Chapter 1

Introduction

1.1 AIR POLLUTION IN DEVELOPING COUNTRIES

The air quality of developing countries is of concern due to industrial development, economic growth and large-scale migration of rural residents to urban areas. Consequences of this include a decline in food security, an increase in respiratory related illnesses, and a degradation of both the quality of life and the environment (Mmolawa, 2006). Comprehensive and reliable air monitoring data is key to the improvement of air quality, as without this information it is impossible to identify and apportion emission sources (Hight and Ferrier, 2006).

Whilst it is acknowledged that significant progress has been made in organic air pollutant monitoring in many developing countries in Asia and South America, here we focus on southern Africa. The geographic delineation for the region was used, i.e. the portion of Africa south of the Cunene and Zambezi rivers. This incorporates the countries of Botswana, Lesotho, Namibia, Mozambique, South Africa, Swaziland and Zimbabwe, as shown in Figure 1.1.
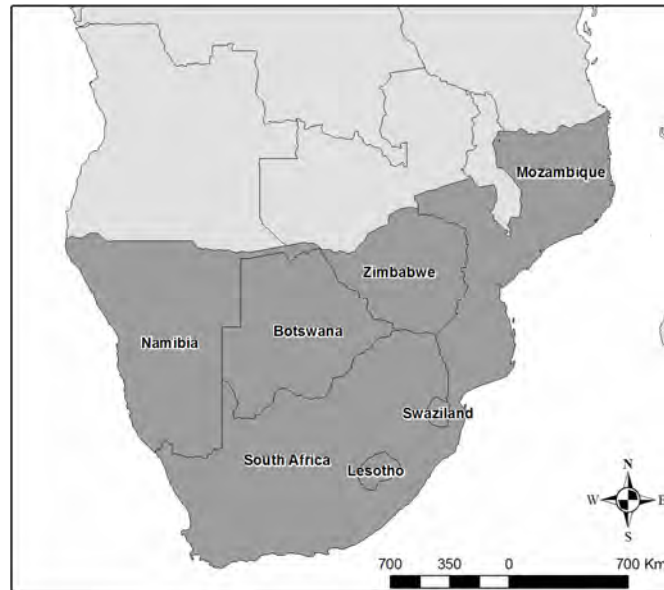
Figure 1.1: Southern African countries.

In addition to industrial emissions, major sources of air pollutants in developing countries include dependence on fossil fuels, and increasing traffic densities in urban areas, mainly involving an aged vehicle fleet without catalytic converters. Poor indoor air quality is also often of concern, due to the use of open fires for cooking and heating purposes. Besides the relatively commonly monitored inorganic pollutants which are released from these combustion processes, for example, nitrogen oxides, sulphur dioxide and carbon dioxide; organic pollutants may also be released in the gaseous form or associated with particles. Hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) are examples of such pollutants, as are polychlorinated dibenzodioxins and furans which may be generated when chlorinated material is combusted. Although the organic pollutants would generally be present at lower concentrations than the inorganic species, they are nevertheless of environmental significance due to their potential impacts (including health effects) at low levels.

1.2 HINDRANCES TO AIR POLLUTANT MONITORING IN DEVELOPING COUNTRIES AND MEANS BY WHICH THESE ARE BEING ADDRESSED

Organic air pollutant monitoring has been minimal in many developing countries to date, particularly those on the African continent. This is due to a number of reasons, some of which are the result of socio-political priorities. In addition, a lack of resources is often the most prominent hindrance, where funding, skilled human capital, and suitable equipment may be unavailable.

Various initiatives have been established in order to address these issues. For example, the Air Pollution Information Network for Africa (APINA) is a sub-Saharan regional network of scientists, policy-makers and non-governmental organizations, and its member countries include Botswana, Mozambique, South Africa and Zimbabwe. APINA aims to address air pollution problems, as part of the RAPIDC (Regional Air Pollution in Developing Countries) programme. RAPIDC is funded by the Department of Infrastructure and Economic Cooperation (INEC) of SIDA, the Swedish International Development Cooperation Agency and includes initiatives in both Asia and Africa (APINA, 2008).

The Southern and Eastern Africa Network of Analytical Chemists (SEANAC) was established to assist with capacity building and collaboration in the region, specifically in the areas of health, food security and environmental monitoring. One of the problems cited as being faced by African analytical chemists is that many of them received training abroad in techniques which are much more appropriate to the developed world (SEANAC, 2008).

The Organisation for Economic Cooperation and Development (OECD) has investigated the impact of monitoring equipment on air quality management in developing countries (Hight and Ferrier, 2006). Capacity building is achieved through case studies, where participant countries are assisted with monitoring equipment and training. The case studies conducted to date do not include southern African countries, and have focused on inorganic pollutants, with the exception of one study involving fuel testing in India, where PAHs were monitored.

1.3 OVERVIEW OF ORGANIC AIR POLLUTANT MONITORING IN SOUTHERN AFRICA

It is relevant to consider southern Africa as a region in terms of air quality, as the climate and air circulation of the region south of northern Angola is dominated by a gyre centred on Botswana. The air rotates anti-clockwise, completing one revolution approximately every week and the gyre thus formed remains in place for several weeks, particularly in winter, which leads to a build up of various trapped atmospheric pollutants, resulting in deterioration in visibility and air quality over parts of the subcontinent (Scholes and Biggs, 2004).

Monitoring activities are largely driven by legislation, thus an overview of the existing air quality legislation pertaining to the region is included in this section. It is generally accepted that environmental legislation in many African countries is outdated, or is poorly enforced due to a lack of capacity or poor institutional organisation. In some cases, more modern legislation still allows industries which were in existence before promulgation to continue operating outdated equipment, even if this leads to excessive pollution.

Some monitoring is undertaken by local government municipalities, industries, and research institutions in the different countries of interest, but in most cases such monitoring is currently restricted to inorganic air pollutants. Published organic air pollutant monitoring activities, conducted prior to 2007, are summarised in the following sections. It is acknowledged that additional monitoring may have taken place such as for the purpose of Environmental Impact Assessments (EIAs), where the reports are not readily accessible.

1.3.1 Botswana

Routine air quality monitoring began in Botswana in the mid 1970s, upon the promulgation of the Atmospheric Pollution Prevention Act in 1971. Continuous monitoring of hydrocarbons has been conducted in Botswana at one site since 1999 (Scholes, 2001), but most of the monitoring sites focus on inorganics (SO_2, NO_x, O_3, CO and particulate matter) and associated meteorological data. Ambient air quality objectives for Botswana do not include organic air pollutants. A National Environmental Laboratory was established in 2002, however, which has the capabilities to analyse organic pollutants (Mmolawa, 2006).

1.3.2 Lesotho

The Environment Act 2001 provides for the management of the environment and all natural resources of Lesotho. The Act makes provision for the establishment of environmental quality standards and environmental monitoring, but it is unclear as to whether such provisions have been enacted (Department of Tourism, Environment and Culture, 2001).

1.3.3 Mozambique

Mozambique has an Environmental Law of 1997, but few air pollutant monitoring studies have been conducted in this country (Mmolawa, 2006).

1.3.4 Namibia

The Namibian Directorate of Environmental Affairs has noted that air pollution is a less serious problem than in many other countries, although the need to update the environmental legislation to enable effective law enforcement is acknowledged (Namibia Directorate of Environmental Affairs, 2008). No systematic air quality monitoring had occurred in Namibia, as of 2001 (Scholes, 2001).

1.3.5 South Africa

A new era in air quality management in South Africa began with the promulgation of the National Environmental Management: Air Quality Act (Act No. 39 of 2004) (AQA), which replaced the Air Pollution Prevention Act (Act No. 45 of 1965). This has resulted in a shift from an emission control focus to an airshed approach, which culminated in the establishment of national standards for permissible ambient concentrations of air pollutants (Department of Environmental Affairs and Tourism, 2006).

This has implications in terms of air quality monitoring, as methods are required which are suitable for monitoring pollutants at ambient concentrations, which are generally lower than emission levels. Alternative methods, which allow for pre-concentration of analytes of interest and which have lower detection limits, are therefore of importance. Sampling methods employed in ambient and emission air monitoring are also different. Development of the capacity and capabilities to perform ambient air monitoring (as well as in air quality

management) is therefore receiving attention in South Africa, particularly at local government level.

At present, benzene is the only organic air pollutant for which ambient standards have been set (an annual average of 5 $\mu g.m^{-3}$), although the AQA makes provision for the Minister of Environmental Affairs and Tourism to make notice of additional air pollutants, as necessary.

In terms of monitoring, local municipalities in South Africa currently monitor Volatile Organic Compounds (VOCs) (specifically benzene, toluene, ethylbenzene and xylenes) at nine sites across three provinces. Methane is also monitored at four stations in two provinces, one of which is the World Meteorological Organisation (WMO) Global Atmospheric Watch (GAW) site at Cape Point (Department of Environmental Affairs and Tourism, 2007). Non-methane hydrocarbons are also monitored monthly at the GAW site, by means of grab sampling into canisters which are analysed in Europe. These samples have yielded interesting results in the context of biomass burning episodes, for example (Brunke et al., 2001).

VOCs have been studied in various contexts, including that of emissions from spontaneous combustion of coal (Pone et al., 2007) and the Cape Town brown haze, which forms in winter months under inversion conditions (Burger et al., 2004).

In addition to monitoring campaigns, fundamental research has been conducted in South Africa in terms of novel means of sampling and analysing organic air pollutants. Burger et al. (2006) have developed a high capacity, polydimethylsiloxane (PDMS) rubber sample enrichment probe (SEP), which can be thermally desorbed for GC analysis. A novel thermal modular array for comprehensive two-dimensional gas chromatography has also been produced by these researchers (Burger et al., 2003).

Ortner and Rohwer (1996) developed thick film multi-channel silicone rubber traps, as shown in Figure 1.2, which have been applied in semi-volatile organic air pollutant sampling. These traps serve as pre-concentrators and can be thermally desorbed for gas chromatographic (GC) analysis, thereby negating the need for solvent extraction and concentration, and there is also a low pressure drop across the traps, due to their open geometry. It has been found that the blank runs of PDMS traps, where pre-concentration occurs by sorption of the analytes into

the silicone, are significantly better than those of most adsorbents, such as Tenax TA, and do not deteriorate with continued use (Balthussen et al., 1998). PDMS is also more inert than most adsorbents, and the PDMS degradation products can be easily identified by mass spectrometry. The multi-channel silicone rubber traps of Ortner et al. (1996) are inexpensive to manufacture and can be re-used, therefore they were employed in our study for sampling and pre-concentration of trace organic air pollutants.
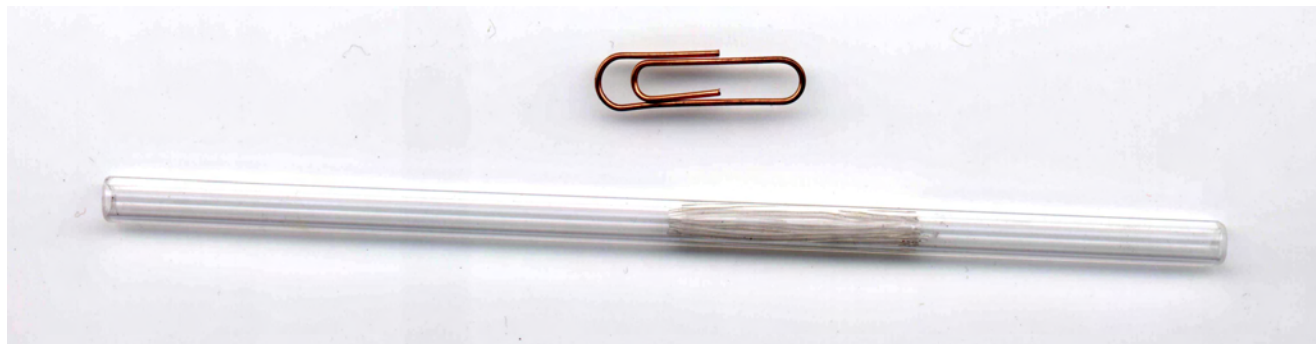

Figure 1.2: A silicone rubber trap containing multiple PDMS channels.

1.3.6   Swaziland

Air Pollution Control Regulations have been drafted for Swaziland, which include air quality objectives for a number of inorganic air pollutants only (Department of Tourism, Environment and Communications, 1999).

1.3.7   Zimbabwe

Zimbabwe has an Atmospheric Pollution Control Act (No. 33 of 1971 as amended by Act No. 22 of 2002) and Atmospheric Pollution Prevention Regulations of 1975. The Environmental Management Act was enacted in December 2002, which will repeal the existing air legislation in due course, and will provide for the establishment of Air Quality Standards (Mmolawa, 2006).

Some random air monitoring studies have been conducted in Zimbabwe, and the Air Pollution Control Unit of the City of Harare Health Department has carried out routine air pollution monitoring of SO_2, NO_2 and soot at eight sites over the past 20-30 years. Other

parameters which have been monitored include methane and VOCs, in addition to inorganic analytes (Pb, NH_3, HCl and particulate matter) (Mmolawa, 2006).

1.3.8 Other African studies

Few published organic air pollutant monitoring campaigns have been conducted in other African countries, such as the monitoring of PAHs from charcoal burning in Kenya (using liquid chromatography with fluorescence detection) (Gachanja and Worsfold, 1993). The majority of these studies were carried out in collaboration with developed countries, which assisted primarily with analyses. Studies of organic pollutants, particularly pesticides, in other environmental media (Torto et al., 2007), also indicate that there is some existing capacity that could provide a basis for air monitoring. An example is the determination of PAHs in surface runoff and sediments in Nigeria (Ogunfowokan et al., 2003). A study of relevance to Africa was the ship-board monitoring of atmospheric PAHs and polychlorinated aromatic hydrocarbons (PCNs) along a north-south Atlantic transect between the Netherlands and South Africa. The highest levels of these pollutants were found near to the land masses (Europe, West Africa and South Africa) (Jaward et al., 2004a).

1.3.9 Involvement of southern Africa in international conventions

In terms of organic pollutant monitoring, the Stockholm Convention on Persistent Organic Pollutants (POPs) is of relevance. The majority of southern African countries have become signatories to this convention, and as such have a responsibility to manage and monitor POPs (Bouwman, 2004). Existing monitoring progammes, activities and datasets have recently been compiled (United Nations Programme, 2007), and are summarised in Table 1.1. Although concentrations of POPs were determined in ambient air in Durban, South Africa (Batterman et al., 2006), all analyses were performed in the United States of America (USA). It is evident that capabilities in the region require further development.

Table 1.1: Existing national monitoring programmes, activities and datasets for southern African countries (United Nations Programme, 2007).

Country	Monitoring activities
Botswana	No data
Lesotho	No data
Mozambique	No data
Namibia	Limited data
South Africa	No existing national POPs information gathering activities. Academic research studies have been conducted and published to assess POPs in various media (Note: air was not included).
Swaziland	No data
Zimbabwe	Limited data

1.3.10 Southern African air monitoring campaigns

The Southern Africa Fire-Atmosphere Research Initiative of 1992 (SAFARI-92) and the Southern African Regional Science Initiative of 2000 (SAFARI 2000) provided scientists in the region with the opportunity to participate in large research projects with international experts. SAFARI-92 investigated the role of savanna fires in atmospheric chemistry, climate and ecology, where organic monitoring included CH_4 and non-methane hydrocarbons (Lindesay et al., 1996). More than 150 scientists from 14 countries were involved, including the southern African countries of Botswana, Namibia, South Africa, Swaziland and Zimbabwe. SAFARI 2000 addressed a broad range of phenomena related to land-atmosphere interactions and biogeochemical functioning of the southern African system. Here biogenic volatile organic compounds (BVOCs), VOCs, oxygenated VOCs, and semi-volatile organic compounds (SVOCs) were also monitored (Swap et al., 2003).

1.4 USE OF ALTERNATIVE MONITORING METHODS

In light of the hindrances experienced in developing countries, as discussed under section 1.2, alternative monitoring methods to the standard comprehensive methods may be more appropriate. Such methods should be cost effective and simple, in order to allow for

more widespread monitoring in the region. A few options in this regard, with respect to organic air pollutants are briefly discussed in this section.

1.4.1 Passive sampling

Passive air samplers provide a useful means of monitoring in developing countries due to their simplicity, cost effectiveness and non-reliance on provision of a power source. Passive sampling may provide pre-concentration of analytes, thereby increasing analytical sensitivity, and may reduce or eliminate solvent consumption for sample preparation purposes. Sampling is based on diffusion or permeation of the analyte into the sampler, as reviewed by Seethapathy (Seethapathy et al., 2008). Passive samplers have found widespread application in airborne POPs monitoring, for example (Shoeib and Harner, 2002; Jaward et al., 2004b).

Besides the use of evacuated canisters for passive organic air pollutant sampling, passive samplers of interest include solid phase microextraction (SPME), polyurethane foam (PUF) based samplers, and samplers containing adsorbents such as graphitised charcoal or Tenax.

Studies have been conducted in South Africa to assess the chronic health impacts of exposure to VOCs (as well as naphthalene), by means of passive sampling, using 3M badges (John, 1998) and IVL passive samplers (Wichmann, 1999). There is significant scope to implement passive sampling more widely in the field of organic air pollutant monitoring in southern Africa, and to utilise this technique for a wider range of organic analytes. It should be noted, however, that passive samplers may not provide the time resolution required in some monitoring campaigns, due to the relatively long sampling intervals usually employed (one to several weeks).

1.4.2 Indicator compounds

The monitoring of by-products (indicator compounds) of reaction pathways which generate the analyte of interest has been successfully utilised for various classes of chemicals. A relevant example is the monitoring of chlorobenzenes and chlorophenols as indicators for dioxins and furans, where correlation coefficients are used to relate the indicator compound

concentrations to that of the target analyte (Kaune et al., 1998). Precursor compounds may be similarly utilised where intermediates in the synthesis of the target analyte are monitored.

The choice of indicator compound is based on the existence of a correlation with the target compound(s), ease of sampling, as well as other characteristics which simplify analysis, such as a higher concentration and existence of fewer congeners compared to the target analyte(s). The monitoring of indicator or precursor compounds for organic air pollutant monitoring therefore has significant potential for application in developing countries, where resources and capacity are limited.

1.4.3 Screening methods

Screening methods find application in large sampling campaigns, in that numerous samples can be taken and analysed in order to determine whether more comprehensive analysis (by standard accepted methods) is required, such as of those samples which screen positive. A screening method should ideally be fast, simple and of low cost, yet meet the sensitivity and selectivity requirements of the application. It is therefore evident that the advantages of screening methods would be particularly beneficial in a developing country context.

1.5 PURPOSE OF THIS STUDY

This study was initiated in order to develop methods for organic air pollutant monitoring, which are more applicable to developing countries and which have benefits over comprehensive, detailed methods in this context, thereby allowing for significantly more sampling campaigns to be conducted, particularly in southern Africa. The techniques are required to be rapid, and have acceptably low limits of detection for the envisaged applications thereof. In addition, sufficient selectivity is needed and sample clean-up and separation processes prior to analysis should be minimal. Interface with more comprehensive techniques for further comprehensive, quantitative analysis post screening should ideally also be possible. Although equipment cost considerations are important, it is possible that some techniques may be more suitable for application in a centralized environmental laboratory for the southern African region.

1.6 STRUCTURE OF THE THESIS

Following the background to organic air pollutant monitoring and the objectives of this study, as provided in this chapter, the generation of trace organic gas standards for such monitoring is detailed in Chapter 2. The development of a novel, laser induced fluorescence screening method for PAH monitoring with PDMS based sampling is presented in Chapter 3, whilst the use of the multi-channel silicone rubber traps in a novel denuder configuration is described in Chapter 4. Chapter 5 covers the applications of these methods, whilst overall conclusions are drawn in Chapter 6.

1.7 REFERENCES

Air Pollution Information Network for Africa (APINA), **2008**, accessed online at www.sei.se/rapidc/apina.htm

Balthussen, E., David, F., Sandra, P., Janssen, H.-G. and Cramers, C.A., *Journal of High Resolution Chromatography*, **1998**, *21*, 332-340.

Batterman, S., Chernyak, S., Gounden, Y. and Matooane, M., *Organohalogen Compounds*, **2006**, *68*, 1111-1114.

Bouwman, H., *South African Journal of Science*, **2004**, *100*, 323-328.

Brunke, E.-G., Labuschagne, C. and Scheel, H.E., *Atmospheric Environment*, **2001**, *35*, 777-786.

Burger, B.V., Marx, B., le Roux, M. and Burger, W.J.G., *Journal of Chromatography A*, **2006**, *1121*, 259-267.

Burger, J.W., Pienaar, J.J., Fourie, L. and Jordaan, J.H.L., *Air Pollution 2004*, **2004**, WIT Press, UK, 631-640.

Burger, B.V., Snyman, T., Burger, W.J.G. and van Rooyen, W.F., *Journal of Separation Science*, **2003**, *26* (1-2), 123-128.

Department of Environmental Affairs and Tourism, South Africa, 9 June **2006**, National Environmental Management: Air Quality Act No. 39 of 2004, Government Notice No. 528, Government Gazette No. 28899.

Department of Environmental Affairs and Tourism, South Africa, May **2007**, *Technical Compilation to inform the Initial State of Air Report*, National Air Quality Management Programme.

Department of Tourism, Environment and Communications, Swaziland, **1999**, Air Pollution Control Regulations, accessed online at www.ecs.co.sz

Department of Tourism, Environment and Culture, Republic of Lesotho, **2001**, Environment Act, accessed online at www.faolex.fao.org/faolex

Gachanja, A.N. and Worsfold, P.J., *Science of the Total Environment*, **1993**, *138*, 77-89.

Hight, J., and Ferrier G., **2006**, *The impact of monitoring equipment on air quality management capacity in developing countries*, Organisation for Economic Cooperation and Development, Joint Working Party on Trade and Environment, Report COM/ENV/TD(2006)7/FINAL, France.

Jaward, F.M., Barber, J.L., Booij, K. and Jones, K.C., *Environmental Pollution*, **2004a**, *132*, 173-181.

Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J. and Jones, K.C., *Environmental Science and Technology*, **2004b**, *38*, 34-41.

John, J., January **1998**, *Research to quantify atmospheric volatile organic compounds in the major metropolitan areas of South Africa*, CSIR internal report ENV-P-C-98016, South Africa.

Kaune, A., Lenoir, D., Schramm, K.-W., Zimmermann, R., Kettrup, A., Jaeger, K., Rückel, H.G. and Frank, F., *Environmental Engineering Science*, **1998**, *15* (1), 85-95.

Lindesay, J.A., Andreae M.O., Goldammer, J.G., Harris, G., Annegarn, H.J., Garstang, M., Scholes, R.J. and van Wilgen, B.W., *Journal of Geophysical Research*, **1996**, *101* (D19), 23521-23530.

Mmolawa, M.D., **2006**, Scoping report on existing monitoring activities in the 7 APINA member countries, Issued as part of Phase III Activity 2.3 of the RAPIDC Programme 2005-07, Botswana.

Namibia Directorate of Environmental Affairs, **2008**, accessed online at www.met.gov.na/dea

Ogunfowokan, A.O., Asubiojo, O.I. and Fatoki, O.S., *Water, Air, and Soil Pollution*, **2003**, *147*, 245-261.

Ortner, E.K. and Rohwer, E.R., *Journal of High Resolution Chromatography*, **1996**, *19*, 339-344.

Pone, J.D.N., Hein, K.A.A., Stracher, G.B., Annegarn, H.J., Finkleman, R.B., Blake, D.R., McCormack, J.K. and Schroeder, P., *International Journal of Coal Geology*, **2007**, *72*, 124-140.

Scholes, R.J. and Biggs, R. (eds), **2004**, *Ecosystem services in Southern Africa: A regional assessment*, CSIR, ISBN 0-7988-5527-4, 55, South Africa.

Scholes, R., February **2001**, *Regional Implementation Plan for Southern Africa*, *Global Terrestrial Observing System GTOS-21*, CSIR internal report ENV-P-R 2001-002, South Africa.

Seethapathy, S., Górecki, T. and Li, X., *Journal of Chromatography A*, **2008**, *1184*, 234-253.

Shoeib, M. and Harner, T., *Environmental Science and Technology*, **2002**, *36*, 4142-4151.

Southern and Eastern Africa Network of Analytical Chemists (SEANAC), **2008**, accessed online at www.seanac.org

Swap, R.J., Annegarn, H.J., Suttles, T., King, M.D., Platnick, S., Privette, J.L. and Scholes, R.J., *Journal of Geophysical Research*, **2003**, *108* (D13), SAF 1-1 – 1-15.

Torto, N., Mmualefe, L.C., Mwatseteza, J.F., Nkoane, B., Chimuka, L., Nindi, M.M. and Ogunfowokan, A.O., *Journal of Chromatography A*, **2007**, *1153*, 1-13.

United Nations Environmental Programme, **2007**, Stockholm Convention on Persistent Organic Pollutants (POPs), *Compilation of existing national monitoring programmes, activities and datasets*, Document UNEP/POPS/GMP/TWG-2/6, Geneva.

Wichmann, J., October **1999**, *Human health risk assessment case study – value addition of passive sampler generated data*, CSIR internal report ENV-P-I-99008, South Africa.

Chapter 2

The generation of trace gas standards

2.1 INTRODUCTION

In trace gas analysis, it is important that reliable gas standards can be produced at the appropriate concentrations. For initial analytical method development, liquid injections of standards onto the sampling traps may suffice. During method optimization for application purposes, however, gas phase standards may be more appropriate.

A number of means of generating gas standards have been developed, as reviewed by Barratt (1981), Namieśnik (1984) and Naganowska-Nowak et al. (2005), which may be broadly classified into static and dynamic methods. Static techniques involve the introduction of a specific amount of analyte into a known volume of diluent gas in a closed container, such as a gas cylinder, whilst with dynamic methods, the analyte enters the diluent gas stream on a continuous basis (Naganowska-Nowak et al., 2005).

Static systems are used primarily for small volumes of mixtures and fairly high concentrations, but losses of components of the mixture to the wall of the container may occur, and these systems are usually not very portable. They have been used primarily in the calibration of GC detectors. Dynamic systems can produce larger volumes, with surface losses being lower than in static systems due to the existence of equilibrium conditions after saturation of contact surfaces, and are thus more suitable for polar and reactive species (Barratt, 1981).

In deciding on an appropriate means of generating a gas standard, the particular application needs to be considered, such as the vapour pressure of the analyte concerned, the need for portability, and so on.

In order to generate gas standards of organic air pollutants at trace levels in our study, a number of techniques were utilized, as detailed in this Chapter, where sampling was performed onto the multi-channel silicone rubber traps referred to in Chapter 1.

2.2 PERMEATION TUBES

2.2.1 Theory

The principle of permeation was first used in 1966 to prepare primary standards for trace gas analysis (Barratt, 1981). Since then, permeation tubes have found application in air pollution, occupational hygiene and instrumental analysis, as evidenced by their current commercial availability.

Permeation methods are based on the dissolution of the compound of interest into and permeation through a sealed polymeric tube or membrane, at a constant and reproducible rate. Polyethylene, polytetrafluoroethylene (PTFE or Teflon) and silicone rubber have been used as tube or membrane material (Namieśnik, 1984), although Teflon is commonly used due to its durability, low reactivity, and commercial availability in a range of diameters and wall thicknesses (Mitchell, 2000; O'Keeffe and Ortman, 1966). The configurations of permeation tubes commonly used are sealed Teflon tubes, Teflon tubes with sample storage reservoirs (sometimes called permeation vials), and membrane devices for highly volatile compounds, which have a wafer structure, with a small area for permeation. Permeation tubes can be prepared for gases, liquids or solids. The latter two cases consist of two-phase systems, where the liquid or solid and its vapour (at a fixed vapour pressure) are present.

Fick's law of diffusion governs the permeation process, due to the difference in partial pressure of the compound of interest between the inner and outer walls of the tube. After construction of a permeation device, a period of equilibration is required before steady-state

conditions are reached, when the permeation rate is constant as long as a two phase system is present. After a period of time, the compound of interest will become depleted, and the permeation rate will consequently decrease to zero. The lifetime of a particular permeation device depends on the permeation rate and the mass of compound of interest placed inside the tube.

The permeation rate is given by the equation (Namieśnik, 1984):

$$R = DS(p_1 - p_2)\frac{A}{L}, \qquad\qquad \text{Equation 2.1}$$

where R is the permeation rate of the gas through the plastic membrane; D is the diffusion coefficient; S is the solubility constant; p_1 and p_2 are the partial pressures on the two sides of the membrane; A is the surface area of the membrane; and L is its thickness.

The permeation rate (and the vapour pressure) is temperature dependant, as shown in equation 2.2 (Namieśnik, 1984), thus accurate temperature control is vital in their application.

$$\log\frac{R_2}{R_1} = 2950\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \qquad\qquad \text{Equation 2.2}$$

where R_1 and R_2 are the permeation rates at temperature T_1 and T_2, respectively. The equation was empirically derived for various permeation materials, and it allows for the permeation rate to be predicted at temperatures different from the calibration temperature. It is also evident that the permeation rate would change by ~10 % for each 1°C change in temperature.

Under standard temperature and pressure conditions (STP), the concentration of the compound of interest (C) in a gas stream flowing over the permeation tube can be calculated from (Namieśnik, 1984):

$$C = \frac{22.45R}{MQ}, \qquad\qquad \text{Equation 2.3}$$

where R is the permeation rate; M is the molar mass of the compound of interest; and Q is the flow rate of the diluting gas.

A number of means of calibrating permeation tubes have been reported (Namieśnik, 1984), however, the gravimetric method of determining permeation rates from mass loss over an extended time period is most commonly used. Theoretical calculation of permeation rates is hindered by a lack of data regarding diffusion coefficients and solubility constants in the polymer materials of interest. Errors in determining small mass losses gravimetrically, however, may arise from static electricity effects, dust in the weighing room, and air currents.

Advantages of permeation tubes as sources of trace gas standards include their versatility, portability and ease of use. They do, however, require long initial equilibration times, and they are a continuous source of the component (i.e. it is not possible to "switch them off"). In addition, they are not suitable for compounds which have very low vapour pressures and low diffusion rates.

Various permeation systems have been developed (Scaringelli et al., 1970; Barrat, 1981), which include temperature controlled systems (provided by a water bath, for example). Such permeation systems are, however, bulky and fragile for field use, and are therefore more suitable for laboratory environments. A permeation-based dynamic gas generator system was developed for naphthalene (Temime et al., 2002), which allowed for the generation of a range of PAH concentrations. The permeation cell consisted of a glass tube containing crystals of the PAH of interest, which was sealed with a PTFE membrane, and was housed in a temperature controlled water bath. The flow rate of the carrier (diluent) gas was between 20 and 40 $m\ell.min^{-1}$, and gravimetric calibration was employed (1 mg mass loss was recorded after a 2 day period, which equates to 6 $ng.s^{-1}$).

In our study, individual permeation tubes were prepared for a number of chorophenols, chlorobenzenes and naphthalene, as discussed in the following sections. Mixed gas standards were also generated from these permeation tubes by placing the selected permeation tubes together in a holder, through which clean diluent air was passed.

2.2.2 Experimental method

2.2.2.1 Permeation tube preparation

Permeation tubes were manufactured using shrink fit PTFE Teflon tubing (Supelco, Sigma Aldrich, 1.4 mm o.d., which shrinks to 0.81 mm, ~40 mm long) into which the standard of interest was placed using a 5 $\mu\ell$ microcap (chlorobenzenes and chlorophenols: Riedel-de-Haën, analytical grade, Pestanal®; naphthalene: Fluka, GC grade). The open ends of the Teflon tubing were heat sealed onto short (~40 mm long, 10 mm o.d.) solid glass capillaries, which served as stoppers (Figure 2.1). Duplicate permeation tubes were prepared for 1,2-dichlorobenzene; 1,2,4-trichlorobenzene; 2,3,4,6-tetrachlorophenol; and naphthalene, in order to determine the repeatability of this method, and to ensure that the heat seals were effective closures for the permeation tubes (loss of analyte through a leak at the seal would result in differences in permeation rates between the duplicate permeation tubes). In the case of 1,2,4-trichlorobenzene, short and long permeation tubes of the same compound were prepared (43 mm and 61 mm long, respectively).

The permeation tubes were stored in a temperature controlled room (20 ± 2 $^{\circ}$C), and were calibrated gravimetrically using a semi-micro balance (Mettler, readability of 0.01 mg) over a period of > 5000 hours.

2.2.2.2 Permeation tube usage

When using the permeation tubes as gas standards, the tubes of interest were placed in a cylindrical glass holder (body: 165 mm long with 25 mm o.d.; end connections: 40 mm long with 9 mm i.d., Figure 2.2) and allowed to equilibrate without air flow. Clean air (laboratory air which had passed through an activated charcoal bed) was drawn through the holder followed by the silicone rubber trap(s) at a defined flow rate (~500 mℓ.min^{-1}). In this manner, a known concentration of each analyte was loaded onto the sample trap.

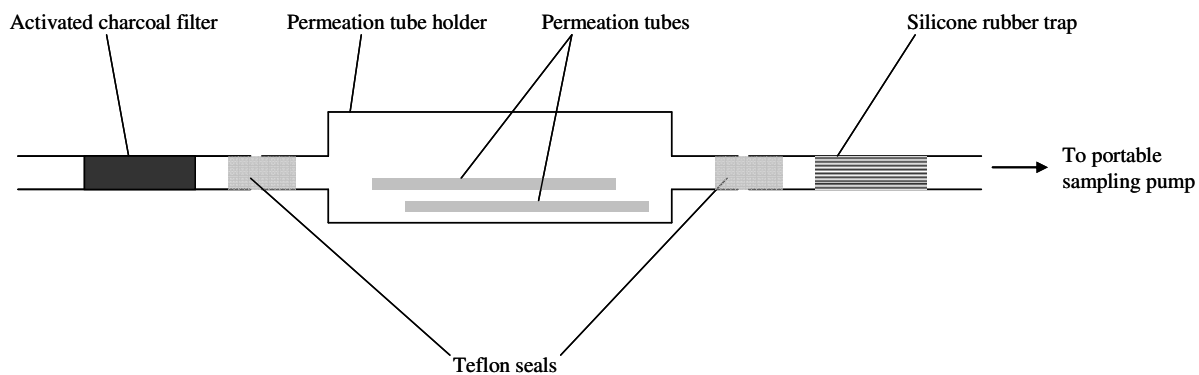Figure 2.1: Examples of chlorobenzene permeation tubes.

Figure 2.2: Usage of permeation tubes.

2.2.3 Results and discussion

The permeation rates, as determined gravimetrically for each permeation tube, are given in Table 2.1.

Table 2.1: Permeation rate of analytes through Teflon permeation tubes.

Compound	Molar mass (g.mol^{-1})	Purity (%)	Vapour pressure (Pa)	Average permeation rate (ng.min^{-1})	r^2
Chlorobenzenes					
Chlorobenzene[a]	112.6	99.9	1.57 x 10^3 (at 25 ^{o}C)	41.7	0.986
1,2-dichlorobenzene (A)[a]	147.0	99.9	160 (at 20 ^{o}C)	9.62	0.997
1,2-dichlorobenzene (B)[a]	147.0	99.9	160 (at 20 ^{o}C)	7.07	0.996
1,3-dichlorobenzene[b]	147.0	99.3	200 (at 20 ^{o}C)	18.3	0.992
1,2,4-trichlorobenzene (A; short)[b]	181.5	99.4	130 (at 20 ^{o}C)	6.92	0.984
1,2,4-trichlorobenzene (B; long)[b]	181.5	99.4	130 (at 20 ^{o}C)	18.3	0.981
1,2,3,4-tetrachlorobenzene	216.0	99.1	Not available	NSC	NA
1,2,4,5-tetrachlorobenzene	216.0	99.3	Not available	NSC	NA
Chlorophenols					
3-chlorophenol[b]	128.6	99.5	100 (at 44 ^{o}C)	NSC	NA
4-chlorophenol[b]	128.6	99.8	15 (at 20 ^{o}C)	NSC	NA
2,4-dichlorophenol[c]	163.0	99.4	16.0	2.33	0.982
2,4,5-trichlorophenol[c]	197.5	99.6	2.9	NSC	NA
2,3,6-trichlorophenol	197.5	98.9	Not available	NSC	NA
2,3,4,6-tetrachlorophenol (A)	232.0	99.9	Not available	NSC	NA
2,3,4,6-tetrachlorophenol (B)	232.0	99.9	Not available	NSC	NA
Pentachlorophenol[c]	266.3	99.0	0.019	NSC	NA
PAHs					
Naphthalene (A)[c]	128.2	99.8	10.4	NSC	NA
Naphthalene (B)[c]	128.2	99.8	10.4	NSC	NA

NOTES: NSC refers to "no significant change" and NA is not applicable.

[a] refers to vapour pressure data obtained from the material safety data sheets as provided by Sigma Aldrich.

[b] refers to vapour pressure data obtained from ChemDat ® (Merck, 1999).

[c] refers to vapour pressure data obtained from the Danish Environmental Protection Agency (2006) for Standard Temperature and Pressure.

The permeation rate graphs for all the compounds which showed a significant mass loss are also presented in Figures 2.3 to 2.6 (i.e. chlorobenzene; 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,2,4-trichlorobenzene and 2,4-dichlorophenol). Permeation rates were considered to be insignificant for the purpose of gas standard generation when permeation rates were < 1 ng.min^{-1}.
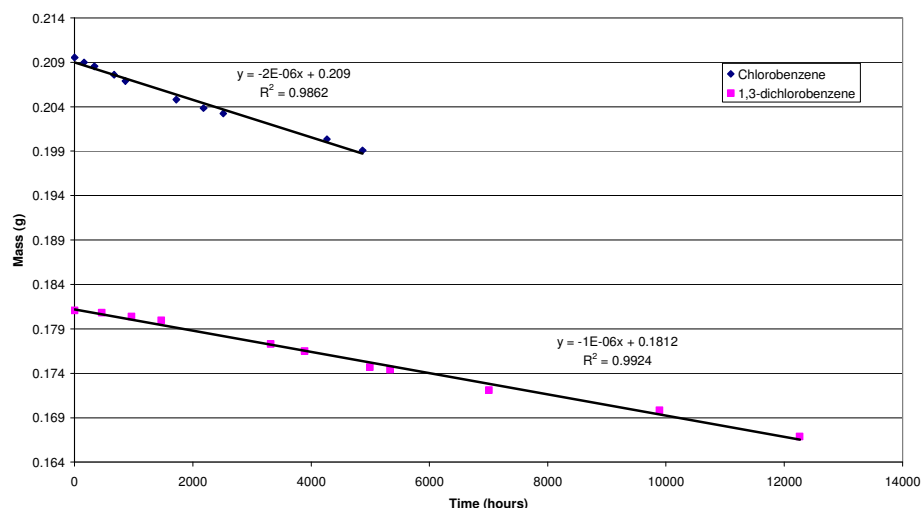

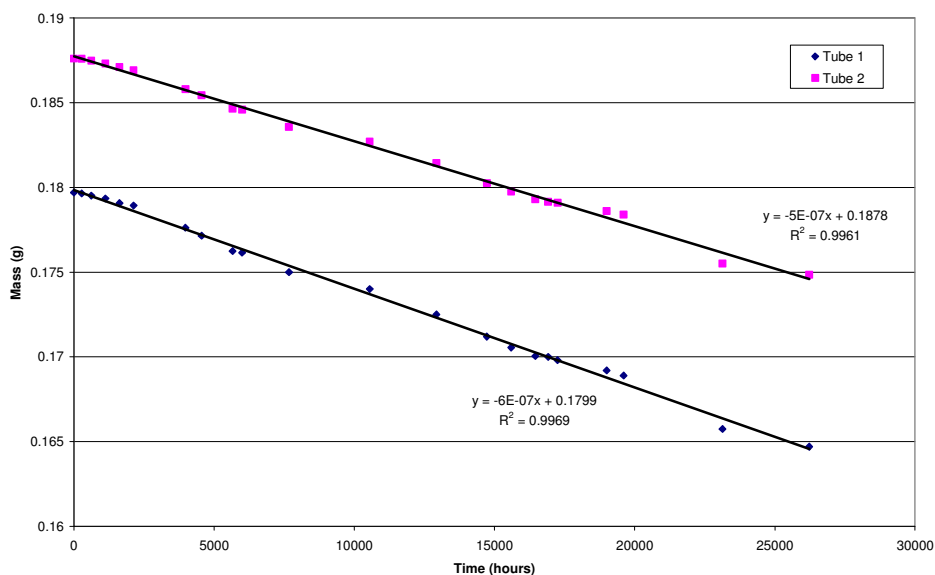Figure 2.3: Mass loss from the chlorobenzene and 1,3-dichlorobenzene permeation tubes.

Figure 2.4: Mass loss from the two 1,2-dichlorobenzene permeation tubes over ~26 000 hours.
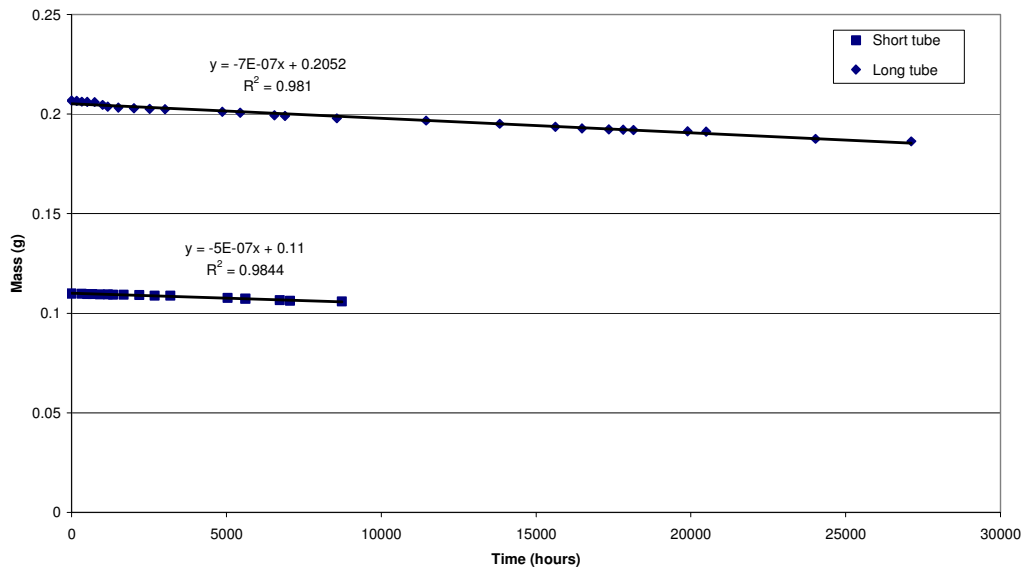
Figure 2.5: Mass loss from the short and long 1,2,4-trichlorobenzene permeation tubes.
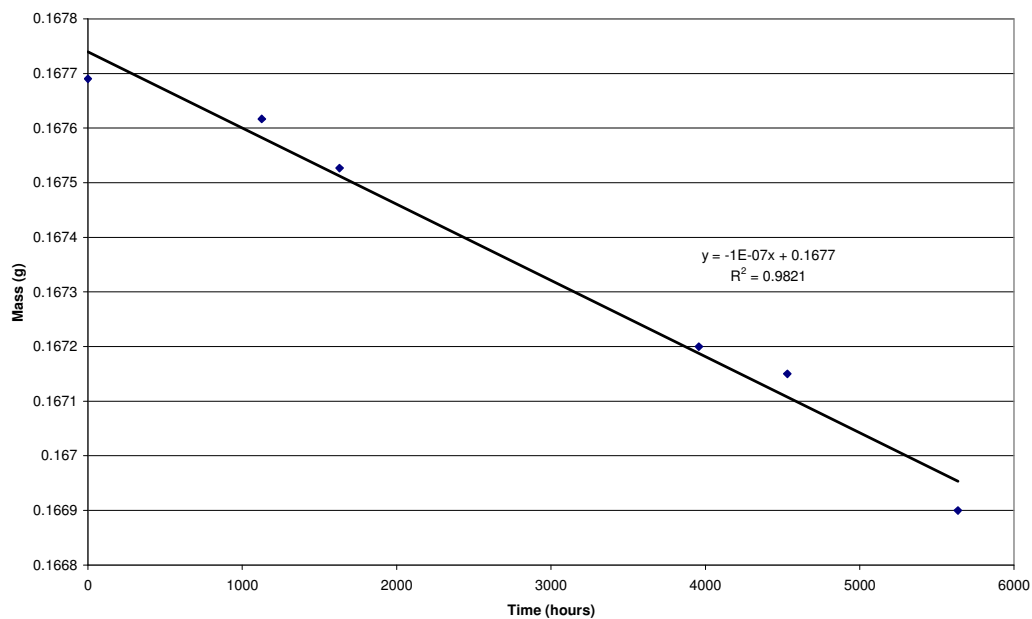

Figure 2.6: Mass loss from the 2,4-dichlorophenol permeation tube over ~5500 hours.

The mass loss of the permeation tubes for which permeation rates could be calculated was found to be relatively constant, as can be seen from the r^2 values in Table 2.1, which were all > 0.98. The permeation rates ranged from 2.3 to 42 ng.min^{-1}.

23

Due to the very slow rate of permeation of naphthalene, one of the permeation tubes (A) was sandpapered to reduce the wall thickness, i.e. *L* in equation 2.1, which should have increased the permeation rate. However no significant change in the permeation rate occurred, as no significant change in the mass of the permeation tube could be detected.

The duplicate permeation tubes for 1,2-dichlorobenzene were of a similar order of magnitude and differed by 27 %. The permeation rate has a standard deviation of 20 %, however, based on the smallest mass loss of 0.05 mg recorded between readings for 1,2-dichlorobenzene, and a mass accuracy of 0.01 mg. The repeatability between the two 1,2-dichlorobenzene permeation tubes is therefore considered to be acceptable. There was no significant mass loss for the other two duplicate permeation tubes (naphthalene and 2,3,4,6-tetrachlorophenol). No losses from the heat seals were therefore evident.

For the two 1,2,4-trichlorobenzene permeation tubes of different lengths, the increased area of the Teflon tube in the case of the long permeation tube, increased the permeation rate almost three fold. This is expected from equation 2.1, as the area of the long tube was 1.4 times that of the short tube, and the walls of the long tube were thinner at one end due to stretching of the Teflon tubing during the heating stage of the permeation tube manufacture, which would have also increased the permeation rate.

2.2.4 Conclusion

Permeation tubes were not suitable for gas standard generation for naphthalene, the tetrachlorobenzenes, and most of the chlorophenols, as the rates of mass loss (permeation rates) were insignificant in these cases. It appears that the vapour pressure of the compound of interest needs to be greater than that of the trichlorobenzenes for permeation tubes to be a viable option for gas standard generation (approximately > 100 Pa at 20 $^{\circ}$C).

The duplicate permeation tubes for 1,2-dichlorobenzene were of a similar order of magnitude and differed by 27 %, whilst the standard deviation of the permeation rate for these tubes was ~20 %, based on the smallest mass loss between readings and the mass accuracy of the balance.

Reducing the diffusion length by sandpapering the wall of the naphthalene permeation tube did not significantly change the permeation rate, whilst increasing the permeation area by increasing the length of the permeation membrane (Teflon tubing) did result in a significant increase in permeation rate of 1,2,4-trichlorobenzene.

It can be concluded that permeation tubes are a cost effective means of generating portable gas standards of the more volatile trace organic air pollutants.

2.3 DIFFUSION TUBES

2.3.1 Theory

Diffusion tubes provide a simple and useful means of preparing a mixture of low concentrations of a vapour in a gas, which is based on the diffusion of the vapour from a tube of accurately known dimensions. The technique was originally used to determine diffusion data, but was then used to generate known concentrations of vapours in 1956 (Barratt, 1981). Diffusion tubes are often used for vapour generation from volatile organic liquids, however, they may also be applied to organic solids of sufficiently high vapour pressure.

Diffusion is the process which transports material from one part of a system to another as a result of random molecular motions and concentration gradients, in the absence of mixing (Cho et al., 1992).

Diffusion tubes consist of a reservoir of the pure compound of interest, which evaporates (or sublimates) under constant temperature conditions. The vapour thus generated diffuses along a capillary tube of known dimensions into a flowing gas stream. The rate of diffusion can be determined gravimetrically, and is used in conjunction with the flow rate of the diluent gas in order to calculate the vapour concentration in the resultant gas mixture.

The diffusion rate can also be calculated from theoretical considerations:

$$S = \frac{DMPA}{RTL} \ln \frac{P}{P-p}, \qquad \text{Equation 2.4}$$

where S is the diffusion rate in g.s^{-1}; D is the diffusion coefficient (cm^2.s^{-1}); M is the molar mass of the compound (g.mol^{-1}); P is the pressure in the diffusion cell at the open end of the capillary (atm); A is the cross-sectional area of the diffusion tube (cm^2); R is the molar gas constant (mℓ.atm.mol^{-1}.K^{-1}); T is the absolute temperature (K); L is the diffusion path length (cm), and p is the partial pressure of the diffusing vapour at temperature T (atm).

The diffusion rate will only become constant once steady-state conditions have been reached.

This can be estimated from the function (Altshuller and Cohen, 1960):

$$t > \frac{L^2}{2D},$$
$\qquad\qquad$ Equation 2.5

where t is the total time for steady-state conditions to be reached, in seconds.

The diffusion rate can be changed by altering the length or bore of the capillary after sufficient time has been allowed for re-equilibration after such changes have been made. Alternatively, the flow rate of the diluent gas can be varied in order to adjust the volumetric concentration of the vapour of interest, although it is important that this flow rate does not result in turbulent flow regimes at the diffusion tube outlet, which would impact on the diffusion rate. The diffusion rate is also temperature dependant, thus temperature control is very important.

Various diffusion vessel geometries have been successfully utilized in different applications (Barratt, 1981; Namieśnik, 1984). The diffusion tube design used in this research for PAH standards is discussed under section 2.3.2. The use of these tubes was attempted for the PAHs, due to their lower vapour pressures, which prevented the use of permeation tubes for these compounds.

2.3.2 Experimental method

2.3.2.1 Diffusion tube preparation

The diffusion tube assembly consisted of a glass vessel (45 mm long, 8 mm i.d.), which was attached to a glass capillary (35 mm long, 6 mm i.d.) by means of a ground glass joint (Figure 2.7). The PAH standard of interest (naphthalene: Fluka, 99.8 % purity, GC grade; phenanthrene and pyrene: Supelco, 99.9 % and 96.6 % purity, respectively) was placed inside the vessel, and the capillary was then positioned and the joint tightly closed. The diffusion tube was allowed to equilibrate under temperature controlled conditions, and was then weighed at various time intervals to 0.01 mg (Mettler analytical balance).

Figure 2.7: Naphthalene diffusion tube.

2.3.2.2 Diffusion tube usage

The diffusion tube was placed in a glass diffusion chamber, which comprised two portions joined by a tightly sealed ground glass joint, as shown in Figure 2.8. This allowed for easy insertion and removal of the diffusion tube. The diffusion chamber consisted of both an inlet and outlet port for the diluent gas flow. Sufficient re-equilibration time was allowed after insertion of the diffusion tube into the diffusion chamber prior to usage of the device. A

battery operated portable sampling pump was used to draw air at ~ 500 mℓ.min^{-1} into the sample holder and then onto the silicone rubber trap, in order to load the trap with naphthalene, as shown in Figure 2.9.

The GC-MS laboratory room air was also sampled onto a trap for 5 and 60 min, respectively, at 477 mℓ.min^{-1} prior to TD-GC-MS analysis, in order to verify that all the naphthalene present on loaded traps originated from the diffusion tube. Laser laboratory room air was similarly sampled onto a clean trap for 85 min, after a laser induced fluorescence (LIF) scan had been recorded of the blank trap, as detailed in Chapter 3. After sampling, a LIF scan was recorded again. The trap was then end-capped, wrapped in aluminium foil and refrigerated prior to TD-GC-MS analysis.

The loaded silicone rubber traps were thermally desorbed using a thermal desorber system (TDS) (Gerstel TDS 3) and the desorbed analytes were cryogenically focused via a cooled injection system (CIS). The traps were desorbed from 0 °C (0.2 min) to 270 °C (2 min) at 120 °C.min^{-1} in the solvent vent mode (100 mℓ.min^{-1} until 0.2 min). Cryo-focusing of the PAHs was achieved using liquid nitrogen at -40 °C (0.5 min) followed by rapid heating at 12 °C. s^{-1} to 300 °C (1 min). The GC-MS system was an Agilent GC 7890A coupled to a Hewlett Packard 5975 inert XL electron ionisation/chemical ionisation (EI/CI) mass selective detector (MSD). The GC inlet was in the split mode (10:1) with helium (Ultra High Purity, Afrox) as the inlet gas. The flow rate through the column was 1.3 mℓ.min^{-1} at 40 °C. An Agilent HP5 (30 m x 250 µm x 0.25 µm) GC column was used and the column head pressure was 68.8 kPa using helium as the carrier gas. The GC oven was temperature programmed from 40 °C (1.5 min) at 20 °C.min^{-1} to 150 °C (0 min) and at 30 °C.min^{-1} to 300 °C (1 min). The GC-MS transfer line was at 300 °C, the mass scan range was 80-250 atomic mass units (amu), the solvent delay 6.8 min, and the electron multiplier voltage ~1070 V. Calibrations were performed with 1 µℓ naphthalene standard injections onto blank silicone rubber traps (100, 200 and 300 ng for the analysis of the GC-MS laboratory room air, and 50, 250, 500, 1000 and 2000 ng for the analysis of the laser laboratory air samples).

The limit of detection (LOD) of this TD-GC-MS method (CIS split of 10:1) was determined by the analysis of silicone rubber traps onto which 1 µℓ of PAH standards in toluene had been injected (0; 0.2; 1; 2; 4; 8; 20; 40 and 80 ng, respectively).
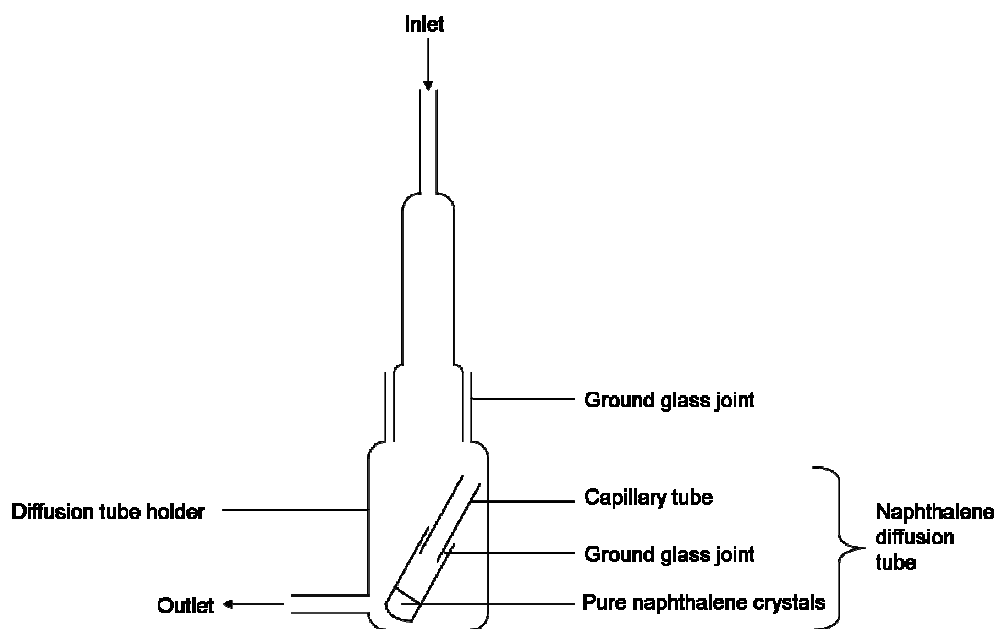
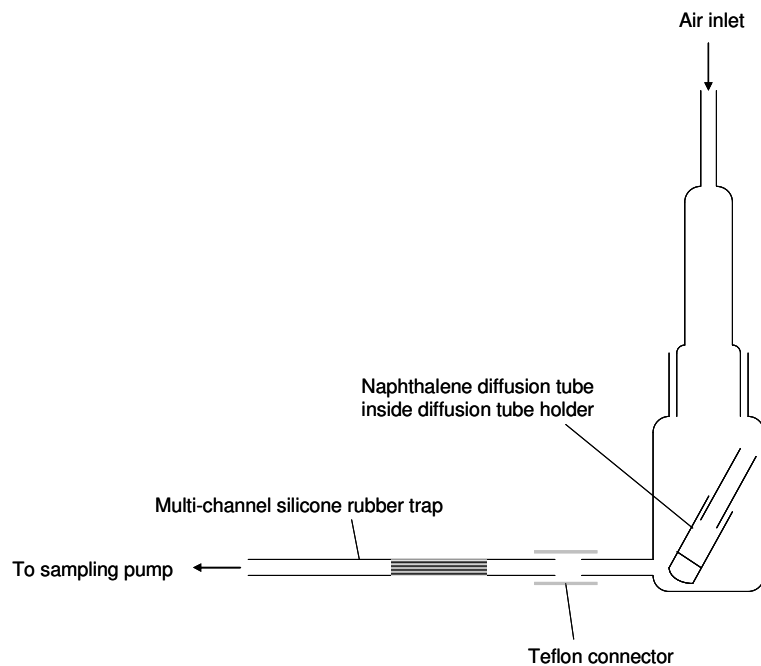Figure 2.8: Naphthalene diffusion tube inside the diffusion tube holder.

Figure 2.9: Use of the naphthalene diffusion tube to load a silicone rubber trap with gaseous phase standard.

2.3.2.3 Alternative diffusion tube orientation

The direction of air flow through the diffusion tube chamber was reversed, as shown in Figure 2.10, in order to determine whether the flow regime was inducing turbulent conditions, which would impact on the rate of diffusion. A trap was repeatedly loaded for a period of 5 min. TD-GC-MS analyses were performed using the method detailed under section 2.3.2.2, with 50, 100, 200 and 500 ng naphthalene standards and a sample CIS split of 100:1.
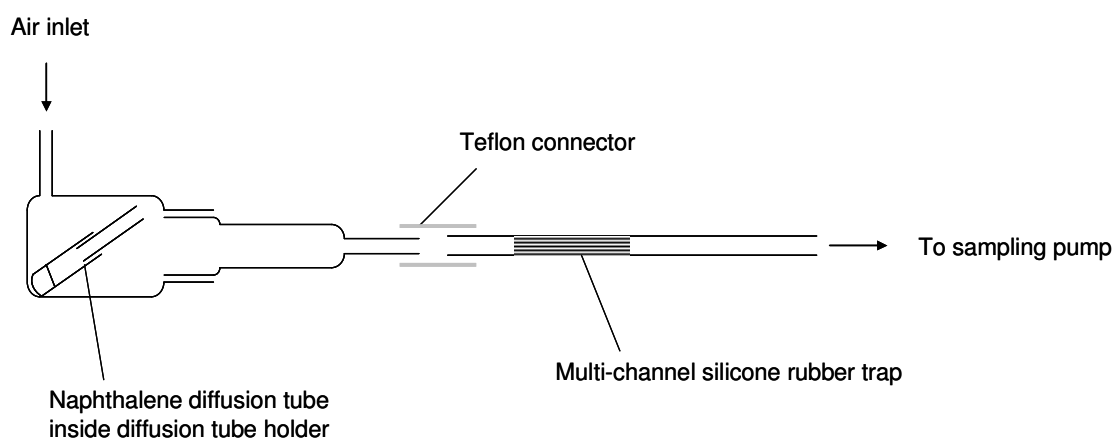
Air inlet

Teflon connector

To sampling pump

Multi-channel silicone rubber trap

Naphthalene diffusion tube
inside diffusion tube holder

Figure 2.10: Alternative diffusion tube configuration.

2.3.2.4 Evaluation of the effect of air flow on the rate of diffusion

The mass loss of the diffusion tube was determined over a period of 1096 min, whilst placed in the diffusion tube holder and connected to the sampling pump, operating at the usual sampling flow rate of 489 mℓ.min^{-1}, in order to determine whether there were any effects of air flow on the rate of diffusion.

2.3.3 Results and discussion

2.3.3.1 Theoretical calculations

From equation 2.4, diffusion rates were calculated for the diffusion tubes at 20 ^{o}C (due to availability of vapour pressure and diffusion rates at this temperature), and P = 0.859 atm (average atmospheric pressure in Pretoria, South Africa, as obtained from the National Metrology Institute of South Africa, 2007), with R = 82.06 mℓ.atm.mol^{-1}.K^{-1}, as presented in Table 2.2. An average value for the diffusion path length was used for fluoranthene for comparative purposes.

Table 2.2: Theoretical diffusion rates, for L = 35 mm.

Compound	D (cm^2.s^{-1})[#]	M (g.mol^{-1})	p (atm)[#]	S (ng.s^{-1})
Naph	0.069	128.2	1.03 x 10^{-4}	3.1
PhA	0.058	178.2	1.58 x 10^{-7}	5.5 x 10^{-3}
FlA	0.055	202.3	1.28 x 10^{-8}	4.8 x 10^{-4}
Py	0.055	202.3	6.02 x 10^{-9}	2.2 x 10^{-4}

[#] Obtained from the Danish Environmental Protection Agency (2006).

From these calculations, it is evident that the theoretical diffusion rate for naphthalene was in the low ng.s^{-1} range, whilst that for the other, less volatile PAHs were much lower at pg.s^{-1} levels.

The time required for steady-state conditions to be reached for each of the diffusion tube configurations was calculated from equation 2.5, and are shown in Table 2.3. Steady-state conditions would thus have been reached within 1 – 2 min.

Table 2.3: Time required for steady-state conditions to be reached for the PAH diffusion tubes.

Compound	t (s)
Naph	89
PhA	106
FlA	111
Py	111

2.3.3.2 Experimental results and discussion

The results obtained for the naphthalene diffusion tube over an extended period of ~250 days are presented in Figure 2.11. The linear trendline obtained from this data had an r^2 value of 0.95, which is a reasonable fit. The experimental diffusion rate can be obtained from the slope of this trendline, which was 7.0×10^{-6} $g.hr^{-1}$, or 1.9 $ng.s^{-1}$. This is in good agreement with the theoretical diffusion rate of 3.1 $ng.s^{-1}$ (refer to Table 2.2), even though there was a high mass ratio of the tube to its contents, and the diffusion path length was relatively short.
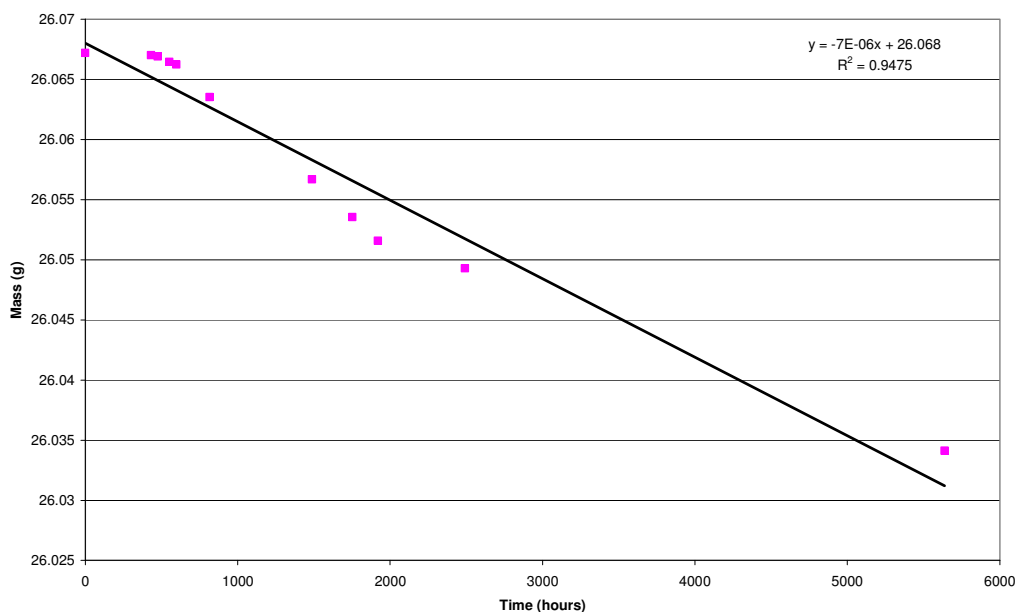

Figure 2.11: Experimental diffusion rate obtained for the naphthalene diffusion tube.

The LOD of the TD-GC-MS method was found to be <0.5 ng for each PAH, where the LOD was based on three times the standard deviation of the blank divided by the slope of the calibration graph for each PAH.

The GC-MS laboratory air loading experiments yielded concentrations of < 1 ng naphthalene after 5 min loading, and ~ 1 ng for a 60 min loading time (using a calibration curve of $y = 3.17 \times 10^3 x$ with $r^2 = 0.98$). There was no difference evident in the LIF spectra of the blank trap and the trap after sampling of the laser laboratory air for 85 min, and subsequent TD-GC-MS analysis of the trap revealed a concentration of 10 ng naphthalene (using a calibration curve of $y = 3.81 \times 10^3 x$ with $r^2 = 0.996$). It was therefore deemed unnecessary to pre-clean laboratory air prior to its passage through the diffusion tube. This had the advantage of not increasing the back pressure through the system.

The gravimetric results for the other two diffusion tubes (phenanthrene and pyrene) showed very low mass changes over an extended period, which made them unsuitable for use as trace gas standards in our study. The diffusion tube containing pyrene, for example, showed a 60 μg loss over a period of approximately 6.5 months; whilst the diffusion tube containing phenanthrene decreased by 120 μg over 5 months (relating to an experimental diffusion rate of 7×10^{-3} ng.s^{-1}). These low diffusion rates are in agreement with the diffusion rates determined theoretically, as shown in Table 2.2, as the diffusion rates were in the pg.s^{-1} range. Although a diffusion tube was not prepared for fluoranthene, the theoretical diffusion rate indicates that the diffusion rate would also be very low for this compound.

The chromatographic peak area for naphthalene doubled when the alternative diffusion tube configuration was employed (calibration curve of $y = 1.38 \times 10^4 x$ with $r^2 = 0.98$), which would indicate that the flow regime of the original configuration was more stable, and was therefore used for trap loading purposes. We ascribe the measured differences to the small length to diameter ratio of the diffusion tube, where even slight turbulence at the tube outlet can alter the diffusion rate of the analyte. This clearly means that wider and shorter tubes should not be used to increase the diffusion rate of the less volatile standards.

A diffusion rate of 2.1 ng.s^{-1} was found under air flow conditions, which is in good agreement with that obtained when there was no air flow, thus it was determined that the air flow was not disturbing the diffusion process.

2.3.4 Conclusion

The theoretical and experimental diffusion rates for the naphthalene diffusion tube showed good agreement, which indicates that the tube can be used as a trace gas standard for naphthalene. Although the capillary was relatively short (the area to length ratio was ~1 mm), constant diffusion rates were obtained.

Diffusion tubes proved to be unsuitable for gas standard generation of the less volatile PAHs (phenanthrene, pyrene, and fluoranthene), due to the very low diffusion rates obtained, which were below that required, and were also too low for accurate gravimetric determinations. This was verified by the theoretical calculations, which gave values in the pg.s^{-1} range for the configurations employed.

The diffusion tube holder geometry allowed for easy gas phase loading of sampling traps, whilst maintaining a constant rate of diffusion for naphthalene at the sampling flow rate of interest (~500 mℓ.min^{-1}).

2.4 PDMS TRAP LOADING VIA GAS CHROMATOGRAPHIC FRACTION COLLECTION

2.4.1 Background

In order to load the less volatile PAHs onto traps in the gas phase, an alternative method to permeation and diffusion tubes was needed. Although injection of a liquid standard onto a trap, followed by passing a fixed volume of nitrogen gas through the trap has been reported (Wauters et al., 2008), this method is not ideal for multi-channel silicone rubber traps in the laser induced fluorescence application developed in this study, as it is difficult to equally distribute a small volume of liquid over the 22 inlets of the silicone tubes. It was therefore decided to attempt to load these compounds onto traps by injecting known concentrations of

the individual liquid standard onto a GC column inside a GC oven with collection of the analyte vapour on a trap placed on the flame ionization detector (FID) tip. This method is essentially a chromatographic fraction collection technique, where knowledge of the retention time of the analyte under the GC conditions employed allowed for the collection of the analyte only, and not the solvent or other impurities. A similar method has been used to collect individual components of beer (Lim Ah Tock, 2008) and milk (Naudé et al., 2009) aroma, in this case for organoleptic evaluation of such fractions. The practicality of this collection method is based on the negligible pressure drop of the open tubular structure of the trap, which does not influence the flow rate through the GC column. It was necessary to optimize the experimental setup in order to minimize analyte loss and to maximize trapping efficiencies.

2.4.2 Experimental method

Liquid standards of the PAHs (naphthalene: Fluka, 99.8 % purity, GC grade; phenanthrene, pyrene, fluorene and anthracene: Supelco, 99.9 %, 96.6 %, 98.6 % and 99.0 % purity respectively, GC grade) were prepared in toluene (Riedel de Haen, GC grade, 99.7 % purity), and were manually injected onto an EQUITY^{TM}-5 fused silica capillary column (Supelco, 30 m x 0.25 mm x 0.25 μm) of an Agilent 7890A GC equipped with an FID, which was maintained at 250 ^{o}C. In order to minimize losses at the FID outlet, the top assembly of the detector, as well as the collector/insulator were removed and the multi-channel silicone rubber trap was connected directly to the flame tip by means of a small piece of Teflon tubing and was manually pressed into position at the appropriate time during collection runs. The FID is shown in Figure 2.12 and the experimental setup is presented in Figure 2.13.
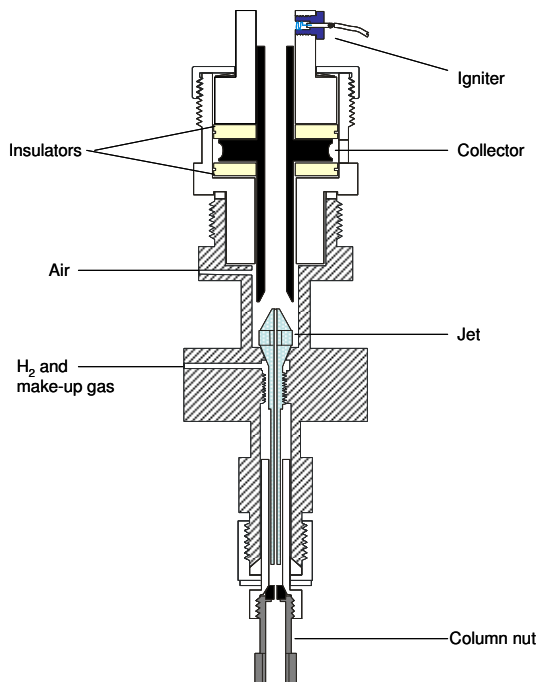
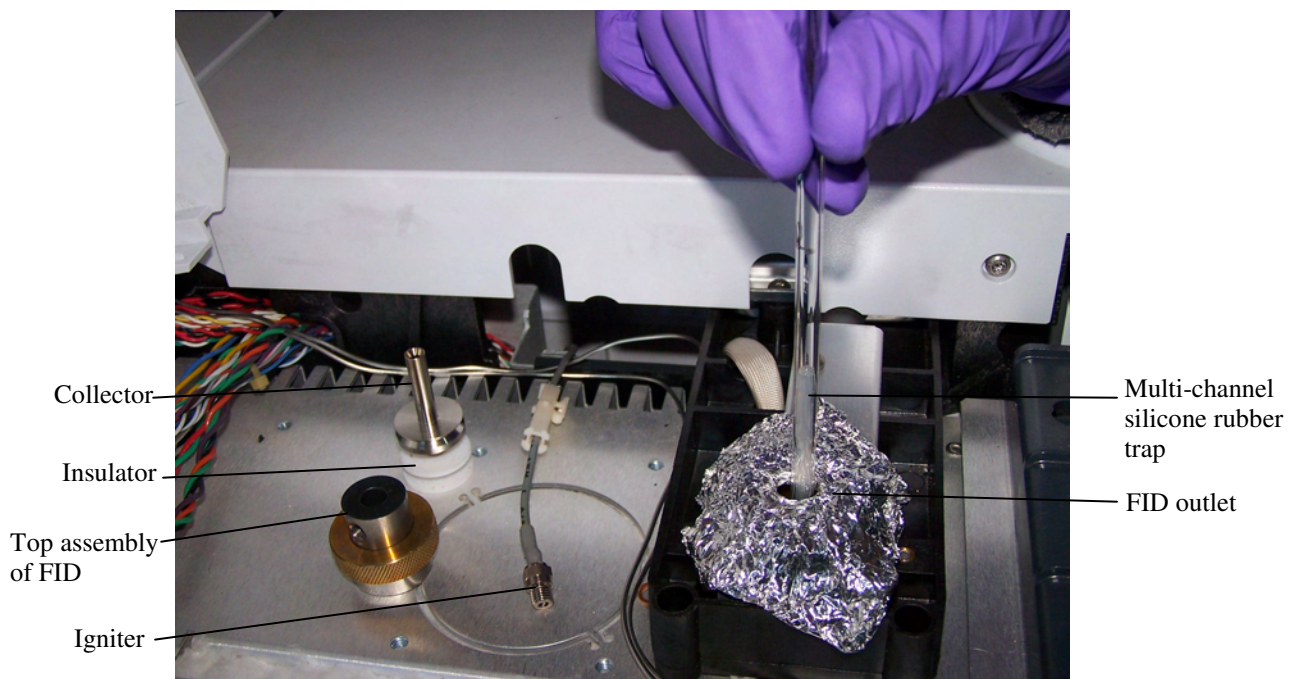Figure 2.12: Cross section of the Agilent FID (Agilent Technologies, 2008).

Figure 2.13: Experimental setup for the loading of PAHs onto multi-channel silicone rubber traps from the FID outlet. FID components which were removed from the detector are also shown on the left hand side of the figure.

The efficiency of loading was determined by comparison of TD-GC-MS peak areas obtained for GC loaded traps to that obtained for the direct injection of 1 µℓ of the mixed PAH standard (equivalent to 20 ng of each PAH) initially onto an empty glass tube and later onto a sample trap, as specified for each experiment. A similar TD-GC-MS method to that detailed in section 2.3.2.2 was used with a CIS split of 10:1, except for the analyses of traps relating to sections 2.4.2.1, 2.4.2.2 and 2.4.2.3, where the solvent vent mode was employed (100 mℓ.min^{-1} until 0.1 min). The desorption hold time at 270 ^{o}C was 10 min; the CIS final temperature hold time at 300 ^{o}C was 10 min and the initial GC hold time at 40 ^{o}C was 2 min for all samples.

2.4.2.1 Optimization of the FID make-up flow rate

20 ng of a mixed PAH standard (containing fluorene, anthracene, naphthalene, phenanthrene and pyrene) was injected as 1 µℓ using different FID make-up flow rates: 5; 10; 20; 50 and 100 mℓ.min^{-1}. Initially, after a hold time of 10 min at 40 ^{o}C, the GC oven was ramped to 150 ^{o}C at 20 ^{o}C.min^{-1} and then to 300 ^{o}C at 30 ^{o}C.min^{-1}. PAHs were collected onto a trap between 14 and 21 min and were analysed by TD-GC-MS using an empty glass tube for standard injection comparisons.

In later experiments, the hold time at 40 ^{o}C was decreased to 1.5 min, and the PAHs were collected from the FID outlet from 6 to 14.5 min after injection.

2.4.2.2 Repeatability

a) Initial experiments

Four traps were loaded using the method described under section 2.4.2.1 (10 min GC hold time at 40 ^{o}C). They were then end-capped and refrigerated overnight prior to TD-GC-MS analysis (using standard injections onto empty glass tubes for comparison purposes).

This experiment was then repeated (n = 4) with a slightly shorter PAH collection time from 15 to 21 min.

b) Optimised conditions

The loading method was optimized by shortening the inner Teflon spacer between the FID tip and the trap from 14 mm to 4 mm in order to prevent losses by bringing the trap into closer contact with the flame tip thereby minimizing cooling and contact with the Teflon. The system was checked for leaks by measuring the flow rate of the gas exiting the trap to that of the detector make-up and column flow rate (using a Porter Instrument Company B495 flow meter).

The repeatability experiment was then re-done using a mixed PAH standard (1 $\mu\ell$ of 20 mg.ℓ^{-1}), with the shorter initial GC hold time and collection at the FID outlet from 6 to 14.5 min after injection (n = 7). Collection efficiencies were determined upon comparison with standards injected directly onto silicone rubber traps.

2.4.2.3 Breakthrough experiments

During the repeatability experiments described under section 2.4.2.2, one trap was loaded whilst a second trap was positioned in series (connected to the primary trap by means of a short piece of Teflon tubing). The secondary trap was then analysed by TD-GC-MS, using injections of standards onto empty glass tubes for comparison.

This experiment was also repeated after optimization of the collection time and the FID connection.

2.4.2.4 Cooling of traps during loading

In order to determine whether losses during loading could be decreased by cooling of the trap, nitrogen vapour from a small liquid nitrogen dewar was directed onto the portion of the trap where the silicone rubber tubes are located (refer to Figure 2.14). Loading was performed with and without cooling 0; 2; 4 and 6 min after injection of 1 $\mu\ell$ of 50 μg.mℓ^{-1} naphthalene standard (i.e. the most volatile PAH was tested), with n = 2 for each time delay, and the peak areas were compared to direct loading onto a silicone rubber trap. The different time delays post loading were used in order to verify that no naphthalene was lost during the early stages of the process.
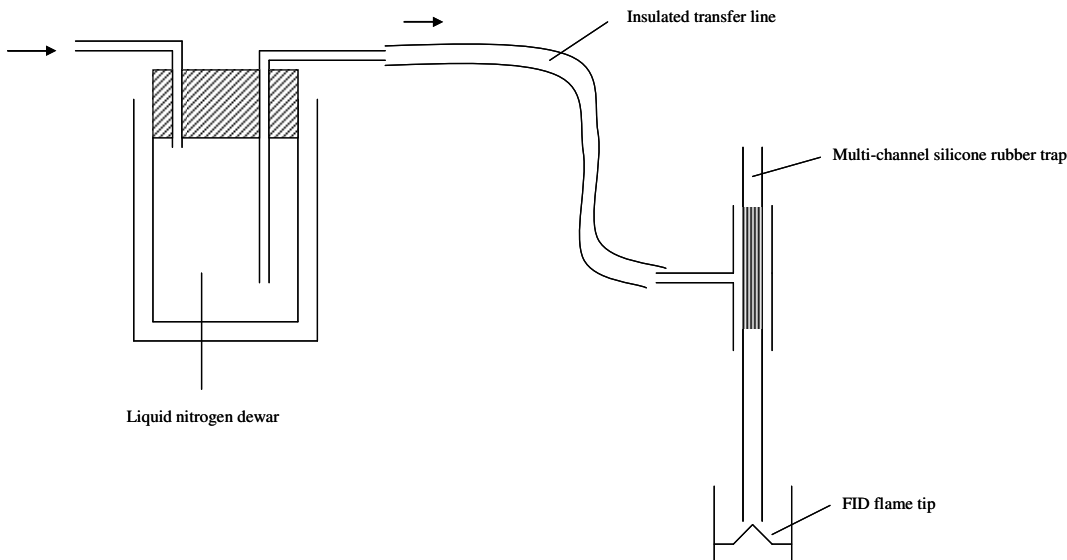
Insulated transfer line

Multi-channel silicone rubber trap

Liquid nitrogen dewar

FID flame tip

Figure 2.14: Liquid nitrogen cooling during gas chromatographic loading.

2.4.2.5 Stability of loaded traps

In order to determine whether traps could be loaded with phenanthrene and pyrene the day before they were required as standards for analytical method development, five traps were loaded from the FID outlet with phenanthrene and pyrene, respectively (1 $\mu\ell$ of 100 μg.mℓ^{-1}) according to the procedure described under section 2.4.2.1, with the shorter initial GC hold time at 40 $^{\circ}$C and with a three min hold time at 300 $^{\circ}$C. The PAHs were collected onto the traps from 8 to 13 min, after which they were analysed by TD-GC-MS. The results were compared to the analysis of five direct injections of a standard solution (1 $\mu\ell$ of 100 μg.mℓ^{-1}) onto a silicone rubber trap. Three traps were then loaded again with phenanthrene and pyrene, respectively. These traps were end-capped and stored in the refrigerator overnight. They were analysed the next day by TD-GC-MS, and the results were compared to that of direct injection onto a trap.

2.4.3 Results and discussion

When the system was checked for leaks, by measuring the flow rate of the gas exiting the trap to that of the detector make-up and column flow rate, no losses were evident.

2.4.3.1 Optimization of the FID make-up flow rate

The results of these experiments are presented in Figure 2.15. It was decided to proceed with make-up flow rates of 50 mℓ.min^{-1}, as this appeared to give the best recoveries in most cases, particularly for phenanthrene and pyrene, for which gas standard loading was most needed.
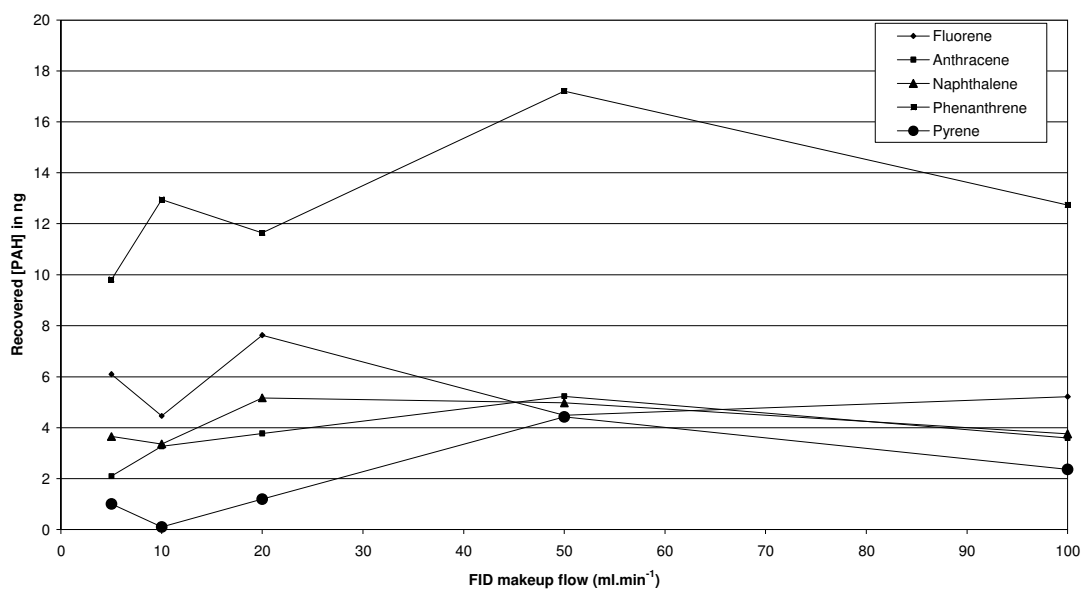
Figure 2.15: Recovery of 20 ng of individual PAHs from multi-channel silicone rubber traps after gas chromatographic loading of a mixed standard using different FID make-up flow rates.

2.4.3.2 Repeatability

a) Initial experiments

The results of the two sets of repeatability experiments are presented in Table 2.4. The delayed collection time improved the repeatability for most of the PAHs, except phenanthrene and pyrene, but decreased the collection efficiency in most cases. It was evident that the collection efficiencies and repeatability required further optimization.

40

Table 2.4: Percentage recoveries for PAHs from GC loading of a 20 ng mixed standard, using different traps and different collection times.

PAH	Trap A	Trap B	Trap C	Trap D	Average % trapped	% RSD
14-21 min collection, n = 4						
Fluorene	44	35	54	33	41	23
Anthracene	12	18	33	22	21	41
Naphthalene	21	28	39	52	35	38
Phenanthrene	64	68	80	50	66	19
Pyrene	27	48	79	53	52	41
15-21 min collection, n = 4						
Fluorene	26	23	33	25	27	17
Anthracene	27	19	33	26	26	22
Naphthalene	34	19	31	27	28	24
Phenanthrene	74	42	53	72	60	26
Pyrene	40	18	56	40	39	40

b) Optimized conditions

The results of the later set of experiments under optimized conditions (as detailed in section 2.4.2.2 (b)) are presented in Table 2.5.

Table 2.5: Percentage recoveries for PAHs from GC loading of a 20 ng mixed standard using optimized collection conditions.

PAH	Average % trapped	% RSD
6-14.5 min collection, n = 7		
Fluorene	61	12
Anthracene	71	27
Naphthalene	57	14
Phenanthrene	52	18
Pyrene	61	16

It is evident that the recoveries had improved compared to the initial experiments, with the exception of phenanthrene, and that the repeatability had improved.

2.4.3.3 Breakthrough experiments

The peak areas obtained for the secondary trap for each PAH are given in Table 2.6, from which it is evident that breakthrough from the primary trap was minimal (< 1 %).

Table 2.6: Breakthrough of PAHs from the primary trap upon GC loading of a 20 ng mixed standard with a make-up flow rate of 50 mℓ.min^{-1}.

PAH	Primary trap peak area	Secondary trap peak area	% breakthrough
Fluorene	94691	73	0.08
Anthracene	72711	462	0.64
Naphthalene	60610	405	0.67
Phenanthrene	255669	1421	0.56
Pyrene	21751	151	0.69

No significant breakthrough was also found when the experiment was repeated under optimized conditions, as the peak areas found on the secondary trap for each PAH were all less than 0.75 % of the primary trap.

2.4.3.4 Cooling of traps during loading

The results of the experiments conducted with and without cooling are presented in Table 2.7. It is evident that cooling did not improve recoveries, but actually had a negative impact. Cooling was therefore deemed unnecessary and was not used in the final method. The collection efficiency was poorer for earlier (and therefore longer) collection times, which was most likely due to the breakthrough volume of naphthalene on the trap being exceeded under these conditions, leading to loss of the analyte. Collection was therefore only conducted from 6 min after injection in the final loading method.

Table 2.7: Effect of trap cooling on analyte recoveries and repeatability during GC loading (n = 2 for each time interval).

Delay between injection & loading (min)	0	2	4	6	Direct injection onto trap
With cooling					
% recovery	30	47	43	51	100
% RSD	50	9	16	14	8
Without cooling					
% recovery	35	66	76	75	100
% RSD	40	24	1	1	9

2.4.3.5 Stability of loaded traps

The results of these experiments are summarized in Table 2.8. The recovery of GC loaded traps was ~50 % for both phenanthrene and pyrene when compared to direct injection, and the recovery did not decrease significantly when the loaded traps were stored overnight. The repeatability was generally good, with % RSDs of less than 15 %, with the exception of the stored phenanthrene traps, which had a % RSD of 29 %. This may have been improved by increasing the number of stored traps analysed.

Table 2.8: Effect of storage of GC loaded traps on analyte recoveries.

PAH	Direct loading n = 5	GC loading, immediate analysis n = 5	GC loading, stored overnight n = 3
Phenanthrene			
Average peak area	173 635	94 865	87 824
% RSD	6	10	29
% recovery	100	55	51
Pyrene			
Average peak area	172 019	85 360	92 944
% RSD	11	12	5
% recovery	100	50	54

2.4.4 Conclusion

It was found that there were no detectable gas leaks from the experimental setup described, and that an FID make-up gas flow of 50 mℓ.min^{-1} was best for loading purposes. Repeatability experiments revealed that % RSDs of < 20 % were possible with a short Teflon connection between the FID outlet and the silicone rubber trap. Analyte was collected over a period of ~8 min and recoveries were 57; 52; and 61 % for naphthalene, phenanthrene, and pyrene, respectively, based on loading of 20 ng of each PAH via a 1 $\mu\ell$ injection of a mixed standard. As the repeatability was fairly good, correction for losses can be made by injection of a larger amount of analyte. It is possible that losses occur via the mandatory septum purge flow on the split/splitless injector. It was verified that complete analyte desorption occurred during TD-GC-MS analysis, as no significant concentrations of the PAHs of interest were detected upon a second desorption analysis, therefore losses due to incomplete desorption are not likely.

Experiments on the effect of the presence of solvent in traps analysed by TD-GC-MS indicated an increase in peak area with increase in solvent volume up to 20 $\mu\ell$ and even resulted in peak splitting in some cases. Solvent injection volumes onto traps or empty tubes, as appropriate, were therefore maintained at 1 $\mu\ell$ for calibration and comparison purposes, although it is possible that this effect contributed to the perceived losses.

No significant breakthrough occurred for any of the PAHs investigated under the loading conditions employed, as evidenced from the analysis of a secondary backup trap. Cooling of the trap during loading did not improve recoveries and storage overnight did not significantly decrease the recoveries obtained.

It was later found that slight carryover between loading runs was occurred in some cases (refer to Chapter 3, section 3.2.3), therefore it is advisable to bake out the system between loading events.

The loading of PAHs, specifically phenanthrene and pyrene, via GC injection of liquid standards and collection of the vapours on the GC outlet was therefore shown to be a viable means of loading less volatile analytes onto the silicone rubber traps in the vapour phase. This method allowed for the comparison of LIF and GC-MS analyses of the less volatile PAHs, as described in Chapter 3, and is cost effective for laboratories equipped to analyse the analytes of interest, where standards and GC equipment is available. It offers the additional advantage of loading analytes after capillary chromatographic purification in cases where high purity standards are not readily available and may find application in other spectroscopic studies.

2.5 OVERALL CONCLUSION

In trace gas analysis, it is important that reliable gas standards can be produced at concentrations which are appropriate both in terms of the relevant applications as well as the method detection limits. In addition, portability and cost are also important factors. Various means of generating gas standards have therefore been developed.

In our study, the permeation tubes we prepared were found to be a cost effective means of providing portable gas standards for the more volatile trace organic air pollutants, such as chlorobenzene and the dichlorobenzenes, with permeation rates in the range of a few to ~40 ng.min^{-1}. Constant permeation rates were obtained within a month from manufacture, and duplicate tubes had permeation rates of a similar order of magnitude. Storage of the permeation tubes adjacent to activated charcoal or inside a fumehood is necessary, as permeation is a constant process.

Of the PAHs which were investigated, only the naphthalene diffusion tube had a sufficiently high rate of diffusion to be of experimental use in our studies ($\sim$2 ng.s^{-1}). Good correlation was found in this case between the theoretical and experimental diffusion rates, which was not altered by the flow of gas through the diffusion tube holder. Steady-state conditions were calculated to be attained in under 5 min. Diffusion tubes are therefore a useful, cost-effective and portable means of generating gas phase standards for the somewhat more volatile trace organic air pollutants, but are not suitable for the heavier semi-volatile compounds. Storage considerations are also relevant here, as diffusion is a constant process, as for permeation.

Vapour loading of liquid injected analytes at the FID outlet of a GC via the fraction collection technique developed here proved useful for the PAHs which were less volatile than naphthalene, specifically phenanthrene and pyrene. Repeatability experiments revealed that % RSDs of < 20 % were possible and recoveries were of the order of 50-60 %, based on the loading of 20 ng of each PAH via a 1 $\mu\ell$ injection of a mixed standard. Possible reasons for the low recoveries include losses at the manual injection inlet during trap loading, or errors in comparing peak areas of FID loaded traps with peak areas obtained with liquid standards for recovery calculations. No significant breakthrough occurred from the multi-channel silicone rubber traps during loading for any of the PAHs investigated under the conditions employed. Although this method is not portable, it is cost effective for laboratories equipped to analyse the analytes of interest, where standards and GC equipment is available. It offers the additional advantage of loading analytes after capillary chromatographic purification in cases where high purity standards are not readily available.

It has been shown that the methods and devices investigated have different applications, based on the volatility of the analyte of interest. It is possible to generate gas standards using devices which are not costly and do not require sophisticated apparatus in manufacture or use, therefore they have potential application in developing countries for trace organic air pollutant method research and development, as well as implementation.

2.6 REFERENCES

Agilent Technologies, *Gas Chromatograph Detectors*, **2008**.

Altshuller, A.P. and Cohen, I.R., *Analytical Chemistry*, **1960**, *32* (7), 802-810.

Barratt, R.S., *Analyst*, **1981**, *106* (1265), 817-849.

Cho, K., Irvine, T.F. and Karni, J., *International Journal of Heat and Mass Transfer*, **1992**, *35* (4), 957-966.

Danish Environmental Protection Agency, **2006**, Guidelines on remediation of contaminated sites, Appendix 5.5 Physical and chemical data, accessed on 17 February 2006 at http://www.mst.dk/udgiv/publications

Lim Ah Tock, M.J., April **2008**, Aroma analysis of alcoholic beverages using multi-channel silicone rubber traps, MTech Thesis, Tshwane University of Technology.

Merck, **1999**, ChemDat ®, The Merck Chemical Database, 99'2, available on CD.

Mitchell, G.D., *Separation and Purification Methods*, **2000**, *29* (1), 119-128.

Naganowska-Nowak, A., Konieczka, P., Przyjazny, A. and Namieśnik, J., *Critical Reviews in Analytical Chemistry*, **2005**, *35*, 31-55.

Namieśnik, J., *Journal of Chromatography A*, **1984**, *300*, 79-108.

National Metrology Institute of South Africa, personal communication with Angelique Botha, **2007**.

Naudé, Y., van Aardt, M. and Rohwer, E.R., *Journal of Chromatography A*, **2009**, *1216* (14), 2798-2804.

O'Keeffe, A.E. and Ortman, G.C., *Analytical Chemistry*, **1966**, *38* (6), 760-763.

Scaringelli, F.P., O'Keeffe, A.E., Rosenberg, E. and Bell, J.P., *Analytical Chemistry*, **1970**, *42* (8), 871-876.

Temime, B., Francois, S., Monod, A. and Wortham, H., *Environmental Pollution*, **2002**, *120*, 609-616.

Wauters, E., Van Caeter, P., Desmet, G., David, F., Devos, C. and Sandra, P., *Journal of Chromatography A*, **2008**, *1190*, 286-293.