In conclusion it was determined that the TD technique based method could be used as an alternative method for the measurement of CTPVs.

Keywords: coal tar pitch volatiles, polycyclic aromatic hydrocarbons, smelter, furnace, NIOSH 5515, OSHA 58, thermal desorption technique.

Introduction

Platinum is both a commercial and a precious metal and is part of the six member family of platinum group metals (PGMs) which also include palladium, rhodium, iridium, osmium and ruthenium. More than 80% of the global platinum production originates from South Africa with PGMs being geographically concentrated in the Bushveld Complex (Nell, 2004).

The beneficiation process of PGMs, the process during which PGMs is separated from the ore containing them, is complex, with each step designed to increase the concentration of PGMs until the individual metals is refined into their pure form. The process may be summarised in three steps namely extraction, concentrating and refining. During the concentration process, the concentrate containing PGMs is smelted in order to separate the oxide and silicate minerals (gangue) from the sulphide minerals associated with the PGMs. In Southern Africa the smelting of concentrate takes place solely in electric furnaces (Jones, 2005).

Most producers of PGMs in South Africa utilises furnaces equipped with vertically submerged Söderberg electrodes. Söderberg electrodes are continuously formed by adding coke and coal tar pitch, usually as anode paste, to steel casings. The steel casing together with the anode paste is fed continuously into the furnace. The anode paste is baked by the heat generated by the electric current flowing through the electrode as well as the heat from the furnace itself. During the baking process the soft, non-conductive paste at the top of the electrode becomes a solid carbon conductor that is continuously consumed (Jones, 2005; Schreiter *et al.*, 2006).

During the baking process of the anode paste, coal tar pitch volatiles (CTPVs) are released into the work environment (Bentsen *et al.*, 1998; Priest and O'Donnell, 1999). CTPVs is a term denoted specific to the emissions of organic compounds from coal tar pitch. These emissions may however include poly-cyclic aromatic compounds (PACs), also known as poly-nuclear aromatics (PNAs) and poly-cyclic aromatic hydrocarbons (PAHs) according to the Agency for Toxic Substances and Disease Registry (ATSDR), (ATSDR, 1995, 2002). According to the International Agency for Research on Cancer (IARC) some of the PAHs contained in CTPVs are carcinogenic, such as benzo(a)pyrene, while others such as naphthalene, benzanthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluorathene, indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene are either probably or possibly carcinogenic to humans (Waterman, *et al.*, 2000; Friesen, 2003; IARC, 2010; 2011*)*.

CTPVs released into the work environment may be inhaled by workers (Waterman, *et al.*, 2000). The respiratory system is the most common route of entry for hazardous chemical substances (HCS) in the occupational and industrial environment. The accurate and reliable measurement of CTPVs' concentration in ambient air is critical to enable the occupational hygienist to assess exposure to CTPVs (Scobbie, 1998; Thorne, 2003).

The measurement of CTPVs' concentration in ambient air has proved to be a challenge for occupational hygienists (Balya *et al.*, 1984). Various techniques or methods are available for the measurement of CTPVs' concentration in ambient air. The Pocket Guide to Chemical Hazards published by the National Institute for Occupational Safety and Health (NIOSH) subscribes to the use of the Occupational Safety and Health Administration's (OSHA) Method 58 (NIOSH, 2005). The Manual of Analytical Methods, also published by NIOSH, on its part subscribes to NIOSH's Method 5042 (NIOSH, 2003). In the South African industrial context Method 5042 is not widely used (Van Rensburg, 2011). The measurement of CTPVs' concentration in ambient air is done mainly with the use of Method 5515 and Method 58. Unfortunately both methods are renowned for problems regarding ease of use, validity and reliability due to their inherent solvent extraction based approach (Sai Hang Ho, 2008; Van Rensburg, 2011). More recently thermal desorption (TD) as a direct analysis technique has been effectively used for the analysis of trace levels of VOCs. Samples collected are adsorped onto charcoal contained in stainless steel tubes and thereafter desorbed in a flow of inert gas to extract the compounds of interest into the vapour stream. The sample is then transferred to an analyzer for analysis (Bates, 2009). In this context a thermal desorption based method, using a direct analysis technique, may prove to be a feasible alternative method that can be used for the measurement of CTPVs' concentration in ambient air.

Methodology

Static ambient air monitoring was used to compare two established methods namely the National Institute for Occupational Safety and Health's (NIOSH) Method 5515 and the Occupational Safety and Health Administration's (OSHA) Method 58 and one proposed alternative method utilizing thermal desorption (TD) as direct analysis technique with each other. Ambient air samples were taken on the paste floor of an electric furnace, used for the smelting of platinum group metals (PGMs), that uses vertically submerged Söderberg electrodes. Sampling was conducted over four days during which all three methods were used concurrently. The sampling position has been determined on the assumption that exposure is highest closest to the contamination source which is the space between the electrode and the hole through which it extend into the furnace. For this reason the sample set was placed on top of the paste floor, 0.8 m above the floor, as close to the furnace electrodes as possible. In order to ensure efficient randomisation, the sample sets were grouped together in an imaginary Latin square configuration. The position of each sampling set were determined using random numbers. During the sampling process a field blank was included for analysis for each method used resulting in three field blanks for each sampling shift. The field blanks was taken in addition to the 8 samples required for NIOSH's Method 5515 and OSHA's Method 58 respectively. The 8 samples were required in order to determine the solvent of choice for both NIOSH's Method 5515 and OSHA's Method 58.

NIOSH's Method 5515

For the evaluation of NIOSH's Method 5515, Gilian (Sensidyne Inc USA, Part No 800885-171) constant flow air sampling pumps were connected to washed XAD-2 (SKC South Africa (Pty) Ltd, Catalogue No 226-30-04) sorbent tubes which were in turn connected in series to cassettes containing polytetrafluoroethylene (PTFE) coated filters (Zefluor) sourced from (SKC South Africa (Pty) Ltd, Catalogue No 225-1713). Prior to calibration, the pumps were switched on with a representative sampling train for 5 minutes in order to stabilize in accordance with the manufactures instructions. After stabilisation of the pumps, the pumps were pre-calibrated to a flow rate of 2 ℓ/min.

After pre-calibration, the pumps together with their respective sampling trains were positioned on the paste floor 0.8 meters above floor level. The cassettes and the sorbent tubes were wrapped in aluminium foil to prevent any degradation of the CTPVs by sunlight or UV light although sampling was done indoors.

The pumps were then switched on, in unison with the other pumps representing the two remaining methods, and left on for a sampling period of 8 hours. After the 8 hours of sampling time has transpired the pumps were switched off in unison with the other pumps representing the two remaining methods. The sorbent tubes were removed from the sampling tubes and capped while the PTFE coated filters were removed from the cassettes and transferred to scintillation vials. Both the capped sorbent tubes as well as the scintillation vials were then wrapped in aluminium foil and placed inside a thermally insulated container with bagged refrigerant at a temperature below 4 °C. The container was then sent for analysis to a South African National Accreditation System (SANAS) accredited laboratory where the samples were analyzed in accordance with NIOSH's Method 5515 using a gas chromatograph.

Sampling pumps were post-calibrated at the field office using a representative sampling train to verify that the flow rate remained within 5% of the intended flow rate of 2 ℓ/min.

OSHA's Method 58

For the evaluation of OSHA's Method 58, Gilian (Sensidyne Inc USA, Part No 800885-171) constant flow air sampling pumps were connected to cassettes containing glass fibre filters (GFF) from (SKC South Africa (Pty) Ltd, Catalogue No 225-709). Prior to calibration the pumps were switched on with a representative sampling train for 5 minutes in order to stabilize in accordance with the manufactures instructions. After stabilisation of the pumps, the pumps were pre-calibrated to a flow rate of 2 ℓ/min.

After pre-calibration the pumps together with their respective sampling trains were positioned on the paste floor 0.8 meters above floor level. The cassettes were wrapped in aluminium foil to prevent any degradation of the CTPVs by sunlight or UV light although sampling was done indoors. The pumps were then switched on, in unison with the other pumps representing the two remaining methods, and left on for a sampling period of 8 hours.

After the 8 hours of sampling time has transpired the pumps were switched off, in unison with the other pumps representing the two remaining methods. The GFF were removed from the cassettes and transferred to scintillation vials. The scintillation vials were then wrapped in aluminium foil and placed inside a thermally insulated container with bagged refrigerant at a temperature below 4 °C. The container was then sent for analysis to a SANAS accredited laboratory where the samples were analyzed in accordance with OSHA's Method 58 using high-performance liquid chromatography.

Thermal desorption technique based method

As little literature existed to the authors' knowledge regarding an appropriate air sampling flow rate when using thermal desorption tubes for the measurement of CTPVs, an acceptable flow rate first had to be established. In order to do this an acceptable flow rate was first established using a ramp-up process whereby the flow rate was increased in a stepwise fashion until an acceptable flow rate for the sampling of CTPVs utilizing thermal desorption tubes was found. This process was followed in order to prevent under sampling which would have led to a failed sample due to non-detects or over sampling which would have led to saturation of the sorption media and resultant under estimation of the CTPVs' concentration in the air.

Flow-rate determination and standardization

Four Gilian (Sensidyne Inc USA, Part No 800885-171) constant flow air sampling pumps with representative sampling trains were pre-calibrated using a dry-cell low volume calibrator. Three of the pumps were calibrated to 0.05 ℓ/min while the remaining pump was calibrated to a flow rate of 0.1 ℓ/min. After pre-calibration has been performed, the stainless steel sorption tubes were connected to their respective sampling pumps. The sampling pumps together with their sampling trains were placed on the paste floor, 0.8 meters above floor level and switched on at the same time. After 14 minutes one of the pumps calibrated to 0.05 ℓ/min was switched off, after another 14 minutes the second pump calibrated to 0.05 ℓ/min was switched off and after another 28 minutes the last pump calibrated to 0.05 ℓ/min as well as the pump calibrated to 0.1 ℓ/min was switched off. The stainless steel sorption tubes were removed and capped using the Luer-locks supplied. The tubes were placed in a thermally insulated container with bagged refrigerant at a temperature below 4 °C and sent for analysis to a SANAS accredited laboratory utilizing gas chromatography mass spectrometry.

Based on the results of the first batch of samples, the second phase of the procedure allowed for five pumps, each calibrated to 0.1 ℓ/min. After pre-calibration has been performed the stainless steel sorption tubes were connected to their respective sampling pumps. The sampling pumps together with their respective sampling trains were placed on the paste floor, 0.8 meters above floor level and switched on at the same time. After 120 minutes have transpired, the pumps were switched off allowing for a sampling volume of 12 litres. The stainless steel sorption tubes were removed and capped using the Luer-locks supplied.

The tubes were placed in a thermally insulated container with bagged refrigerant at a temperature below 4 °C and sent for analysis to a SANAS accredited laboratory utilizing gas chromatography mass spectrometry.

Based on the results of this process, a flow rate of 0.05 ℓ/min over an eight hour period was chosen for the study. At this flow rate an adequate amount of air was sampled while breakthrough of the sampling media was prevented.

Only after having established and appropriate flow rate for the thermal desorption technique the three methods was put to test.

Statistical analysis of results

Statistical analysis included basic statistics (mean, standard deviation and variation), Spearman non-parametric correlation analysis and Bland-Altman tests. Variability was determined within each specific method (intra-variability) in addition to the variability between (inter-variability) the three methods including the thermal desorption technique based method. Finally the variability of exposure during the four different shifts (days) was established. The above mentioned was accomplished by using Statistica Version 10 (Statsoft Inc.) and Graphpad Version 5 (Prism). All differences were evaluated at a significance level of $p \leq 0.05$. All non-detect values of the analysis results were represented as the detection limit of the particular substance divided by the square root of two in order to calculate the concentration of total CTPVs.

Results

The results obtained from this study will now be represented in tables and figures. Although it is the norm to either use tables or figures, for the purpose of this study both will be used in order to represent the data in the most logical format possible.

Average concentration of total CTPVs

The average daily concentrations of total CTPVs in the ambient air of the paste floor as measured with each of the three methods, including the TD technique based method, are provided in Figure 1.

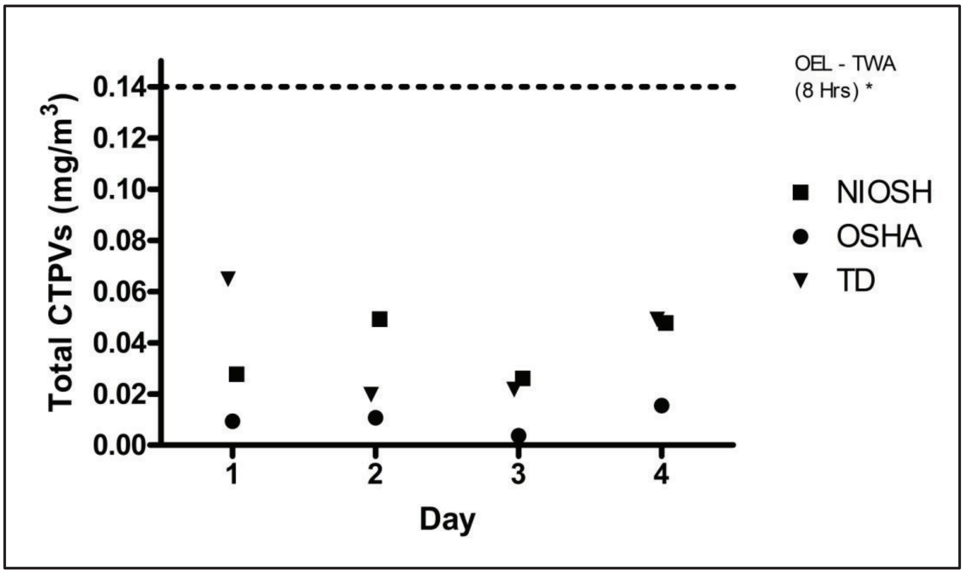


Figure 1: Average concentrations of total CTPVs measured on four different days, asterisk (*) refer to the OEL-TWA as provided by the Mine Health and Safety Regulations (MHSR) of the Mine Health and Safety Act (MHSA) (South Africa, 1996) and the Regulations for Hazardous Chemical Substances (RHCS) of the Occupational Health and Safety Act (OHSA) (South Africa, 1993).

As can be seen from Figure 1 the highest level of total CTPVs was measured on Day 1 by the TD technique based method while the lowest level of total CTPVs was measured on Day 3 by the OSHA method. It is noteworthy that the OSHA method consistently measured the lowest level of total CTPVs over the four day period.

Variation within (intra-variation) and between (inter-variation) methods over sampling period

Two types of variation may be distinguished. Variation within a single method between the different samples taken and variation between the three methods, including the TD technique based method. Results displayed in Figures 2 and 3 and Table 1 reveal these variations.

A summary of results of exposure to the total CTPVs load as measured with the three different methods, including the TD technique based method, over the four consecutive days are provided for in Figure 2 utilizing box and whisker plots.

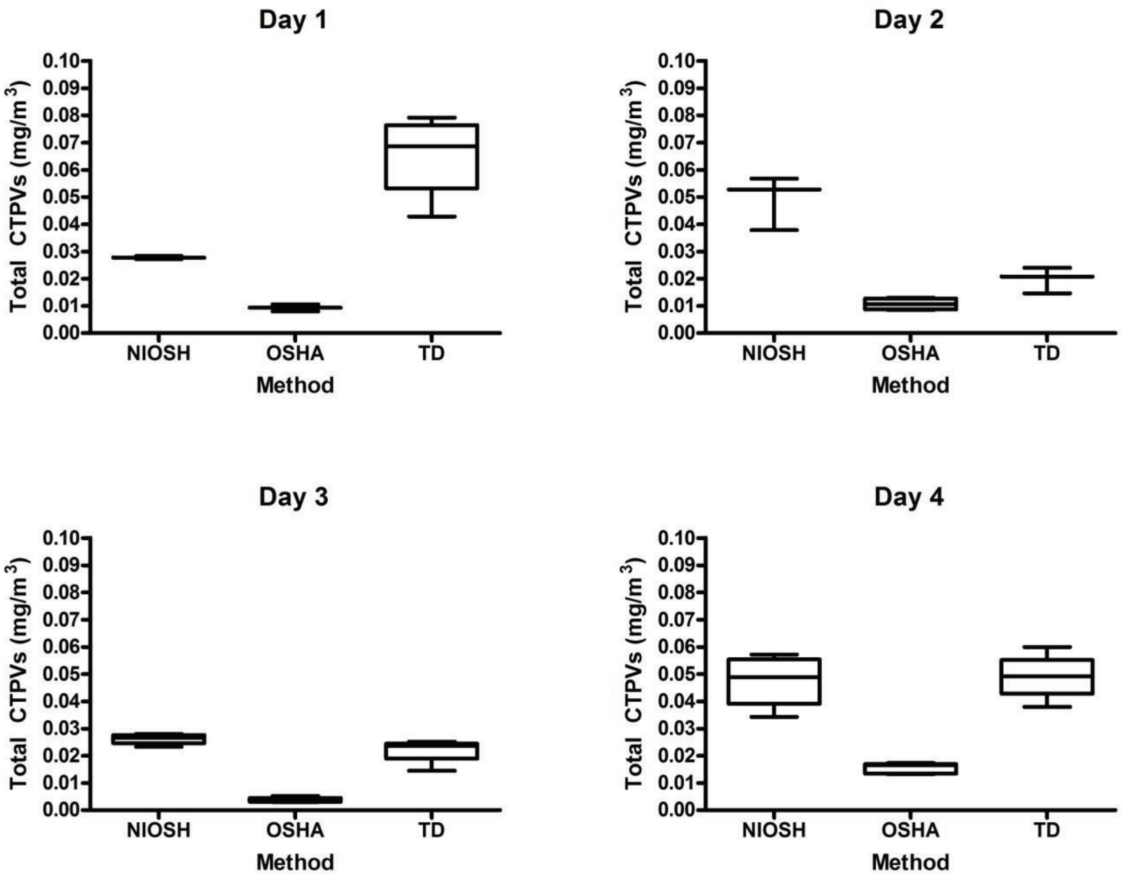


Figure 2: Box and whiskers plots of total CTPVs load over four consecutive days. Upper and lower ends of boxes represent 75th and 25th percentiles respectively with a solid line at the median. Whiskers indicate the maximum and minimum values.

Table 1: Descriptive statistics of the average concentrations of total CTPVs.

Day	Minimum (mg/m^3)	Maximum (mg/m^3)	Median (mg/m^3)	Standard Deviation (mg/m^3)	95% CL	Coefficient of Variation (%)
	NIOSH					
Day 1	0.027	0.028	0.028	0.0009	[0.020; 0.036]	3.23
Day 2	0.038	0.057	0.053	0.0100	[0.024; 0.074]	20.31
Day 3	0.023	0.028	0.027	0.0021	[0.023; 0.029]	7.95
Day 4	0.034	0.057	0.049	0.0081	[0.039; 0.056]	16.91
Average	**0.031**	**0.043**	**0.039**	**0.0053**	**[0.027; 0.049]**	**12.10**
	OSHA					
Day 1	0.008	0.011	0.009	0.0018	[-0.007; 0.026]	19.69
Day 2	0.008	0.013	0.011	0.0020	[0.008; 0.013]	19.01
Day 3	0.003	0.005	0.004	0.0009	[0.003; 0.005]	23.32
Day 4	0.013	0.017	0.016	0.0019	[0.013; 0.018]	12.09
Average	**0.008**	**0.012**	**0.010**	**0.0017**	**[0.004; 0.015]**	**18.53**
	TD					
Day 1	0.043	0.079	0.069	0.0160	[0.039; 0.090]	24.69
Day 2	0.015	0.024	0.021	0.0048	[0.008; 0.032]	24.33
Day 3	0.014	0.025	0.024	0.0049	[0.014; 0.029]	22.48
Day 4	0.038	0.060	0.049	0.0090	[0.035; 0.063]	18.36
Average	**0.029**	**0.047**	**0.041**	**0.0087**	**[0.024; 0.054]**	**22.47**

From the averages of the results over the four days presented in Table 1 it can be gathered that the OSHA method measured on average the smallest minimum and the NIOSH method the biggest. The OSHA method measured on average the smallest maximum while the TD technique method measured the biggest maximum. On average the TD technique method measured the highest concentration of CTPVs with the highest standard deviation over the four days followed closely by the NIOSH method (second highest standard deviation) and lastly the OSHA method with the lowest standard deviation.

The coefficient of variation which is also known as the relative standard variation is a measure of the precision of a method. Using this formula the ranking of precision from high to low for the three methods used is NIOSH, OSHA and then the TD technique based method.

The coefficient of variation for each method for each day as shown in Table 1 is also presented in Figure 3. The standard deviation of the average coefficient of variation for the NIOSH method was 7.883%, 4.690% for the OSHA method and 2.903% for the thermal desorption technique based method. The standard deviation of the coefficient of variation can be interpreted as the variation in precision within the method used over the course of the study.

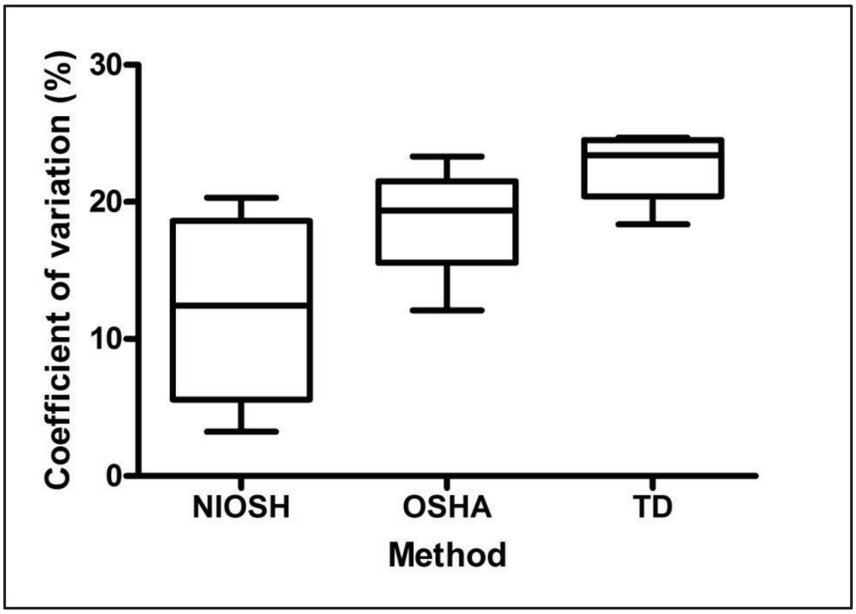


Figure 3: Box and whiskers plots of the relative standard deviation per method. Upper and lower ends of boxes represent the 75th and 25th percentiles respectively with a solid line at the median. Whiskers indicate the maximum and minimum values.

Various statistical techniques are available to compare two or more methods with each other. For the purpose of this study, two statistical analyses were performed on the total CTPVs results for each of the three methods, including the TD technique based method.

The first statistical analysis was a Spearman non-parametric correlation analysis. This statistical technique was chosen as it is appropriate for small sample sizes and for data which is not necessarily of a normal distribution. The results of the Spearman non-parametric correlation analysis is provided for in Table 2.

Table 2: Spearman non-parametric analysis

Day	Method Comparison	Spearman correlation coefficient (r)	P - Value
Day 1	NIOSH vs. OSHA	0.9487	0.0833
	OSHA vs. TD	0.9487	0.0833
	NIOSH vs. TD	0.9487	0.0833
Day 2	NIOSH vs. OSHA	0.8944	0.0833
	OSHA vs. TD	0.8944	0.0833
	NIOSH vs. TD	1.0000	**0.0167**
Day 3	NIOSH vs. OSHA	1.0000	**0.0167**
	OSHA vs. TD	1.0000	**0.0167**
	NIOSH vs. TD	1.0000	**0.0167**
Day 4	NIOSH vs. OSHA	1.0000	**0.0028**
	OSHA vs. TD	0.9856	**0.0028**
	NIOSH vs. TD	0.9856	**0.0028**
All Days	NIOSH vs. OSHA	0.9975	**P < 0.0001**
	OSHA vs. TD	0.9975	**P < 0.0001**
	NIOSH vs. TD	1.0000	**P < 0.0001**

The second statistical technique used to assess the agreement between the three methods was Bland – Altman plots. In 1986 Martin Bland and Douglas Altman published a paper namely "Statistical methods for assessing agreement between two methods of clinical measurement". (Bland and Altman, 1986). In the paper it is put forth that the use of correlation coefficients to compare a new method with an established one is misleading. The reasoning is that two or more methods that measures the same variable will due to their purpose show a significant degree of correlation. A high degree of correlation between methods does however not guarantee agreement between them. If one method consistently measured ten times as much as another method their correlation will be perfect, their agreement will however be entirely different. They concluded that an alternative technique should be used where the difference between measurands are graphically plotted against their means. Bland – Altman plots of the three different methods, including the TD technique based method, are provided for in Figure 4.

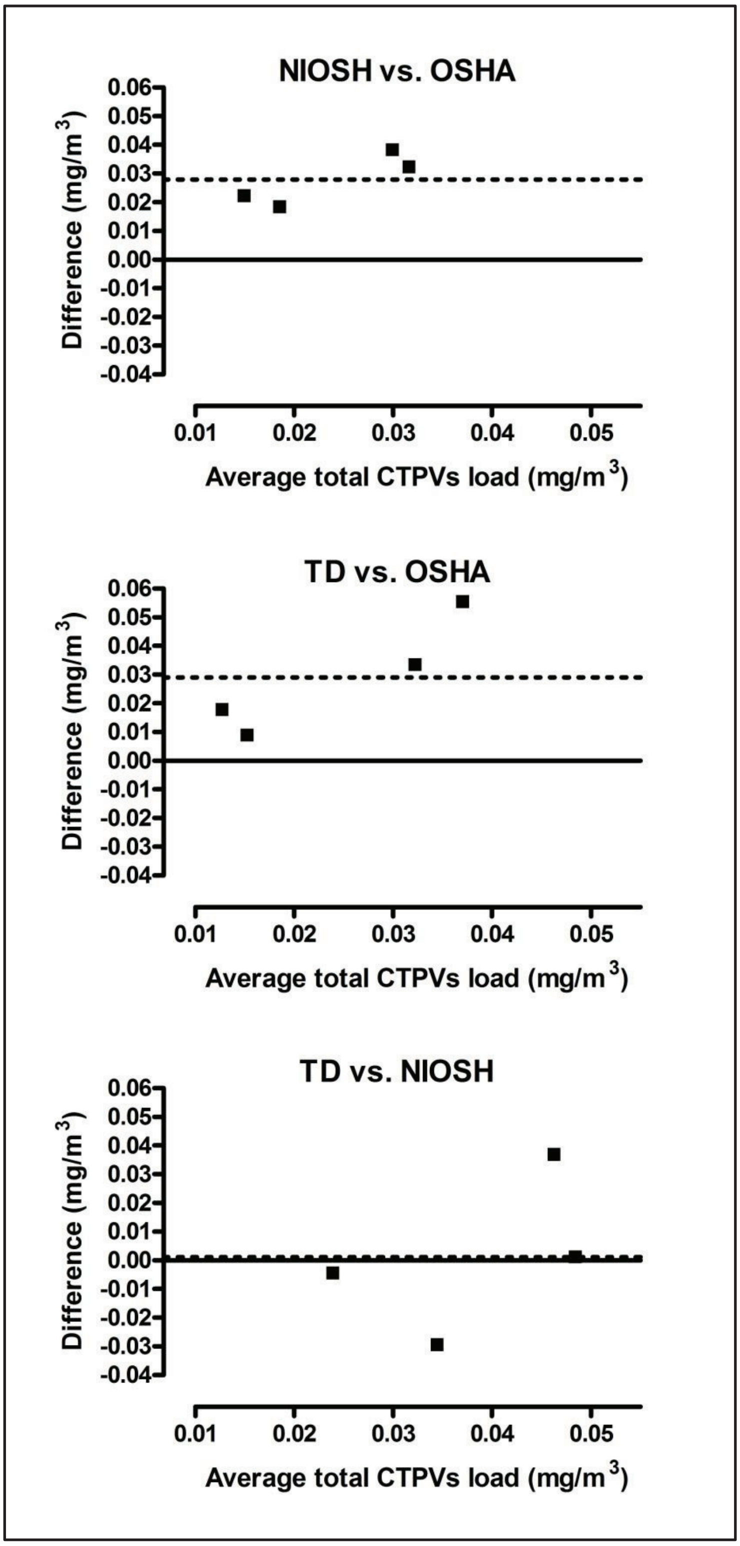


Figure 4: Difference in average total CTPVs (mg/m^3) between methods. Bias is indicated as a dotted line and zero difference as solid line. Confidence limits: NIOSH vs. OSHA (0.010 mg/m^3 – 0.046 mg/m^3), TD vs. OSHA (0.011 mg/m^3 – 0.069 mg/m^3) and TD vs. NIOSH (-0.053 mg/m^3 – 0.059 mg/m^3).

Average concentration of individual CTPVs

The average concentration of individual CTPVs in the ambient air of the paste floor as measured with each of the three methods are provided in Figure 5.

As can be seen from Figure 5, the individual CTPV for which the highest concentration level was measured was Naphthalene. The individual compound for which the lowest concentration level was measured was for Indeno(1,2,3-cd)pyrene. It is noteworthy to note that the concentrations measured for individual CTPVs decreased as the molecular weight of the compounds increased and that the OSHA method favoured the measurement of compounds with a higher molecular weight. This can be expected as the OSHA method is based on a filter only technique while the NIOSH method and TD technique based method focuses on the vapour phase of CTPVs as well. It is also noteworthy to note that the OSHA method measured higher concentration levels for Chrysene and Benzo(b)fluoranthene than the NIOSH or TD technique based method while Acenaphthylene was almost exclusively measured by the TD technique based method.

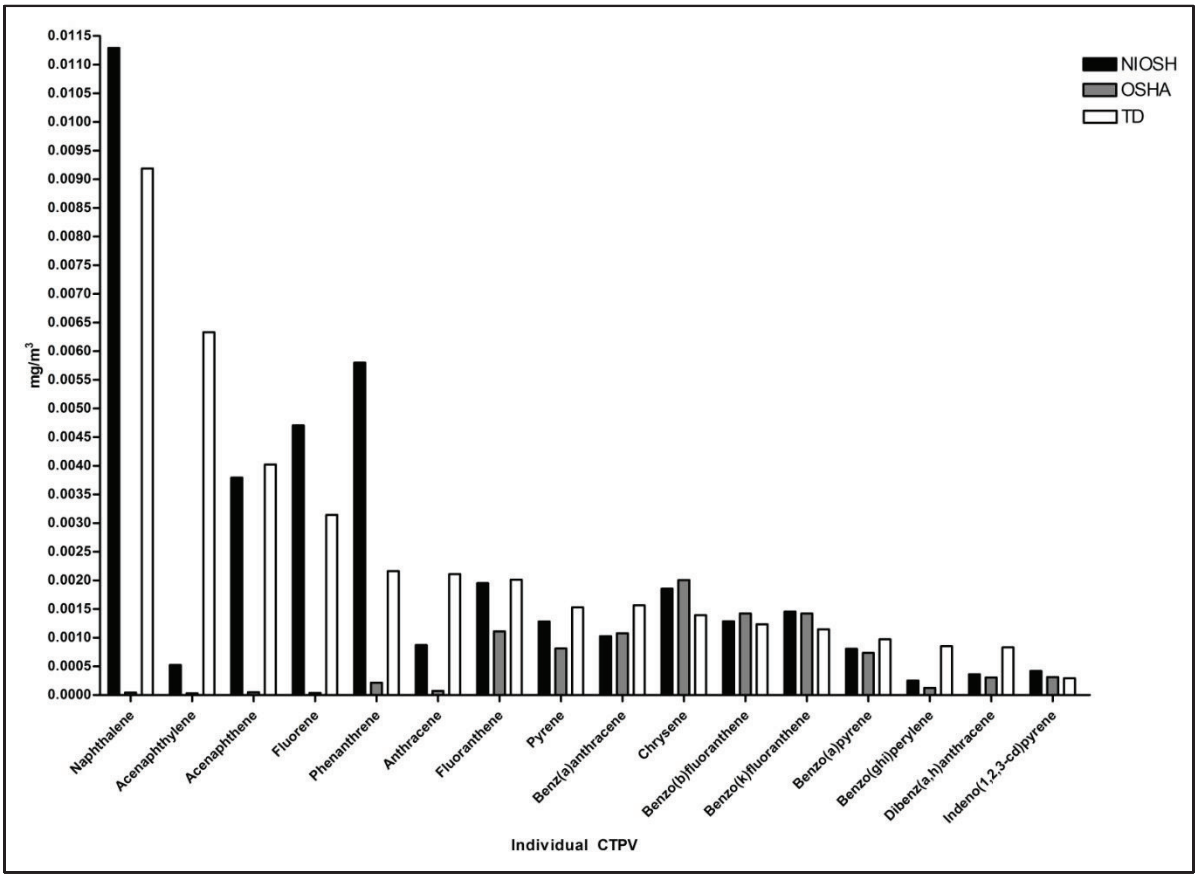


Figure 5: Average concentration of individual CTPVs.

Variation within (intra-variation) and between (inter-variation) methods over sampling period for individual CTPVs.

Concentrations of the individual CTPVs measured over the four day sampling period are presented in Figures 6 – 9. Variation in measurements was highest for the individual compounds with a lower molecular weight. Furthermore it is evident that the NIOSH method and TD technique based method measured individual compounds irrespective of their molecular weight whereas the OSHA method seemed to favour compounds with a higher molecular weight. The individual CTPVs of which the highest concentrations were measured on average, based on the results of all three methods were Naphthalene (0.007 mg/m^3), Phenanthrene (0.003 mg/m^3) and Fluorene (0.003 mg/m^3).

Concentrations of the individual CTPVs measured revealed the highest variation when measured by the TD technique based method except for Fluorene as measured by the NIOSH method on Day 2 and for Naphthalene as measured by the NIOSH method on day 4. Of all three methods used the TD technique based method was the only method able to reasonably measure Acenaphthylene.

If the three methods be paired with the IARC classification of individual CTPVs for which it measured the highest concentration, the results may be presented as is done in Table 3. The highest concentration of Naphthalene, Benzo(k)fluoranthene and Indeno(1,2,3-cd)pyrene was measured by the NIOSH method while the highest concentration of Chrysene and Benzo(b)fluoranthene was measured by the OSHA method. The TD technique based method measured the highest concentration of Benzo(a)pyrene, Dibenz(a,h)anthracene and Benz(a)anthracene.

Table 3: Method selection based on highest concentration measured of individual CTPVs with carcinogenic properties.

IARC Classification	**NIOSH**	**OSHA**	**TD**
I – Carcinogenic to humans.	0	0	1
II A – Probably carcinogenic to humans	0	0	1
II B – Possibly carcinogenic to humans.	3	2	1
Total for Group I to IIB	**3**	**2**	**3**
III – Not classifiable as to its carcinogenicity to humans.	2	0	5
IV – Probably not carcinogenic to humans.	0	0	1

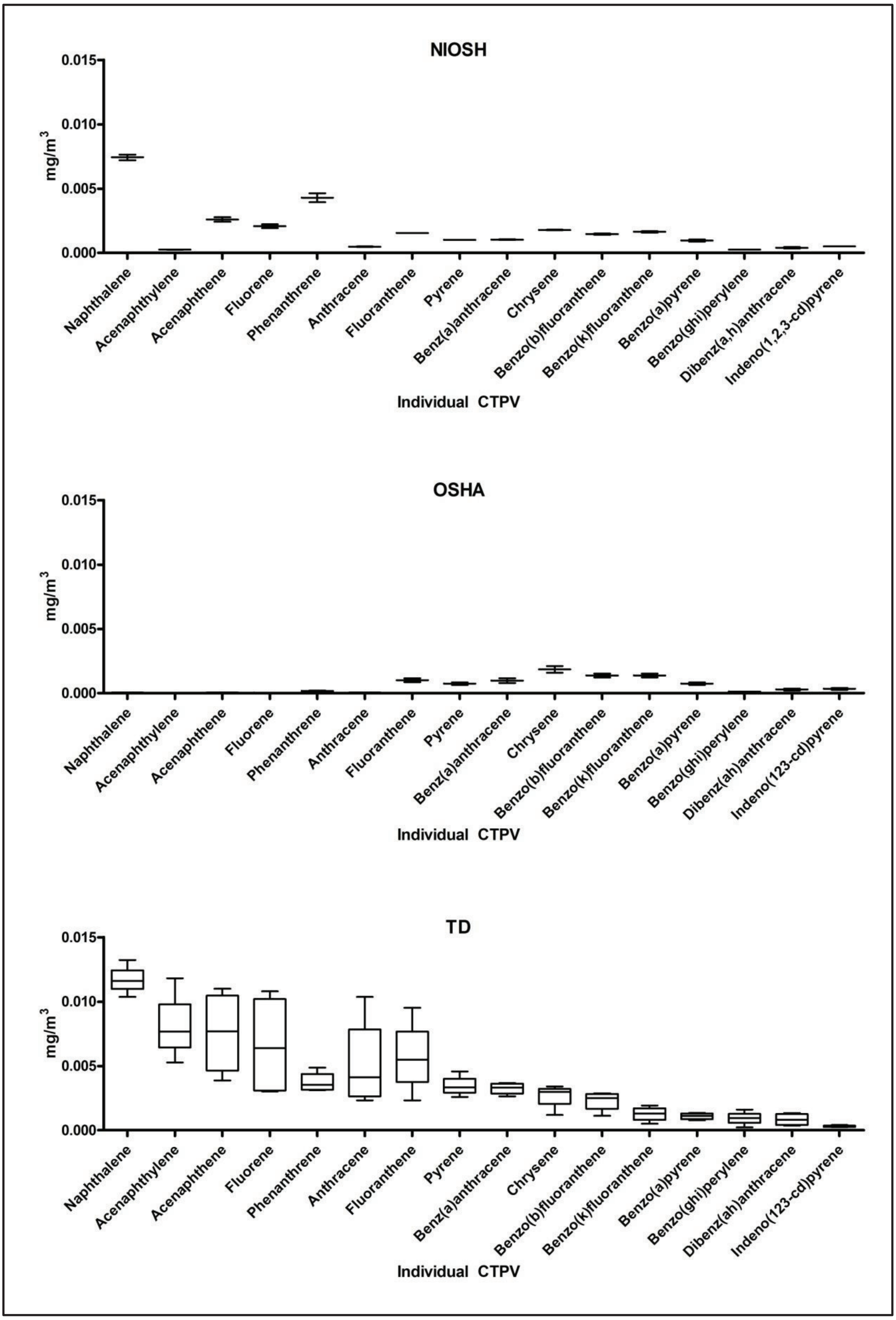


Figure 6: Box and whiskers plots of individual CTPVs on Day 1. Upper and lower ends of boxes represent 75th and 25th percentiles respectively with a solid line at the median. Whiskers indicate the maximum and minimum values.

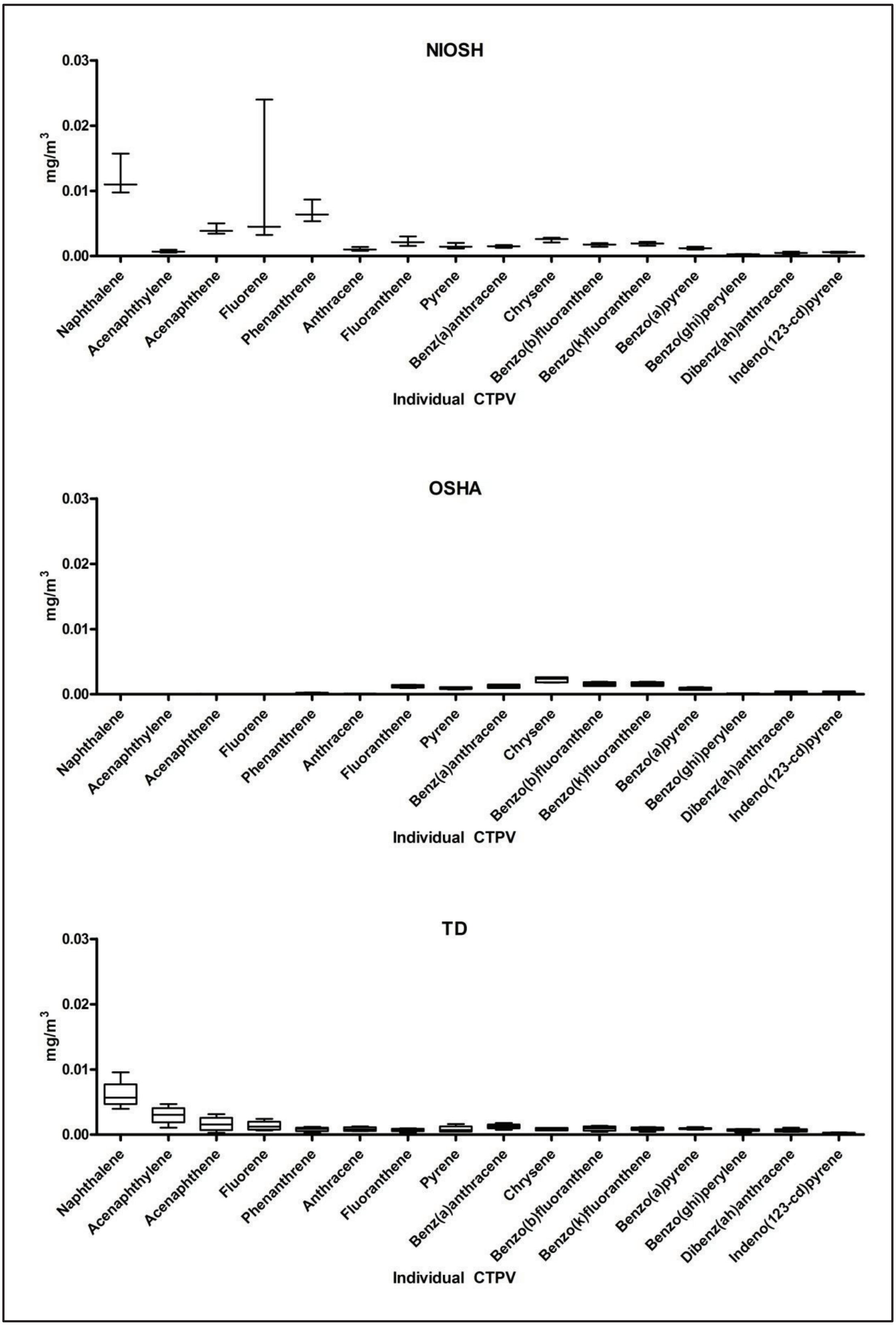


Figure 7: Box and whiskers plots of individual CTPVs on Day 2. Upper and lower ends of boxes represent 75th and 25th percentiles respectively with a solid line at the median. Whiskers indicate the maximum and minimum values.

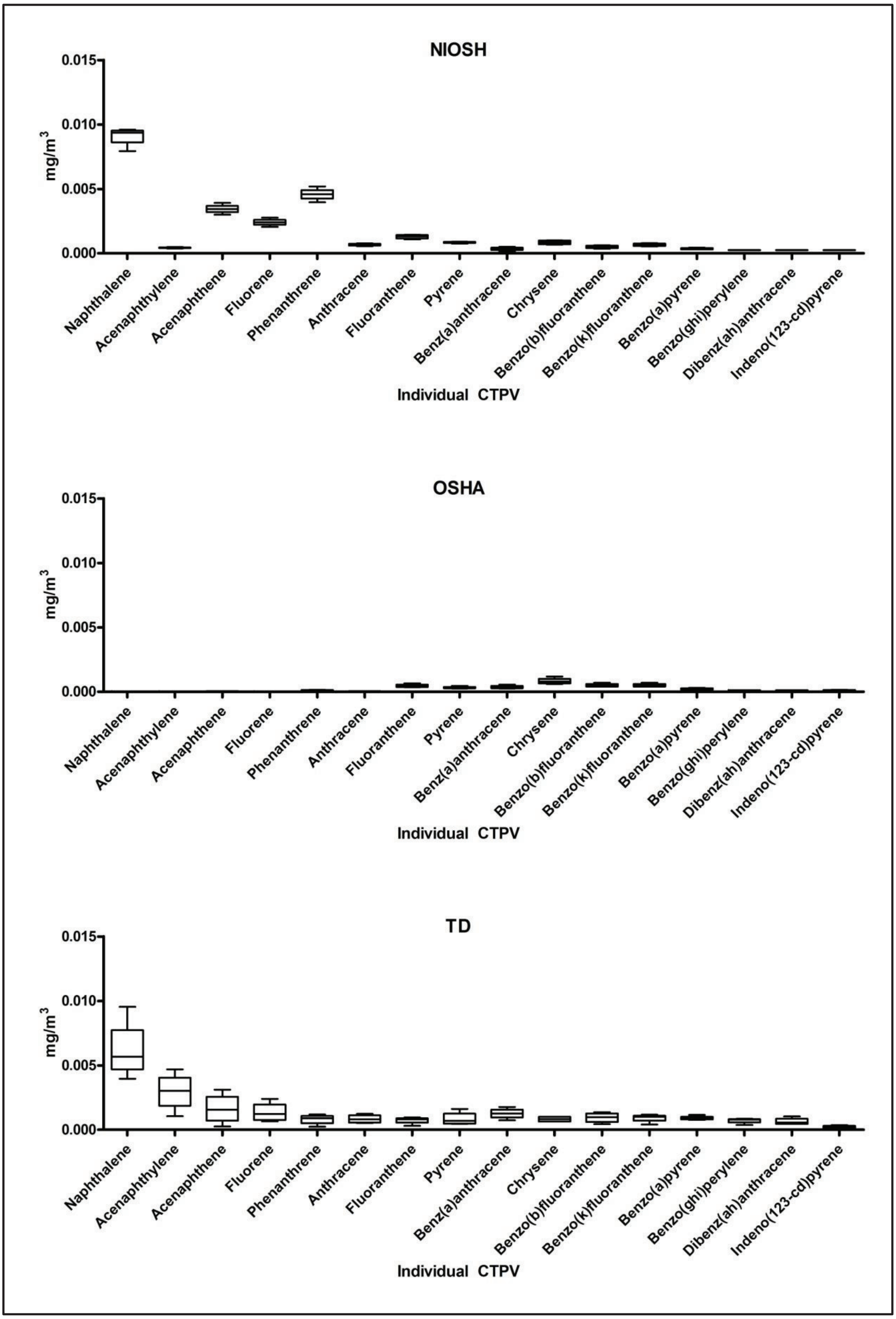
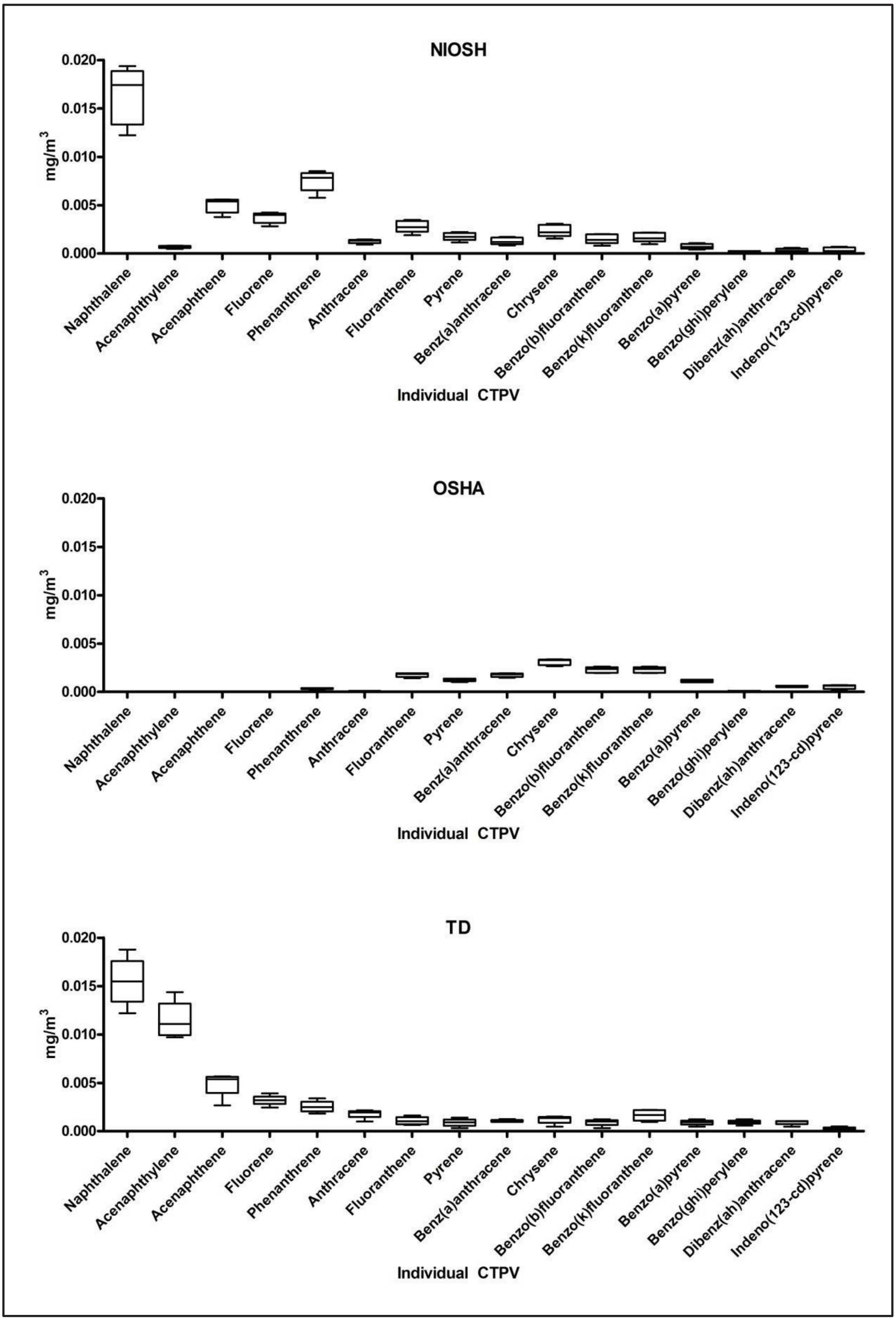


Figure 8: Box and whiskers plots of individual CTPVs on Day 3. Upper and lower ends of boxes represent 75th and 25th percentiles respectively with a solid line at the median. Whiskers indicate the maximum and minimum values.


NIOSH

OSHA

TD

Figure 9: Box and whiskers plots of individual CTPVs on Day 4. Upper and lower ends of boxes represent 75th and 25th percentiles respectively with a solid line at the median. Whiskers indicate the maximum and minimum values.

Comparison between sample costs of the three methods including the TD technique based method.

The average cost per sample, covering the cost of the sampling media as well as the analysis, for a sample taken with the NIOSH method is R 420, R 350 per sample for a sample taken with the OSHA method and R 550 for a sample taken with the TD technique based method. The cost per sample taken using the TD technique based method is thus the most expensive. It should however be kept in mind that a set of eight area samples should accompany samples taken by either the NIOSH or OSHA method. In Figure 10, the cost of sampling based on the above prices is provided. One sample taken using the NIOSH method would cost R 3780, R 3150 when using the OSHA method and R 550 when using the TD technique based method. The cost benefit of the NIOSH and OSHA method only outweighs the total cost of sampling when more than 26 samples need to be taken using the NIOSH method and 14 samples using the OSHA method.

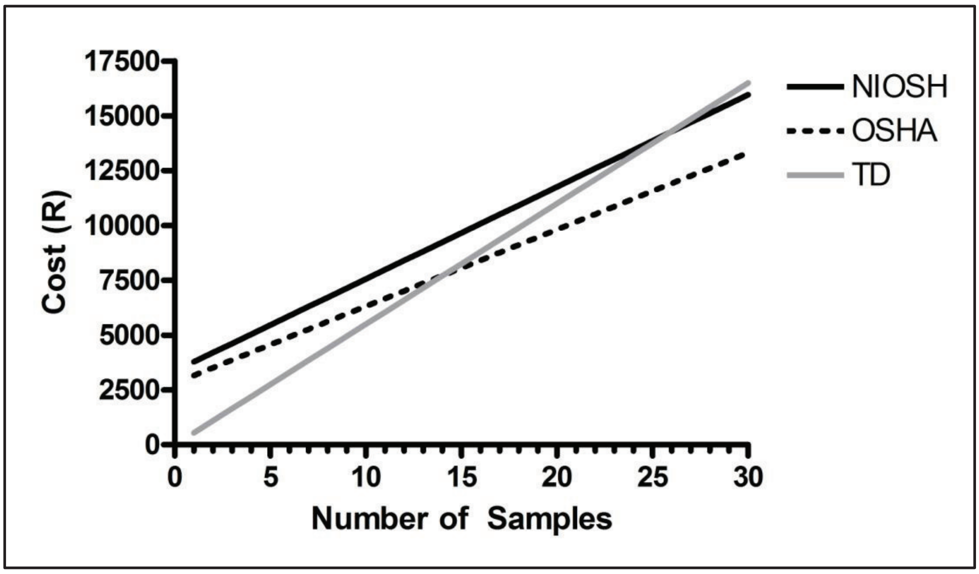


Figure 10: Cost comparison between the three methods including the TD technique based method.

Discussion

The results gathered from this study will now be discussed under headings appropriate to the general aims of the study.

Average concentrations of total CTPVs

From Figures 1 and 2 and Table 1 it can be seen that the highest concentration of total CTPVs in the ambient air was measured on the first day by the TD technique based method. The analysis of one sample revealed a total CTPV concentration of 0.079 mg/m^3. This concentration of total CTPVs is in the region of 56% of the Occupational Exposure Limit Time Weighted Average over eight hours (OEL-TWA) of 0.14 mg/m^3 provided by both the Mine Health and Safety Regulations (MHSR) of the Mine Health and Safety Act (MHSA) (South Africa, 1996) and the Regulations for Hazardous Chemical Substances (RHCS) of the Occupational Health and Safety Act (OHSA) (South Africa, 1993).

The average concentration level for total CTPVs as determined by the NIOSH Method, OSHA Method and TD based method was 0.038 mg/m^3, 0.010 mg/m^3 and 0.039 mg/m^3 respectively over the four day period. When compared to the OEL-TWA (8-hours) of 0.14 mg/m^3 it becomes evident that the average concentration level for total CTPVs as determined at the paste floor is in a region of 28% of the OEL. As none of the average concentration of total CTPVs as measured by the three methods exceeded the OELs provided by either the MHSR or the RHCS it may be concluded that exposure to total CTPVs was on average below the OEL during the duration of the study.

As the median concentration level for total CTPVs ranged from 0.027 mg/m^3 to 0.053 mg/m^3 as measured by the NIOSH method, 0.004 mg/m^3 to 0.016 mg/m^3 by using the OSHA method and 0.021 mg/m^3 to 0.069 mg/m^3 by using the TD technique based method it may be concluded that a large variation in the average concentration level for total CTPVs can be expected. A variation in the concentration of total CTPVs from day to day can be expected due to process related factors for example output at which the furnace is operating or environmental factors such as wind speed, wind direction and ambient temperature amongst others.

Variation within (intra-variation) method over sampling period

When considering the representation of results in Figures 2 and 3 as well as Table 1 it should be noted that different kinds of variance may present itself. There may be variance in the concentration of total CTPVs measured from one sample to the next as measured by the same method. This kind of variance is presented in the box and whisker plots of Figure 2. The amount of variance can be identified by looking at the distance between the whiskers of each box and whisker plot and quantified by the minimum, maximum and standard deviation listed in Table 1. The OSHA method reveals the least amount of variance between samples whereas the TD technique based method reveals the highest amount of variance between samples.

In order to compare variance between different methods, and taking into account that the average concentration of total CTPVs differs from one method to the next, the variance or standard deviation in relation to the mean had to be considered. This was done by calculating the coefficient of variation which takes the mean concentration of total CTPVs into account. These values are presented in Table 1 and the averages thereof are displayed in Figure 3.

From Figure 3 it can be seen that the variance in the average concentration of total CTPVs as measured by the NIOSH method was the smallest (median line) although it varied the most from day to day (25th, 75th percentiles and median). The variance in the average concentration of total CTPVs as measured by the OSHA method was higher than that of the NIOSH method but lower than that of the TD technique based method. The TD technique based method revealed the least variance from day to day (25th, 75th percentiles and median) but the highest variance between samples (median).

As variation within the method can be interpreted to comment on the precision of the method it can be concluded that the NIOSH method measured the concentration level of total CTPVs in the ambient air with the highest precision.

Variation between (inter-variation) methods over the sampling period

The NIOSH method measured the highest average concentration of total CTPVs on Day 2 and 3 while the OSHA method measured the lowest average concentration of total CTPVs on all of the four days. The TD technique based method measured the highest average concentration of total CTPVs on Day 1 and Day 4.

The difference between the average concentration of total CTPVs measured by the NIOSH and the TD technique based method on Day 3 and Day 4 were very small with a difference in average concentration of total CTPVs of 0.004 mg/m^3 on Day 3 and 0.001 mg/m^3 on Day 4.

When considering the average concentration of 0.010 mg/m^3 of total CTPVs measured over all four days by the OSHA method and comparing that to the average concentration of 0.038 mg/m^3 as measured by the NIOSH method and the 0.039 mg/m^3 measured by the TD technique method it becomes clear that the OSHA method measured an average concentration of total CTPVs of almost four times less than with either of the NIOSH or TD technique based method.

Should the assumption be made that false positives, i.e. measuring a concentration of total CTPVs which is not present, is unlikely when using any of the three methods it may be concluded, in the absence of knowing the true concentration of total CTPVs present in the ambient air of the paste floor, that the method which measured the highest concentration of total CTPVs is the most accurate. Based on this assumption it may then be argued that the TD technique based method, followed closely by the NIOSH method, is the most accurate method.

Furthermore, and more importantly it can be argued that the OSHA method may fail to measure the true concentration of total CTPVs in the ambient air of the paste floor by a factor of four. As the OSHA method uses only a filter for the collection of CTPVs, CTPVs in the vapour phase will not be captured during monitoring. Failure to include CTPVs in the vapour phase into the total CTPVs load will result in an under estimation of the concentration of total CTPVs.

Correlation and differences between methods

As all three methods are designed to measure substances in ambient air, one should expect to find a certain extent of correlation between the three methods. In Table 2 the results of a Spearman non-parametric analysis is provided. The NIOSH method correlated perfectly ($r = 1$) with the OSHA method on Days 3 and 4 and well with the TD technique based method on Days 2 through 4 ($r \geq 0.9856$). The OSHA method correlated well with the TD technique based method on Days 3 and 4 ($r \geq 0.9856$). When the average concentration of total CTPVs for all four days were pooled the correlation between the NIOSH method and the TD technique based method showed a perfect correlation ($r = 1$, $p < 0.0001$). The NIOSH method had a good correlation ($r = 0.9975$) with the OSHA method at a p-value of less than 0.0001 while the OSHA method has a good correlation with the TD technique based method of ($r = 0.9975$) at a p-value of less than 0.0001.

The highly significant correlations between the three methods are however misleading according to Bland and Altman. Bland and Altman proposed that correlation coefficients only measure the strength of relation between two variables and not the agreement between them. They proposed a graphical analysis technique henceforth called a Bland-Altman plot.

From the Bland-Altman plots in Figure 4 it can be concluded that the NIOSH method and the TD technique based method measured consistently higher levels of average total CTPVs in the ambient air than the OSHA method. On average the NIOSH method measured 0.028 mg/m^3 and the TD technique based method 0.029 mg/m^3 more total CTPVs, than the OSHA method. As 0.028 mg/m^3 to 0.029 mg/m^3 may represent 20% - 21% of the OEL for total CTPVs (0.14 mg/m^3) as provided for by both the MHSR and the RHCS, this difference is significant.

As the scatter around the bias line of the Bland-Altman plot for the NIOSH vs. OSHA method stays the same as the average increases, it may be concluded that the variability stays consistent. In contrast, the scatter around the bias line of the Bland-Altman plot for the TD vs. OSHA method increased as the averages increased and it may therefore be concluded that the variability does not stay consistent with changes in averages.

From Figure 4 it may be concluded that the NIOSH method and the TD technique based method gave similar results on Days 3 and 4 as the differences were small. On Day 2 the NIOSH method measured higher average levels of total CTPVs while on Day 1 the TD technique based method measured the highest average levels of total CTPVs.

A distinction between the NIOSH method and the TD technique based method with regards to their ability to measure total CTPVs can therefore not be made as the average difference between the average concentration of total CTPVs is only 0.001 mg/m^3 or 0.7% of the OEL as provided for by both the MHSR and the RHCS and this difference may be insignificant.

As no trend can be established between the differences between the NIOSH method and the TD technique based method and the average or the scatter around the bias and the average, no conclusion can be made regarding a trend or variability.

Average concentration of individual CTPVs

From the results presented in Figure 5 it may be concluded that individual CTPVs with lower molecular weights (compounds to the left) was present in higher concentrations than individual CTPVs with higher molecular weights (compounds to the right). This concurs with the argument that individual CTPVs' volatility is related to their molecular weight. It is known that individual CTPVs with higher molecular weights will tend to adhere to particles while the lower molecular weight individual CTPVs will tend to remain in the vapour phase.

From the results presented in Figure 5 it may be concluded that the NIOSH method and the TD technique based method measured the widest range of individual CTPVs when ranked according to their molecular weight while the OSHA method failed to readily measure compounds with a molecular weight lower than that of Phenanthrene.

As can be concluded from the results, the TD technique based method showed to be the only method that readily measured the concentration of Acenaphthylene as it measured higher concentration of Acenaphthylene by a factor of approximately 12 when compared to that as measured by the NIOSH method.

From the results presented in Figure 5 it may be concluded that the NIOSH method measured five of the highest sixteen concentrations of individual compounds, the OSHA method two and the TD technique based method the remaining nine. Based on the previous assumption that false positives is unlikely i.e. measuring the presence of a individual CTPV which is not present in the ambient air, when utilizing any of the three methods including the TD technique based method, it may be concluded that the TD technique based method measured most individual compounds more accurately.

Variation within (intra-variation) and between (inter-variation) methods over sampling period for individual CTPVs

Should an individual CTPV be targeted for measurement based on its human health effects, say for example based on its carcinogenicity, then this information can be used in combination with the data presented in Table 3. From this it may be concluded that the TD technique based method would be best suited for the measurement of Benzo(a)pyrene, an individual CTPV classified as a Group I or carcinogenic to humans compound by the IARC.

Should only Group IIB (possibly carcinogenic to humans) compounds, excluding Naphthalene, be of interest then either the NIOSH or OSHA method should suffice. Should Naphthalene be included as a target CTPV then either the NIOSH or TD technique based method should be used.

Comparison between sample costs of the three methods including the TD technique based method

As can be concluded from the results presented in Figure 10, the NIOSH and OSHA method is the least expensive method to use when determining the concentration of CTPVs in ambient air. It should however be noted that with both the NIOSH and OSHA method a set of 8 area samples are to be included in the set of samples sent to the analytical laboratory even if only one sample needs to be taken. This set of 8 concurrent area samples is used to determine the solvent of choice. This may negate the cost benefit of analysis of samples taken by using either the NIOSH or the OSHA method. As can be seen from Figure 10, one would indeed need to take 26 samples using the NIOSH method or 14 samples using the OSHA method before the cost benefit associated with these less expensive methods outweighs the cost associated with the TD technique based method.

Conclusion

After having discussed the results obtained through this study the following conclusions may be drawn.

The average concentrations of total CTPVs was measured using three methods, including a TD technique based method, and found to comply with the OEL as specified by both the MHSR of the MHSA and the RHCS of the OHSA irrespective of the method used. It should be noted that although the total CTPVs concentration levels, as measured in the ambient air of the paste floor, complied with national legislation, there may still be some risk attached to human exposure to CTPVs. As some of the individual components in the total CTPVs' make-up have been deemed to be carcinogenic, the lowest possible level of total CTPVs in the ambient air should be targeted, as a safe limit for exposure to carcinogenic compounds does not exists.

It was concluded, based on the amount of variation within the method, that the NIOSH method measured the concentration levels of total CTPVs in the ambient air with the highest precision.

Based on the concentration levels of total CTPVs measured in the ambient air the TD technique based method followed closely by the NIOSH method proved to be the most accurate method while the OSHA method, in contrast, failed to measure the true concentration of total CTPVs in the ambient air by a factor of four.

Correlation between the three methods, when based on the results of a Spearman non-parametric analysis, proved to range from good to perfect. Based on Bland-Altman plots the NIOSH method and the TD technique based method proved to correlate well and be in agreement regarding concentration levels of total CTPVs measured.

The difference between the higher concentration levels as measured by either the NIOSH method or the TD technique based method and the OSHA method may account for up to 21% of the OEL. Again it was shown that the OSHA method failed to provide a true reflection of the concentration levels of total CTPVs in the ambient air of the paste floor.

It was concluded that CTPVs with lower molecular weights was present in higher concentrations than CTPVs with higher molecular weights. It was furthermore concluded that the OSHA method failed to readily measure CTPVs with a molecular weight less than that of Phenanthrene. It could be argued that the OSHA method, based on a filter only technique, captures only particulates and therefore failed to capture and hence measure the concentration of CTPVs in the vapour phase.

The TD technique based method proved to be the only method that readily measured the concentration level Acenaphthylene.

Based on the assumption that false positives is unlikely when using any of the three methods, including the TD technique based method, it can be concluded that the TD method measured most individual compounds more accurately when compared to either the NIOSH or the OSHA method.

Should compound specific sampling be required, for example when the concentration of the Group I carcinogen benzo(a)pyrene needs to be determined, the TD technique proved to be best suited for the application.

The more expensive TD technique method proved to be more cost beneficial should a small amount of samples be taken when compared to either the NIOSH or the OSHA method as no concurrent samples have to be taken.

Based on the above conclusions, it may finally be concluded that the TD technique based method can be used as an alternative technique for the measurement of CTPVs in ambient air. It was found to be on par with the NIOSH method with regards to accuracy and superior to the OSHA and NIOSH method with regards to the range of individual CTPVs to be measured. The OSHA method has proven to be the least recommendable method for the measurement of CTPVs in ambient air.

It may be useful for future research to investigate the advantage of using a filter in line with the TD tube and the performance of the TD technique based method under conditions where total CTPV concentrations are higher than the ones encountered during this study.

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Chapter 4

Concluding Chapter

4.1 Summary

The general aim of this study was to explore the feasibility of a thermal desorption (TD) technique based method as an alternative method to be used for the measurement of coal tar pitch volatiles' (CTPVs) concentration in the work environment. In order to achieve this aim the specific objectives was to assess the TD technique based method along criteria such as ease of use, cost, accuracy and precision while comparing it to two established methods, namely the National Institute of Occupational Safety and Health's (NIOSH) Method 5515 and the Occupational Safety and Health Administration's (OSHA) Method 58 and to determine the levels of exposure to CTPVs on the anode paste floor of an electric furnace used for the smelting of concentrate containing platinum group metals (PGMs).

The concentration level of total CTPVs in addition to the concentration levels of individual CTPVs were determined in the ambient air of the paste floor of a PGMs smelter. Results from the study revealed that the average concentration level of CTPVs (0.029 mg/m^3) did not exceed the South African national Occupational Exposure Limit (OEL) (0.14 mg/m^3) provided by either the Mine Health and Safety Regulations (MHSR) of the Mine Health and Safety Act (MHSA) (South Africa, 1996) or the Regulations for Hazardous Chemical Substances (RHCS) of the Occupational Health and Safety Act (OHSA) (South Africa, 1993) but, as no exposure limit can be deemed as safe regarding exposure to chemicals with carcinogenic characteristics it would be prudent to control exposure levels to an as-low-as-possible level.

Based on the amount of variation within the methods (intra-variation) and between the methods (inter-variation), it was concluded that the NIOSH method had the highest precision while the TD technique based method had the highest accuracy. The OSHA method failed to measure the same concentration of total CTPVs as measured by the NIOSH and TD technique based method with a factor of four or a difference of 21% of the OEL. These observable facts may be ascribed to the OSHA's method filter-only approach which does not cater for CTPVs in the vapour phase. The TD technique based method measured the widest range of individual CTPVs and was the only method to readily measure the concentration of Acenaphthylene and would therefore be best suited should the individual CTPVs make-up of total CTPVs in ambient air needs to be investigated.

It was furthermore concluded that the cost benefit of both the NIOSH method and the OSHA method is negated by the need to take 8 replicate area samples for the determination of the solvent of choice. This results in the costlier TD technique based method to be more cost-efficient for taking samples of a sample size up to 26 samples when compared with the NIOSH method and 14 samples when compared to the OSHA method.

A summary of the conclusion are provided for in Table 4.

Table 1: Summary of conclusions

No.	Assessment criteria	Superior method
1.	Best accuracy.	TD / NIOSH
2.	Best precision.	NIOSH
3.	Widest range of individual CTPVs measured.	TD
4.	Easiest to use.	TD
5.	Lowest cost.	TD

The hypothesis of this project was that: “Thermal desorption is a superior alternative technique to other traditionally used method such as OSHA’s Method 58 and NIOSH’s Method 5515 for the measurement of CTPVs in the work environment”. As it was finally concluded that the TD technique method could be used as an alternative method to determine the concentration level of CTPVs in ambient air at a PGMs concentrate smelter as it was on par with the NIOSH method based on accuracy and superior to both the NIOSH method and the OSHA method with regard to the range of CTPVs that could be determined, the stated hypothesis is accepted.

4.2 Limitations of the study

During this study some limitations were identified that could be addressed in subsequent studies:

- The performance of the TD technique based method should be evaluated under controlled conditions where the concentration of individual as well as the total CTPVs levels are controlled and known.

- The performance of the TD technique based method should be evaluated under conditions where the concentration of individual as well as the total CTPVs are higher than encountered in this study.

- Area monitoring was conducted during this study and while it was the best monitoring strategy for the purpose of this study, personal samples could be included in future studies. This would enable the researcher to determine whether exposure based on area monitoring reflect the personal exposure of workers to CTPVs.

4.3 Recommendations

Based on the findings of this study the following recommendations are made:

- Use of the OSHA's Method 58 should be discontinued since methods which are both more accurate and precise are available for the measurement of the concentration of CTPVs in ambient air.

- Exposure assessment should not be limited to exposure to total CTPVs as the contribution of individual CTPVs, with different physical and chemical properties and hence carcinogenic properties, to the total CTPV load are unknown. Exposure to CTPVs should be assessed based on the exposure to individual CTPVs.

- As measurement methods are available that can quantify the exposure to individual CTPVs the need arises for occupational exposure limits specific to each individual CTPV.