

Chapter 4

The use of multi-channel silicone rubber traps as denuders

4.1 INTRODUCTION

PAHs may be present in air samples both in the gaseous phase and adsorbed onto the surface of particles, where PAHs of molecular mass > 228 are found mainly in the particle phase (Kamens et al., 1986). It is important to be able to quantify the relative contributions of each of these phases of the analyte, as they may have different environmental impacts. This is of particular importance to human health toxicities, as deposition and uptake of inhaled toxic species depends on their phase distribution (Gundel et al., 1995 and Temime-Roussel et al., 2004). The environmental fates of semi-volatile organic compounds are also phase dependant, due to the fact that atmospheric reactions including photodegradation, as well as transport and deposition processes differ for vapour and particle phase species (Bidleman, 1988).

The partitioning of atmospheric semi-volatile organic compounds between the vapour phase and the particle phase is dependent on the vapour pressure of the compound, as well as on the amount of particles available, and can be described by a partition coefficient K_{vp} which varies with particle loading and has the dimensions of $[\text{particle}]^{-1}$ (Krieger and Hites, 1994);

$$K_{vp} = \frac{(F/TSP)}{A}, \quad \text{Equation 4.1}$$

where F is the particulate phase concentration of the compound in the atmosphere (in ng.m^{-3}); TSP is the total suspended particulate loading in the atmosphere (in $\mu\text{g.m}^{-3}$); and A is the vapour phase concentration of the compound in the atmosphere (in ng.m^{-3}).

The partition coefficient is a function of atmospheric temperature, T (Krieger and Hites, 1994);

$$\frac{d(\ln K_{vp})}{d(1/T)} = \frac{H_d}{R}, \quad \text{Equation 4.2}$$

where H_d is the energy required to desorb and vapourise the compound from the particle (in kJ.mol^{-1}), and is of similar magnitude to the compound's heat of vapourisation, and R is the gas constant.

Effective sampling of the two phases is needed to ensure that the analytes adsorbed onto particles which are volatilized upon re-equilibration (after collection onto filters, for example), are not lost from the sampling process (Eatough et al., 1993). Likewise, contact between particles and gas phase analytes should be minimized during sampling in order to prevent adsorption. Volatilization of organic analytes from collected particles may be minimized by ensuring a low pressure drop across the filter and by maintaining constant temperature conditions during sampling (Ligocki and Pankow, 1989).

Partitioning measurements based on high volume samplers containing a glass fibre filter which removes particles from the sample flow prior to adsorption of the gas phase analytes onto an adsorbent such as Tenax, or polyurethane foam (PUF), for example, may introduce analytical artifacts. These may arise from sorption of gas phase analytes onto the filter or particles; from desorption of analytes from the particles collected on the filter; or from reaction of the analyte with reactive species in the air, such as $\text{OH}\cdot$ or O_3 .

Prevention of analyte loss via reaction of PAHs with atmospheric oxidants has been accomplished by the use of "oxidant denuder systems", which are coated with water/glycerol KNO_2 solution in order to retain O_3 and oxidants (Tsapakis and Stephanou, 2005). Coutant et al. (1988) investigated the potential for PAH artifact formation due to volatilization and reaction with ozone. Losses from the filter (particulate phase) were evident during sampling

episodes in both the summer and winter months, but no evidence was found for the reaction of ozone with particles during the field sampling experiments.

The adsorption of gas phase analytes onto the filter medium can be significant and may be estimated from a second particle free backup filter. Ideally no gas phase analytes should adsorb onto either filter. The levels of PAHs of interest found on the secondary filter as a percentage of the primary filter concentrations which were obtained from such a study conducted in an urban residential area of the USA, are presented in Table 4.1.

Table 4.1: Levels of PAHs sorbed onto a glass fibre filter medium, as a percentage of that found on the primary filter (Ligocki and Pankow, 1989).

PAH	% of primary filter (mean \pm 1σ)
PhA	5.5 \pm 13
FlA	19 \pm 27
Py	12 \pm 18

The results of an urban air monitoring study based on a filter/PUF sampling system are shown in Table 4.2 for both winter and summer months, where a significantly lower total PAH concentration is evident for summer (Harrison et al., 1996). Although TSP concentrations were measured in the study, they were not reported.

Table 4.2: Winter and summer gas phase and particulate PAH concentrations, derived from filter and PUF sampling (Harrison et al., 1996).

PAH	Winter filter conc (ng.m⁻³)	Winter PUF conc (ng.m⁻³)	Total winter conc (ng.m⁻³)	Ratio PUF/filter for winter	Summer filter conc (ng.m⁻³)	Summer PUF conc (ng.m⁻³)	Total summer conc (ng.m⁻³)	Ratio PUF/filter for summer
Naph	0.69	12.55	13.24	18.19	0.14	1.73	1.87	12.36
PhA	1.08	23.03	24.11	21.32	0.25	3.59	3.84	14.36
FlA	1.17	11.19	12.36	9.56	0.35	1.76	2.11	5.03
Py	2.36	35.68	38.04	15.12	0.55	2.78	3.33	5.05

Park et al. (2002) noted that the contribution of the vapour phase component to the total PAH concentration exceeded that of the particulate phase by a factor of 2.3 in an urban air monitoring study conducted in Seoul. The particulate and vapour phase concentrations for the PAHs of interest are shown in Table 4.3. The total particulate loading was not given. The vapour to particulate PAH ratios are similar to those reported in Table 4.2, except for naphthalene where higher vapour concentrations were found in the study of Park.

The partitioning results of a similar study conducted in an urban residential area of the USA are shown in Table 4.4. It is evident that a higher proportion of the PAHs shown were present in the gas phase as compared to the study of Park et al. (2002), although the total [PAH] for each analyte was of a similar order of magnitude in the two studies.

Table 4.3: Gas phase and particulate PAH concentrations, derived from filter and PUF sampling (Park et al., 2002).

PAH	Particulate [PAH] (ng.m ⁻³)	Vapour [PAH] (ng.m ⁻³)	Total [PAH] (ng.m ⁻³)	Ratio of vapour [PAH]/particulate [PAH]
Naph	0.14	11.09	11.23	79.2
PhA	1.46	15.03	16.49	10.3
FIA	2.27	5.83	8.10	2.6
Py	2.25	10.31	12.56	4.6

Table 4.4: Gas phase and particulate phase PAH concentrations, derived from filter and PUF (primary and backup plug) sampling (Ligocki and Pankow, 1989).

PAH	Particulate [PAH] (ng.m ⁻³)	Vapour [PAH] (ng.m ⁻³)	Total [PAH] (ng.m ⁻³)	Ratio of vapour [PAH]/particulate [PAH]
PhA	0.28 ± 0.25	26 ± 10	26.28 ± 10.25	93
FIA	0.53 ± 0.31	7.9 ± 3.1	8.43 ± 3.41	15
Py	0.62 ± 0.37	6.7 ± 2.7	7.32 ± 3.07	11

Air samples in an urban and industrialized area of Prato (Italy) during 2002, gave an average total PAH concentration of 59.4 ± 26.5 ng.m⁻³, where a quartz fibre filter preceded two PUF plugs (Cincinelli et al., 2007). The total gas phase concentration was much higher

($45.5 \pm 23.9 \text{ ng.m}^{-3}$) than the total particle phase concentration ($14.0 \pm 5.58 \text{ ng.m}^{-3}$), due to the dominance of more volatile PAHs, particularly phenanthrene.

In a roadway tunnel study utilizing Teflon (or in some cases glass fibre) filters and PUF plugs, 88 % of the phenanthrene was in the vapour phase (184 ng.m^{-3}), as was 45 % of fluoranthene (25.6 ng.m^{-3}), and 49 % of pyrene (28.3 ng.m^{-3}) (Benner, 1989). It should be noted that the PAH concentrations were significantly higher in this impacted environment than those previously discussed in this section.

Denuders are sampling devices which have been effectively employed in partitioning applications. Their principle of operation involves the movement of molecules and particles as a result of two mechanisms (Kloskowski et al., 2002):

- a) movement in the direction of the gas stream, as a result of the gas flow
- b) movement perpendicular to the longitudinal gas flow, due to radial diffusion.

It is interesting to note that denuders were initially used to denude air particulate samples of gaseous components (Ali et al., 1989). In 1979, however, Ferm used an oxalic acid coated denuder as a gas sampling device to sample atmospheric ammonia, whilst interfering particle-borne ammonium ions passed through.

Separation in denuders is achieved as a result of gas phase analytes having high diffusion coefficients, thus they can be retained by a sorptive surface perpendicular to the gas flow (typically on the walls of a denuder). Particles, however, pass through the denuder, and can be collected on a downstream filter. A sorbent cartridge may be employed downstream of the filter, to trap analytes desorbed from the filter, and any gaseous analytes not removed by the denuder (under breakthrough conditions). Gravitational settling of particles is avoided by vertical placement of the denuder, and possible desorption of analyte from particles during transport through the denuder section should be minimized by short transit times (sufficiently high flow rates). The possible contribution of this desorption to the measurement uncertainty would also be small for the more volatile PAHs, for which the particle phase contribution to the total concentration is low (Gundel and Lane, 1998). Cyclones or impactors may be used to remove large particles from the sample gas stream before it enters the denuder system (Ali et

al., 1989 and Koutrakis et al., 1990), although the resulting high pressure drops across the sampling device may enhance evaporative losses from particles (Zhang and McMurry, 1991).

For denudation to be effective, it is important that the gas flow through the device is stable and laminar; and that the temperature distribution is uniform within the sampled gas stream. Steady state conditions of temperature and pressure are also necessary, and longitudinal diffusion of gaseous analytes should be negligible as compared to the linear gas flow velocity (Kloskowski et al., 2002). The sorption material employed should effectively sorb the analytes (they should provide infinitely large, perfect sinks for the analyte), and no chemical reactions and transformations of sorbed analytes should occur (both during the sampling and desorption stages).

In order to ensure laminar flow conditions as well as to allow for sufficient residence time in the denuder, to allow for molecules to diffuse to the denuder walls, low flow conditions are required ($< 20 \text{ l.min}^{-1}$, as compared to high volume samplers which operate at around 1000 l.min^{-1}) (Krieger and Hites, 1994).

A number of denuder geometries have been developed, with cylindrical and annular denuders being the most widely reported (Figures 4.1 and 4.2). Cylindrical denuders consist of a tube with the inner walls providing a sorptive surface, whilst annular denuders contain an additional internal cylindrical rod which provides a larger sorptive surface (Possanzini et al., 1983). This additional surface allows for annular denuders to be almost an order of magnitude shorter than cylindrical denuders ($\sim 0.20 \text{ m}$ versus $\sim 2 \text{ m}$). Coiled cylindrical denuders have also been tested, which improves mass transfer to the sorptive surface coated wall, and thus allows for a reduction in length of the denuder (Pui et al., 1990).

Conventional commercial denuders are usually coated with a sorptive medium which requires replacement after a period of time. They are typically solvent extracted prior to analysis.

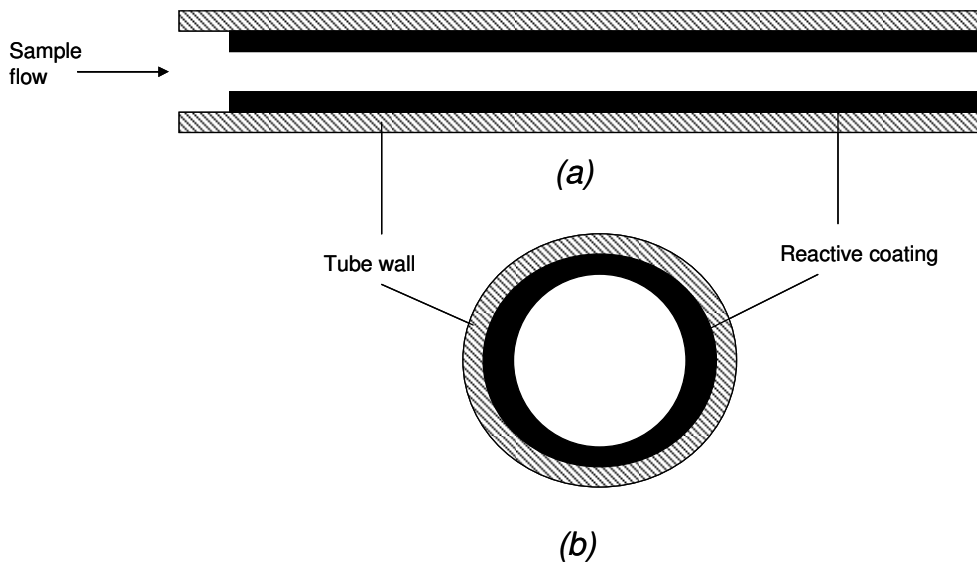


Figure 4.1: Schematic diagram of a cylindrical denuder from a longitudinal (a) view and in cross-section (b) (adapted from Ali et al., 1989)

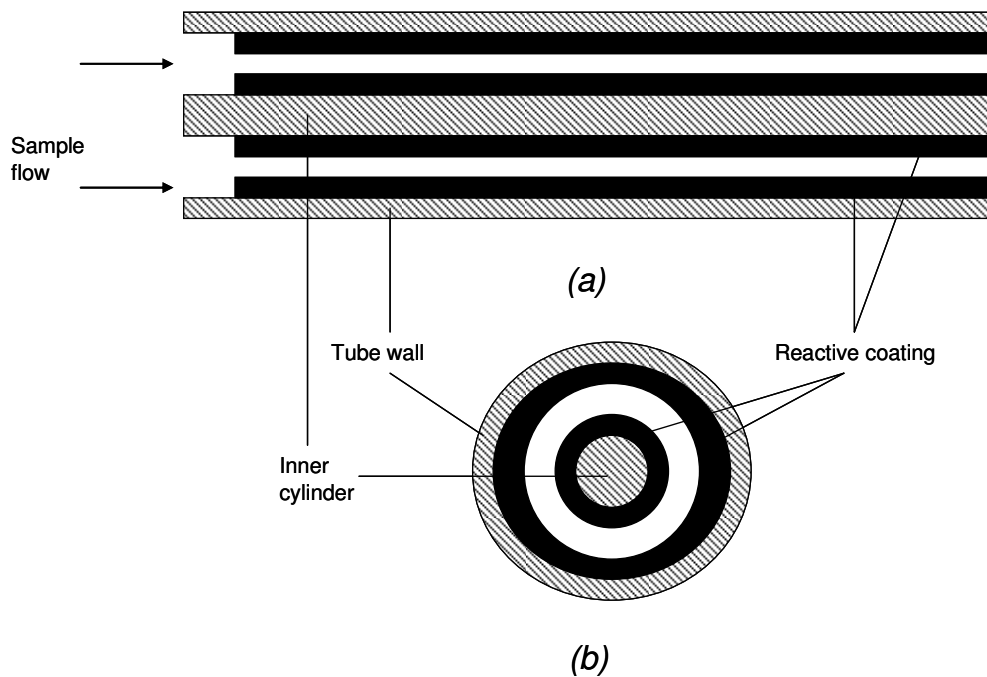


Figure 4.2: Schematic diagram of an annular denuder from a longitudinal (a) view and in cross-section (b) (adapted from Ali et al., 1989)

A high-volume compound annular denuder (consisting of a series of 12 nested denuders, 0.20 m long with an overall outer diameter of 80 mm) was developed for the collection of PAH vapour, which utilized high-vacuum silicone grease as a sorptive medium (coating thickness of 4-100 μm) (Coutant et al., 1989). SE-30 and silicone pump oil had also been tested by these authors, but the SE-30 was found to gradually oxidize upon exposure to air, hindering collection efficiency; and the silicone oil coating was too thin, which decreased the capacity of the device. The compound annular design is rather large and cumbersome, and contamination from impurities in the silicone grease employed in the final design could be of concern.

Compound annular denuders are now available commercially, and these devices have been evaluated for PAH sampling (Temime et al., 2002 and Temime-Roussel et al., 2004). In both these studies and those of Coutant et al. (1989), naphthalene was used as a reference compound in evaluating denuder performance, due to its high volatility, and thus lower collection efficiency than PAHs of lower volatility (Gundel et al., 1995). Any overestimation of the denuder collection efficiency is therefore avoided, and results may be considered as minimum trapping efficiencies for PAHs in general (Temime et al., 2002).

In later studies by Coutant et al. (1992), the silicone grease coated annular denuder was tested for additional PAHs, including phenanthrene and pyrene. A filter placed upstream of the denuder was spiked with perdeuterated PAH standard solutions (200 ng from each 5 $\text{ng}\cdot\mu\ell^{-1}$ PAH standard), which were transferred onto the denuder and XAD trap by means of high purity air flow at 7 $\ell\cdot\text{min}^{-1}$ for 4 hours. The filter, denuder and XAD were then analysed and good repeatability in collection efficiencies (which were between 81 and 94 %, all with $\text{RSD} < 5 \%$) were found for four PAHs.

In the study of Temime-Roussel et al. (2004), the denuder tube was coated with crushed and solvent cleaned Amberlite XAD-4 styrene-divinylbenzene polymer resin, which followed on from previous work by Gundel et al. (1995). The cleaning step is crucial, due to the impurities known to be present in this resin, including naphthalene and its derivatives, thus multiple cleaning steps are required before clean blanks are obtained (Gundel et al., 1995). The resin was applied to the denuder as a slurry in hexane, which could also introduce impurities into the sampling system. After sampling, solvent extraction (30 min), filtration

and pre-concentration sample preparation steps were needed prior to HPLC analysis with fluorescence detection. Collection efficiencies of above 90 % were obtained under a range of environmental and sampling conditions (temperature; relative humidity; gas phase concentration; sampling flow rates; and sampling duration) (Temime-Roussel et al., 2004). It is evident that the main problems of this method are the contamination issues and time consuming denuder preparation and sample extraction processes.

A composite cylindrical denuder, composed of a collection of capillary gas chromatography columns as the sampling tubes, was tested for use in atmospheric PAH (and polychlorinated biphenyls (PCBs)) sampling, as compared to that using a PUF sampler (Krieger and Hites, 1992 and 1994). The denuders were between 15 and 0.5 m long, and the capillary column used was 530 μm i.d. with 8 μm thick methylsilicone stationary phase. Initial experiments utilized 5 μm thick DB-1 fused silica capillary column segments, bonded together with epoxy resin. This yielded a sampling device of 2.4 $\text{m}\ell$ internal volume (operated at 1.5 $\ell.\text{min}^{-1}$) (Krieger and Hites, 1992), which is a factor of 10 larger than that of the silicone rubber trap used in our study (0.23 $\text{m}\ell$). The results obtained from the denuder were not statistically different to those of the PUF sampler, however, a liquid extraction and sample cleanup procedure had to be employed, as the denuder (epoxy resin) was not resilient to thermal desorption conditions (Krieger and Hites, 1994).

The silicone rubber trap used in our study effectively retains gaseous organic analytes whilst transmitting particulates, due to its open geometry allowing laminar air flow. Thus the addition of a downstream particle filter and second denuder (to capture desorbed analytes from the particulates on the filter) would allow for both gaseous and particle phases of PAHs to be separately sampled.

The suitability of these traps as denuders was therefore investigated from a theoretical perspective, as detailed in this Chapter, and then in a number of applications, which are discussed in Chapter 5.

4.2 THEORETICAL CONSIDERATIONS

In order to determine whether the multi-channel silicone rubber trap had potential to perform as a denuder, a number of theoretical calculations were performed to ensure that the requirements for denudation could be met in this sampling device. The silicone rubber trap would be classified as a composite cylindrical type denuder, with each of the 22 silicone tubes effectively performing as a cylindrical denuder (Kloskowski et al., 2002). The non-circular inter-tube channels were ignored in the first calculations to estimate flow conditions inside the composite denuder.

4.2.1 Verification of laminar flow

As discussed under section 4.1, laminar flow is a prerequisite for denudation. The Reynolds number (R_e) relating to the gas flow conditions in the silicone rubber tubes of the traps was therefore calculated as follows.

$$R_e = \frac{VD}{\nu}, \quad \text{Equation 4.3}$$

where V is the linear velocity; D is the internal diameter of the silicone tubes; and ν is the kinematic viscosity.

Further, ν can be determined from

$$\nu = \frac{\mu}{\rho}, \quad \text{Equation 4.4}$$

where μ is the dynamic viscosity; and ρ is the gas density.

Using typical values of $\mu = 1.87 \times 10^{-5} \text{ kg.m}^{-1}.\text{s}^{-1}$ and $\rho = 1.168 \text{ kg.m}^{-3}$ for air at 25 °C and 1 atm, a kinematic viscosity of $1.60 \times 10^{-5} \text{ m}^2.\text{s}^{-1}$ is obtained.

For a sampling flow rate of $500 \text{ m}\ell.\text{min}^{-1}$ through a 22 channel trap, with the internal diameter (i.d.) of the silicone tubes being 0.3 mm; the linear velocity per silicone tube is 5360 mm.s^{-1} . This is a worst case, “high velocity” scenario, where it is assumed that the entire sample flow passes at the same flow rate through each of the silicone tubes only, and not

through any spaces between tubes. This is based on the assumption that each tube is equivalent and that no perturbations in the tube geometries, such as kinks or twists, occurred during trap manufacture.

A Reynolds number of 101 is thus obtained from equation 4.3. As mentioned, this is a worst case scenario, where the linear velocity does not account for a decreased flow rate through the inside of the silicone tubes as a consequence of a portion of the gas flowing through the spaces between the tubes. If the total open cross sectional area of 4.1 mm² for a quartz tube of 3.5 mm i.d. containing 22 silicone tubes of 0.64 mm outer diameter is used, a linear velocity inside the silicone rubber tubes of 2030 mm.s⁻¹ would be obtained, which would yield an even lower R_e of 38.

In both cases, R_e satisfies the condition for laminar flow that $R_e \ll 2300$, thus it can be concluded that the gas flow is laminar in the silicone rubber trap. The low R_e would minimize impaction of large particles on the walls of the denuder.

It should be noted that laminar flow conditions would be achieved a short distance l , from the trap inlet. For a tube of diameter d (Ali et al., 1989):

$$l = 0.07dR_e \quad \text{Equation 4.5}$$

In the case of the silicone tubes, $d = 0.3$ mm and $R_e = 101$. This yields a length of 2.1 mm from the inlet of the silicone rubber tubes, after which laminar conditions would be established. The non-laminar portion accounts for < 5 % of the total length of the silicone tubes (55 mm).

4.2.2 Verification of negligible linear velocity arising from longitudinal diffusion

In order to verify that the contribution of longitudinal diffusion to linear velocity is negligible compared to the linear velocity arising from the pumping of sample gas through the denuder, the Peclet number (P_e) was determined, which needed to meet the following requirement (Kloskowski et al., 2002):

$$P_e = \frac{2Rv}{D_A} > 10, \quad \text{Equation 4.6}$$

where R is the internal radius of the denuder (silicone rubber tube) (cm) ie 0.015 cm; v is the actual linear velocity of air flow ($\text{cm}\cdot\text{s}^{-1}$) at a given distance from the centre; and D_A is the diffusion coefficient of analyte A in the sample gas ($\text{cm}^2\cdot\text{s}^{-1}$) ie: $D_{Naph} = 0.069 \text{ cm}^2\cdot\text{s}^{-1}$; $D_{PhA} = 0.058 \text{ cm}^2\cdot\text{s}^{-1}$; and $D_{FlA} = D_{Py} = 0.055 \text{ cm}^2\cdot\text{s}^{-1}$, where A is the PAH of interest (Danish Environmental Protection Agency, 2006).

Further, for laminar flow the linear flow profile in an open tube is shown in Figure 4.3 and can be given by:

$$v = 2v_{av}\left(1 - \frac{r^2}{R^2}\right), \quad \text{Equation 4.7}$$

where v_{av} is the linear velocity of the sample gas flow ($\text{cm}\cdot\text{s}^{-1}$); and r is the distance from the longitudinal axis of the silicone tube (cm).

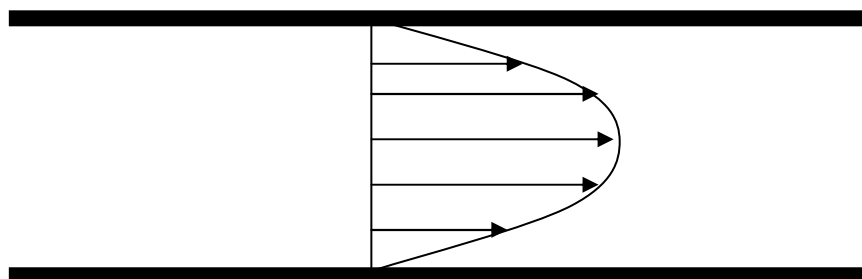


Figure 4.3: Laminar flow conditions inside an open tube.

If the average linear velocity of $203 \text{ cm}\cdot\text{s}^{-1}$ - calculated under section 4.2.1 for a 22 silicone rubber tube trap sampling at a flow rate of $500 \text{ m}\ell\cdot\text{min}^{-1}$ - is used as the actual linear velocity, a Peclet number of 88 is obtained for Naph, 105 for PhA; and 111 for FlA and Py. These results meet the requirement that the Peclet number be greater than 10, thus the contribution to the linear velocity from longitudinal diffusion is indeed negligible. Very close to the silicone walls, however, the linear flow rate would be less than the average value, thus longitudinal diffusion may become important.

4.2.3 Calculation of the efficiency of removal of gaseous components by the denuder

In order to determine the efficiency of analyte removal by the denuder, as well as the parameters which affect this removal efficiency, the rate of change of gaseous concentration of analyte, A , is usually determined from the general mass balance equation for A in a cylindrical, sorption based denuder (where analyte removal is permanent) (Katsanos and Roubani-Kalantzopoulou, 1995):

$$\frac{\partial c_A}{\partial t} = -v \frac{\partial c_A}{\partial z} + D_A \frac{\partial^2 c_A}{\partial z^2} + D_A \left(\frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial c_A}{\partial r} \right) - r_A, \quad \text{Equation 4.8}$$

where $c_A = c_A(t, z, r)$ in the gas phase in mol.cm^{-3} , as a function of t (time) in s; length along the denuder, z , in cm; and distance from the cylinder axis, r , in cm; and r_A is the rate of a gaseous chemical reaction of A in $\text{mol.cm}^{-3}.\text{s}^{-1}$.

The first term on the right hand side of equation 4.8 describes convective movement along the denuder, whilst the second term is due to longitudinal diffusion along the cylinder axis. The third term arises from radial diffusion and the fourth term relates to homogeneous chemical reactions in the denuder.

A number of assumptions can be made in order to simplify equation 4.8 and allow for a solution to be found.

The first of these is to assume steady state conditions, where the composition of the air does not change during its flow along the denuder, ie:

$$\frac{\partial c_A}{\partial t} = 0$$

Further, the second term relating to longitudinal diffusion may be ignored if it is assumed that the linear velocity of analyte A resulting from longitudinal diffusion is negligible compared with the linear velocity resulting from pumped sample air flow, ie:

$$v \frac{\partial c_A}{\partial z} \gg D_A \frac{\partial^2 c_A}{\partial z^2}$$

This was confirmed for the silicone rubber trap in section 4.2.2.

It is also assumed that no homogeneous reactions occur in the denuder, thus equation 4.8 may be simplified to:

$$v \frac{\partial c_A}{\partial z} = D_A \left(\frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial c_A}{\partial r} \right), \quad \text{Equation 4.9}$$

which leads to the Gormley-Kennedy solution of this equation (Gormley and Kennedy, 1949):

$$\frac{c_{av}}{c_0} = 0.8191 \exp(-7.314z^*) + 0.0975 \exp(-44.61z^*) + 0.0325 \exp(-113.9z^*) + \dots,$$

Equation 4.10

where c_0 is the gas concentration entering the denuder; c_{av} is the average gas concentration leaving the tube; and z^* is a dimensionless factor given by:

$$z^* = \frac{\pi D_A L}{2 V}, \quad \text{Equation 4.11}$$

where L is the length of the denuder; and V is the volumetric flow rate.

The assumptions made in this solution are that: analyte A is a trace gas; laminar flow is developed with constant viscosity; the temperature is constant; and the amount of analyte collected on the tube wall is small compared with the available capacity of the denuder (Katsanos and Roubani-Kalantzopoulou, 1995).

For $L = 5.5$ cm (length of silicone rubber tubes); $V = 8.33$ cm³.s⁻¹; and $D_{Naph} = 0.069$ cm².s⁻¹; $D_{PhA} = 0.058$ cm².s⁻¹; and $D_{FIA} = D_{Py} = 0.055$ cm².s⁻¹: $z_{Naph} = 0.072$; $z_{PhA} = 0.060$ and $z_{FIA} = z_{Py} = 0.057$.

$$\text{This gives: } \left(\frac{c_{av}}{c_0} \right)_{Naph} = 0.49; \left(\frac{c_{av}}{c_0} \right)_{PhA} = 0.53 \text{ and } \left(\frac{c_{av}}{c_0} \right)_{FIA} = \left(\frac{c_{av}}{c_0} \right)_{Py} = 0.55.$$

The fraction of analyte retained on the denuder (collection efficiency) can be determined from:

$$\left(1 - \frac{c_{av}}{c_0} \right)$$

Thus for Naph the fraction of analyte retained on the denuder is 0.51 or 51%; whilst that pertaining to PhA is 0.47 or 47 %; and the fraction for FIA and Py is 0.45 or 45 %.

The collection efficiency may be increased by increasing L , and by decreasing the sampling flow rate (V). Collection efficiencies will also be higher for analytes with higher diffusion coefficients, which can be seen from the higher calculated collection efficiency for naphthalene.

A number of alterations to the Gormley-Kennedy solution have been suggested. One of these takes into account an *effective length* of the denuder, which decreases with time as a consequence of the depletion of the active surfaces of the denuder with increasing sample volume, which would decrease the collection efficiency (Ali et al., 1989). This alteration is significant only when the depletion rate is high as a result of high analyte concentrations, high moisture levels, or low surface capacities, and therefore would be of minor significance in trace gas analysis, but would be of relevance under breakthrough conditions. This does not apply in the case of silicone rubber tubes which absorb analytes by dissolution and do not adsorb analytes onto an active surface, which may be easily saturated.

Another alteration is based on the collection surface not performing as a perfect sink and a reaction probability is incorporated into the solution, which requires knowledge of the reaction probability factor and the diffusional behaviour of the analyte (Ali et al., 1989).

In the case of the multi-channel silicone rubber traps, the Gormley-Kennedy approximation is valid for analytes of lower volatility (with higher retention volumes), such as pyrene and phenanthrene; but would not be valid for more volatile analytes (with lower retention volumes) such as naphthalene. Here a chromatographic model is more appropriate due to continuous partitioning behaviour, where the PDMS-air partition coefficients are expected to be proportional to the octanol-air partition coefficients (De Coensel et al., 2007) and experimentally derived breakthrough volumes for each analyte give an indication of the efficiency of removal of gaseous components.

4.2.4 Calculation of the efficiency of particle transmission by the denuder

Loss of particles in denuders, which are configured vertically to prevent gravitational settling and operate under laminar flow conditions, may arise from electrostatic or diffusion effects. These were studied by Ye et al. (1991) by means of particle concentration determinations. It was found that losses in the 0.1 – 1 μm diameter range were only a few percent, which is of relevance as it has been noted that PAHs are found on particles in the size range of < 5 μm (Nikolaou et al., 1984).

Other studies have indicated that 95 % of particulate PAH is found on particles < 3.3 μm in diameter (Harrison et al., 1996); > 80 % are associated with the PM_{2.5} fraction (particulate matter of size \leq 2.5 micron) (Ohura et al., 2004); or that the particle size is bimodal: < 1 μm particles containing the relatively nonvolatile PAHs formed by adsorption which remain airborne for extended time periods and are thus transported long distances; and > 1 μm particles containing the condensed volatile PAHs (Harrison et al., 1996). Another study found that almost half of the particle bound PAHs are associated with the particle size range 0.075 – 0.12 μm (Miguel and Friedlander, 1978).

Particle size is an important consideration in terms of dust retention in the human respiratory tract, and it has been found that more PAHs are associated with the respirable fraction in winter (Van Vaeck et al., 1979). Larger particles have also been observed in

suburban ambient air, as compared to urban air (Horvath et al., 1996), which may be ascribed to particle growth processes during ageing of the urban aerosol.

Higher particle transmission losses are experienced in denuders for smaller particles, due to their higher diffusion coefficients. Losses of charged particles may occur due to localized electrostatic fields on the denuder wall, which may arise due to low humidity or as a result of handling. Experiments to determine electrostatic losses are difficult to repeat (Ye et al., 1991), as they depend on these environmental and localized conditions, thus only losses of neutral particles due to diffusion were considered in this study. In some applications, such as the use of the silicone rubber traps in the denuder configuration for the monitoring of PAHs arising from sugar cane burning in KwaZulu-Natal (Chapter 5), electrostatic effects would have been minimal due to the high humidity at this coastal location. It would also be possible to supplement sample air with moist air, if necessary, and then correct for dilution effects.

Experimental results relating to the diffusional losses of neutral particles in an annular denuder compared favourably to theoretical calculations based on equations developed for a channel of rectangular cross section (Ye et al., 1991). The annular denuder channel was considered in an “unrolled and flattened” state as a parallel plate configuration in order to relate the channel geometry to a rectangle.

For the silicone rubber traps, however, diffusive loss theories for particles traversing tubes of circular cross section were appropriate, as applied in Hermann et al. (2001) and Ferm (1979). The transport efficiency, E_{diff} , is given by:

$$E_{diff} = 1 - 2.564\mu^{2/3} + 1.2\mu + 0.1767\mu^{4/3}, \quad \text{Equation 4.12}$$

for $\mu \leq 0.02$, and

$$E_{diff} = 0.819 \exp(-3.657\mu) + 0.0975 \exp(-22.305\mu) + 0.0325 \exp(-56.961\mu) + 0.0154 \exp(-107.62\mu) \quad \text{Equation 4.13}$$

for $\mu > 0.02$, where

$$\mu = \frac{\pi D_p L}{Q}, \quad \text{Equation 4.14}$$

and where D_p is the diffusion coefficient of a particle of a specific diameter, in $\text{m}^2 \cdot \text{s}^{-1}$; L is the length of the denuder in m; and Q is the volumetric flow rate in $\text{m}^3 \cdot \text{s}^{-1}$.

The particle diffusion coefficients were calculated from

$$D_p = \frac{C_c kT}{3\pi d_p \mu_{abs}}, \quad \text{Equation 4.15}$$

where C_c is the Cunningham slip correction factor (obtained from USA EPA, 2007); k is the Boltzmann constant ($1.3806503 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$); T is the temperature in K; d_p is the diameter of the particle in m; and μ_{abs} is the absolute (or dynamic) gas viscosity in $\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$.

The particle diffusion coefficients, μ values, and corresponding transport efficiencies, E_{diff} , were calculated for a number of particle sizes, ranging from 0.001 to 10 μm at 25 °C, for a silicone rubber trap denuder of length 0.055 m operating at 500 $\text{m} \ell \cdot \text{min}^{-1}$. The results are presented in Table 4.5 and Figure 4.4.

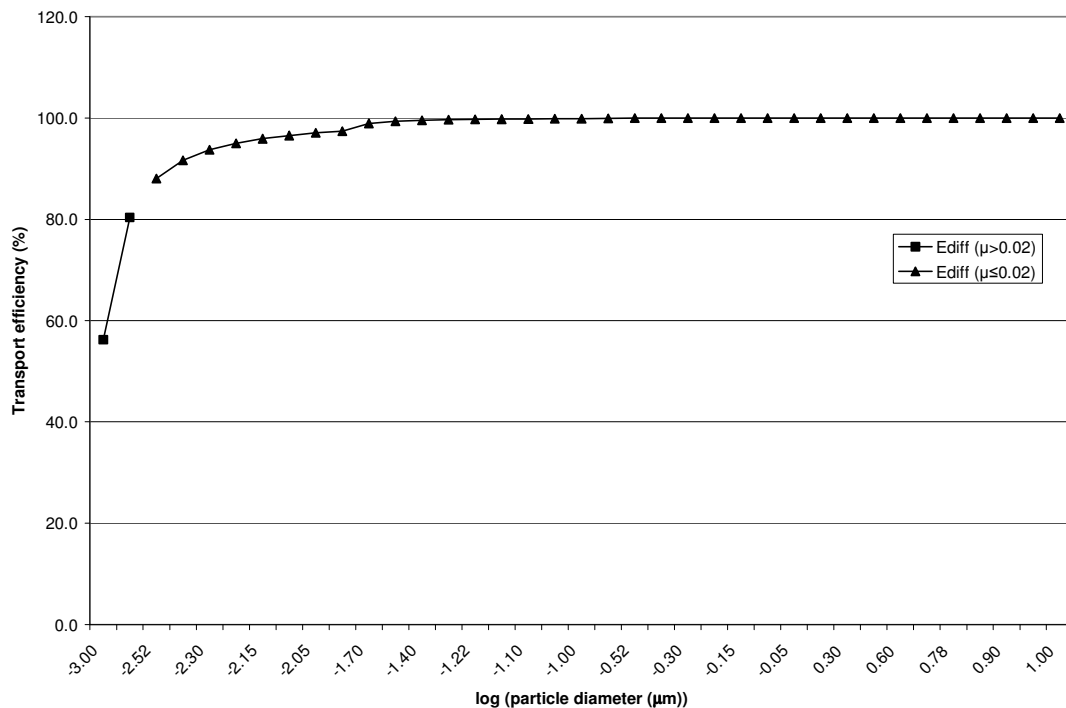


Figure 4.4: Particle transport efficiency through a silicone rubber trap with respect to diffusive losses.

Table 4.5: Neutral particle transport efficiencies for different particle sizes.

d_p (μm)	C_c	D_p ($\text{m}^2 \cdot \text{s}^{-1}$)	μ	Transport efficiency (%)
0.001	222	5.18E-06	1.07E-01	56.2
0.002	111	1.30E-06	2.69E-02	80.4
0.003	74.3	5.78E-07	1.20E-02	88.1
0.004	55.8	3.26E-07	6.76E-03	91.7
0.005	44.8	2.09E-07	4.34E-03	93.7
0.006	37.4	1.46E-07	3.02E-03	95.0
0.007	32.2	1.07E-07	2.23E-03	95.9
0.008	28.2	8.23E-08	1.71E-03	96.5
0.009	25.1	6.52E-08	1.35E-03	97.0
0.01	22.7	5.30E-08	1.10E-03	97.4
0.02	11.7	1.36E-08	2.82E-04	98.9
0.03	7.98	6.21E-09	1.29E-04	99.4
0.04	6.15	3.59E-09	7.45E-05	99.6
0.05	5.06	2.36E-09	4.90E-05	99.7
0.06	4.34	1.69E-09	3.50E-05	99.7
0.07	3.82	1.28E-09	2.65E-05	99.8
0.08	3.44	1.01E-09	2.08E-05	99.8
0.09	3.15	8.16E-10	1.69E-05	99.8
0.1	2.91	6.80E-10	1.41E-05	99.9
0.2	1.89	2.21E-10	4.58E-06	99.9
0.3	1.57	1.23E-10	2.54E-06	100.0
0.4	1.42	8.32E-11	1.73E-06	100.0
0.5	1.34	6.25E-11	1.30E-06	100.0
0.6	1.28	4.98E-11	1.03E-06	100.0
0.7	1.24	4.14E-11	8.58E-07	100.0
0.8	1.21	3.53E-11	7.33E-07	100.0
0.9	1.19	3.08E-11	6.38E-07	100.0
1	1.17	2.73E-11	5.66E-07	100.0
2	1.08	1.27E-11	2.63E-07	100.0
3	1.06	8.22E-12	1.71E-07	100.0
4	1.04	6.08E-12	1.26E-07	100.0
5	1.03	4.83E-12	1.00E-07	100.0
6	1.03	4.00E-12	8.30E-08	100.0
7	1.02	3.42E-12	7.09E-08	100.0
8	1.02	2.98E-12	6.18E-08	100.0
9	1.02	2.64E-12	5.49E-08	100.0
10	1.02	2.38E-12	4.93E-08	100.0

It is evident that the theoretical transport efficiencies of particles larger than 0.05 μm are essentially 100 %. Transmission losses of > 5 % are only evident for the particle size

fraction $< 0.006 \mu\text{m}$. It is of note that the calculated transport efficiency at molecular dimensions (1 nm or $0.001 \mu\text{m}$) was 56.2 %, which would correspond to a collection efficiency of 43.8 %. This correlates well with the gaseous PAH collection efficiencies calculated in section 4.2.3 using the Gormley-Kennedy equation, which ranged from 45 to 51 %. The low Reynolds numbers for the flow rate utilized in this study should also minimize loss of particles due to impaction (as calculated in section 4.2.1).

The particle size fractions of most significance in the monitoring applications investigated in this study are discussed in Chapter 5.

It is also important that the transit time of particles through the denuder is sufficiently fast to prevent re-equilibration of particle bound analyte to the gas phase during transit, as this would produce a positive bias in terms of the gas phase concentration. For semi-volatile organic compounds, a transit time of $\leq 0.3 \text{ s}$ is recommended (Kamens and Coe, 1997 and Gundel and Lane, 1998). In the case of the silicone rubber traps used in our study, a transit time of $\sim 0.03 \text{ s}$ would occur at a $500 \text{ mL}\cdot\text{min}^{-1}$ sampling flow rate, which is far below this cut-off. Re-equilibration during transit was therefore not deemed to be significant, particularly as the target PAHs of interest are found predominantly in the gas phase under the sampling conditions.

4.3 DISCUSSION AND CONCLUSION

Denuders allow for the separation of gas and particulate phases, without the generation of artifacts which may occur with filter-based methods (filtration prior to gas sampling). The method also allows for pre-concentration of the gaseous analyte.

Conventional cylindrical denuders have a number of disadvantages, as their use is labour intensive due to coating and extraction procedures. The silicone rubber traps used in our study do not require coating or solvent extraction therefore the possibility for solvent introduced artifact formation is minimized and the elimination of sample handling steps also reduces the chance of sample contamination and degradation.

A number of denuders have been reported which are analysed by thermal desorption methods. Denuders based on parallel sections of capillary chromatographic columns (typically ~120 parallel 0.25 m long sections), for example, have been used in the sampling of VOCs and SVOCs, followed by thermal desorption using specially designed systems (Krieger and Hites, 1992; Dudek et al., 2000; Dudek et al., 2002 and Tobias et al., 2007). The traps used in our study are unique and are compatible with commercially available thermal desorption systems.

Another problem which may be associated with cylindrical denuders is the need for long sampling times due to the limited flow rates inherent to their design, which may lead to artifact formation, although higher flow rates are possible with annular denuders (Ali et al., 1989). In the case of our denuder, total transfer onto the GC column is possible (as compared to solvent extraction based methods), which enhances sensitivity and allows for shorter sampling times and lower flow rates.

It is evident from the results of the theoretical considerations presented in this Chapter that the multi-channel silicone rubber traps have the potential to serve as efficient denuders. The application of these traps in the denuder configuration was therefore tested experimentally in a number of applications of relevance to South Africa, as described in Chapter 5.

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