The use of multi-channel silicone rubber traps as denuders for polycyclic aromatic hydrocarbons

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HIGHLIGHTS:

- Two multi-channel silicone rubber traps separated by a quartz fibre filter are characterized as a miniature portable denuder
- Gas and particle phase polycyclic aromatic hydrocarbons can be separately sampled and analysed
- Calculated particle transmission efficiencies were 100 % for particles > 50 nm diameter
- Experimental particle transmission efficiencies were 100 % for particles > 200 nm and decreased to < 60 % for particles < 20 nm diameter
- Short sampling intervals are possible which provides high temporal resolution for air pollution studies
Two multi-channel silicone rubber traps separated by a quartz fibre filter are characterized as a miniature portable denuder, which allows for the separate sampling and analysis of gas and particle phase polycyclic aromatic hydrocarbons. Calculated particle transmission efficiencies were 100 % for particles > 50 nm diameter, whilst experimental particle transmission efficiencies were 100 % for particles > 200 nm and decreased to < 60 % for particles < 20 nm diameter. Short sampling intervals are possible which provides high temporal resolution for air pollution studies.
The use of multi-channel silicone rubber traps as denuders for polycyclic aromatic hydrocarbons

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ABSTRACT

Atmospheric polycyclic aromatic hydrocarbons are ubiquitous environmental pollutants, which may be present both in the gaseous phase and adsorbed onto the surface of particles. Denuders are sampling devices which have been effectively employed in such partitioning applications. Here we describe and characterise a novel miniature denuder consisting of two multi-channel silicone rubber traps (each 178 mm long, 6 mm o.d. containing 22 silicone tubes), separated by a quartz fibre filter for particle phase collection. The denuder only requires a small portable personal sampling pump to provide sampling flow rates of ~0.5 L min$^{-1}$. Theoretical considerations indicated that the air flow through the denuder was expected to be laminar, and the linear velocity arising from longitudinal diffusion was found to be negligible. The calculated particle transmission efficiency through the denuder was found to be essentially 100% for particles > 50 nm, whilst the experimental overall efficiency, as determined by CPC and SMPS measurements, was 92 ± 4%. The size resolved transmission efficiency was < 60% for particles below 20 nm and 100% for particles larger than 200 nm. Losses could have been due to diffusion and electrostatic effects. Semi-volatile gaseous analytes are pre-concentrated in the silicone of the trap and may be thermally desorbed using a commercially available desorber, allowing for total transfer and detection of the collected analytes by GC-MS. This enhances detection limits and allows for lower sampling flow rates and shorter sampling times, which are advantageous for studies requiring high temporal resolution.
### 1. INTRODUCTION

Atmospheric polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants, which may be present both in the gaseous phase and adsorbed onto the surface of particles, where PAHs of molecular mass > m/z 228 are found mainly in the particle phase [1]. 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 relevance with respect to human health toxicities, as deposition and uptake of inhaled toxic species depends on phase distribution [2,3]. The environmental fate of these 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 [4].

The partitioning of atmospheric semi-volatile organic compounds between the vapour and particle phases in the atmosphere is dependent upon the vapour pressure of the compound, as well as the amount of particles available, and can be described by a partition coefficient $K_{vp}$ [5]:

$$K_{vp} = \frac{(F / TSP)}{A}, \quad \text{Equation 1}$$

where $F$ is the particulate phase concentration of the compound (in ng m$^{-3}$); $TSP$ is the total suspended particulate loading (in μg m$^{-3}$); and $A$ is the vapour phase concentration of the compound (in ng m$^{-3}$).
In order for sampling of the two phases to be effective, it must be ensured that any analytes adsorbed onto particles which are volatilized upon re-equilibration (after collection onto filters, for example), are not lost from the sampling process [6]. 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 reduced by maintaining constant temperature conditions and a low pressure drop across the filter [7].

Standard 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), may introduce analytical artifacts. These are principally from sorption of gas phase analytes onto the filter or collected particles as well as from desorption of analytes from these particles. The adsorption of gas phase PAHs onto the filter medium can be significant and may be estimated from a second particle-free backup filter [7].

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 [8]:

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.
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 may be employed behind 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 such desorption to the measurement uncertainty would be small for the more volatile PAHs, for which the particle phase contribution to the total concentration is low [9]. Cyclones or impactors have been used to remove large particles from the sample gas stream before it enters the denuder system [10,11], although the resulting high pressure drops across the sampling device may enhance evaporative losses from particles [12].

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 [8]. Ideally 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 for diffusion of molecules to the denuder walls, low flow
conditions are required (< 20 L min\(^{-1}\), as compared to high volume samplers which
operate at around 1000 L min\(^{-1}\)) [5].

A number of denuder geometries have been developed, with cylindrical and annular
denuders being the most widely reported. Conventional commercial denuders are
usually coated with a sorptive medium which requires replacement after a period of
time and they are typically solvent extracted prior to analysis.

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 [13,14]. Crushed Amberlite XAD-4 styrene-divinylbenzene
polymer resin has also been employed in PAH denuder applications [2,3,15]. It is
evident that the main problems of these methods are contamination issues from the
sorbent medium and time consuming denuder preparation and sample extraction
processes.

A composite cylindrical denuder between 0.15 and 0.5 m long, composed of a
collection of capillary gas chromatography columns (methylsilicone stationary phase)
bonded together with epoxy resin as the sampling tubes, was tested for use in
atmospheric PAH sampling [5,16]. A liquid extraction and sample cleanup procedure
had to be employed, as the denuder was not resilient to thermal desorption conditions.
Similar composite denuders have been more recently tested operating at 13 L min\(^{-1}\), as
well as denuders prepared by coating stainless steel honeycombs with
polymethylsiloxane (PDMS) at 300 L min\(^{-1}\), which require custom built thermal
desorption apparatus [17,18].

Multi-channel silicone rubber traps, which consist of 22 parallel PDMS tubes of 0.3
mm i.d. housed in a 178 mm long glass tube [19], retain gaseous semi-volatile organic
analytes. It was expected that airborne particles would be effectively transmitted
through the trap, due to its open geometry allowing laminar air flow. The trap could
therefore serve as a denuder and by the addition of a downstream particle filter and
second denuder (to capture desorbed analytes from the particulates on the filter), both
gaseous and particle phases of PAHs could be separately sampled, as shown in Fig. 1.

The suitability of these traps as denuders was therefore investigated both from a
theoretical perspective and experimentally, as described in this paper. In terms of
theoretical gas phase collection efficiencies, a range of the more volatile PAHs were
studied, namely naphthalene (Naph), phenanthrene (PhA), fluoranthene (FlA) and
pyrene (Py), as their gas phase breakthrough volumes (collection efficiencies) would
be lower than for PAHs of lower volatility. Any overestimation of the denuder
collection efficiency is therefore avoided, and results may be considered as minimum
trapping efficiencies for PAHs in general [2,15]. The PAHs which were studied are
more abundant in the environment, as they are emitted at relatively high
concentrations from numerous sources, and they have been found to be suitable
indicators for PAH contamination [20-22]. Particle transmission efficiencies were
tested over a range of particle sizes, where the transmission efficiency of the denuder
was determined from the ratio of particle concentration transmitted by the denuder to
that of a bypass line.
2. THEORETICAL CONSIDERATIONS

The multi-channel silicone rubber trap can be classified as a composite cylindrical type denuder, with each of the 22 silicone tubes effectively performing as a cylindrical denuder. The non-circular inter-tube channels were ignored to simplify initial calculations in the estimation of flow conditions inside the composite denuder.

2.1 Verification of laminar flow

As previously mentioned, 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.

\[
R_e = \frac{VD}{\nu}, \quad \text{Equation 2}
\]

where \( V \) is the linear velocity; \( D \) is the internal diameter of the silicone tubes; and \( \nu \) is the kinematic viscosity.

Further, \( \nu \) can be determined from

\[
\nu = \frac{\mu}{\rho}, \quad \text{Equation 3}
\]

where \( \mu \) is the dynamic viscosity; and \( \rho \) 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 \( 1.60 \times 10^{-5} \, \text{m}^{2} \, \text{s}^{-1} \) and thus a Reynolds number of 101 is obtained.

For a sampling flow rate of 0.5 L min\(^{-1}\) through a 22 channel trap, with the internal diameter (i.d.) of each silicone tube 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. It is also 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. If the total open cross sectional area of 4.1 mm\(^2\) for a quartz tube of 3.5 mm i.d. containing 22 silicone tubes of 0.64 mm outer diameter is rather employed, an average linear velocity inside the silicone rubber tubes of 2030 mm s\(^{-1}\) would be obtained assuming uniform flow across the open area, which would yield an even lower \(R_e\) of 38.

In both cases, \(R_e\) satisfies the condition for laminar flow that \(R_e < 2000\) [23], 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 \(d\) [10]:

\[ l = 0.07dR_e \]  \hspace{1cm} \text{Equation 4}

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), but may impact on the overall particle transmission rate.

### 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 [8]:

\[
P_e = \frac{2 R \nu}{D_A} \geq 10, \quad \text{Equation 5}
\]

where \(R\) is the internal radius of the denuder (silicone rubber tube) i.e. 0.015 cm; \(\nu\) is

the actual linear velocity of air flow (cm s\(^{-1}\)) at a given distance from the centre; and

\(D_A\) is the diffusion coefficient of PAH analyte \(A\) in the sample gas (cm\(^2\) s\(^{-1}\)) i.e. \(D_{Naph}\)

\(= 0.069\) cm\(^2\) s\(^{-1}\); \(D_{PhA} = 0.058\) cm\(^2\) s\(^{-1}\); and \(D_{FlA} = D_{Py} = 0.055\) cm\(^2\) s\(^{-1}\) [24].

Further, for laminar flow the linear flow profile in an open tube is shown in Fig. 2 and

can be given by:

\[
\nu = 2 \nu_{av} \left(1 - \frac{r^2}{R^2}\right), \quad \text{Equation 6}
\]

where \(\nu_{av}\) is the linear velocity of the sample gas flow (cm s\(^{-1}\)); and \(r\) is the distance

from the longitudinal axis of the silicone tube (cm).

If the average linear velocity of 203 cm s\(^{-1}\) 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 would appear to be

negligible. Very close to the silicone walls and in the small inter-tube channels, the

linear flow rate would be less than the average value, thus longitudinal diffusion may

become important.
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) [25]:

\[
\frac{\partial c_A}{\partial t} = -\nu \frac{\partial c_A}{\partial z} + D_A \frac{\partial^2 c_A}{\partial z^2} + D_A \left( \frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial c_A}{\partial r} \right) - r_A, \quad \text{Equation 7}
\]

where \( c_A = c_A(t, z, r) \) in the gas phase in \( \text{mol cm}^{-3} \), 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 7 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 7 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, i.e.

\[
\frac{\partial c_A}{\partial t} = 0.
\]

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,
as was shown for the silicone rubber trap i.e. \( \nu \frac{\partial c_A}{\partial z} >> D_A \frac{\partial^2 c_A}{\partial z^2} \).

It is also assumed that no homogeneous reactions occur in the denuder, thus equation 7 may be simplified to:

\[
\nu \frac{\partial c_A}{\partial z} = D_A \left( \frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial c_A}{\partial r} \right),
\]

Equation 8

which leads to the Gormley-Kennedy solution of this equation [26]:

\[
\frac{c_{av}}{c_0} = 0.8191 \exp(-7.314 z^*) + 0.0975 \exp(-44.61 z^*) + 0.0325 \exp(-113.9 z^*) + ...
\]

Equation 9

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:

\[
z^* = \pi \frac{D_A L}{2 \nu},
\]

Equation 10

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 [25].
For $L = 5.5$ cm (length of silicone rubber tubes); $V = 8.33$ cm$^3$ s$^{-1}$; and $D_{\text{Naph}} = 0.069$ cm$^2$ s$^{-1}$; $D_{\text{PhA}} = 0.058$ cm$^2$ s$^{-1}$; and $D_{\text{FlA}} = D_{\text{Py}} = 0.055$ cm$^2$ s$^{-1}$; $z_{\text{Naph}} = 0.072$;

$z_{\text{PhA}} = 0.060$ and $z_{\text{FlA}} = z_{\text{Py}} = 0.057$. This gives: \[
\frac{c_{av}}{c_0}_{\text{Naph}} = 0.49;
\]

\[
\frac{c_{av}}{c_0}_{\text{PhA}} = 0.53 \text{ and } \frac{c_{av}}{c_0}_{\text{FlA}} = \frac{c_{av}}{c_0}_{\text{Py}} = 0.55.
\]

The fraction of analyte retained on the denuder (collection efficiency) can be determined from: \[
1 - \frac{c_{av}}{c_0}.\]

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 FlA 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 [10]. 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 then incorporated into the solution, which requires additional knowledge of the reaction probability factor [10].

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 the continuous partitioning of analytes, where the PDMS-air partition coefficients are expected to be proportional to the octanol-air partition coefficients [27] and experimentally derived breakthrough volumes for each analyte give an indication of the efficiency of removal of gaseous components. The experimentally derived 10 % breakthrough volume of the silicone rubber traps for naphthalene is ~4 L, for example [28], and would be larger for the other, less volatile PAHs.

2.4 Calculation of the efficiency of particle transmission through the denuder

Loss of particles in denuders, operating under laminar flow conditions and which are configured vertically to prevent gravitational settling, may arise from electrostatic or diffusion effects.

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 [29], as they depend on these environmental and localized
conditions, thus only losses of neutral particles due to diffusion were considered in
this study, which would increase for lower flow rates [30].

Diffusional losses of neutral particles traversing the tubes of circular cross section in
the silicone rubber trap, were estimated from the theory derived by Hermann et al.
[31] and Ferm [32] where the transport efficiency, $E_{\text{diff}}$, is given by:

$$E_{\text{diff}} = 1 - 2.564\mu^{2/3} + 1.2\mu + 0.1767\mu^{4/3},$$  \hspace{1cm} \text{Equation 11}

for $\mu \leq 0.02$, and

$$E_{\text{diff}} = 0.819\exp(-3.657\mu) + 0.0975\exp(-22.305\mu) + 0.0325\exp(-56.961\mu) + 0.0154\exp(-107.62\mu)$$  \hspace{1cm} \text{Equation 12}

for $\mu > 0.02$, where

$$\mu = \frac{\pi D_p L}{Q},$$  \hspace{1cm} \text{Equation 13}

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

The particle diffusion coefficients were calculated from

$$D_p = \frac{C_c k T}{3\pi d_p \mu_{abs}},$$  \hspace{1cm} \text{Equation 14}

where $C_c$ is the Cunningham slip correction factor (obtained from [33]); $k$ is the
Boltzmann constant (1.3806503 x 10$^{-23}$ m$^2$ kg s$^{-2}$ K$^{-1}$); $T$ is the temperature in K; $d_p$ is
the diameter of the particle in m; and $\mu_{abs}$ is the absolute (or dynamic) gas viscosity in kg m\(^{-1}\) s\(^{-1}\).

The particle diffusion coefficients, $\mu$ 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 0.5 L min\(^{-1}\). The results are presented in Fig. 3 and are tabulated in the Supplementary Information (Table S1).

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 μm. It is of note that the calculated transport efficiency at molecular dimensions (1 nm or 0.001 μm) was 56%, which would correspond to a collection efficiency of 44%. This correlates well with the gaseous PAH collection efficiencies calculated in section 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, especially the large particles, which have high kinetic energy [34]. Loss due to impaction is also greater for thicker capillary walls.

It is 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 ≤ 0.3 s is recommended [9,35]. In the case of the silicone rubber traps used in our study, a transit time of ~0.03 s would be achieved at a 0.5 L min\(^{-1}\) sampling flow rate, which is far below this cut-off. Re-equilibration during transit was therefore not deemed to be significant, particularly for
the more volatile PAHs which are found predominantly in the gas phase under ambient conditions.

It was evident from the results of these theoretical considerations that the multi-channel silicone rubber traps have the potential to serve as efficient denuders, and the experimental confirmation of these results was therefore sought, as detailed in the following section.

3. EXPERIMENTAL METHODS

3.1 Laboratory particle transmission tests

A multi-channel silicone rubber trap was tested as a denuder in terms of particle transmission. The trap consisted of 22 parallel PDMS tubes (55 mm long, 0.3 mm i.d. and 0.64 mm o.d.) housed in a 178 mm long glass tube (for trap preparation details refer to [19]). The denuder tube and a bypass line were connected in parallel via electrically conducting polyamide tubes (4 mm i.d.) with two three-way-valves (Fig. 4), such that either the denuder or the bypass was supplied with an aerosol flow. Switching between the lines was achieved in under 1 s, and each was tested three times. The bypass consisted of a silicone tube which was squeezed by a crimp in order to adjust the bypass pressure difference and flow rate to be the same as for the denuder (0.5 L min$^{-1}$). The total length and horizontal distances of the tubing were identical for the denuder and bypass and all other sampling lines were the same for all analyses, therefore any difference in particle size distribution between the denuder and bypass could be assigned to the denuder / restrictor combination.
Aerosol particles were generated by a jet nebulizer (“Trijet” nebulizer, Model 3460, TSI, USA), using an ammonium sulphate solution (42 mg (NH$_4$)$_2$SO$_4$ in 100 ml H$_2$O). Particle size distribution output was approximately lognormal, with a modal diameter of ~50 nm and a number concentration of more than 10$^5$ particles per cm$^3$. Dilution was performed with filtered N$_2$ via valve #1, whilst valve #2 diluted the denuder/bypass flow in order to maintain a constant sampling flow rate of 1.6 L min$^{-1}$ through the particle sizer and counter instruments. A sampling flow splitter (Model 3708, TSI, USA) was used to distribute the sample flows to the instruments. All sampling lines between manifold and instruments were of identical diameter and length.

A scanning mobility particle sizer (SMPS, model 3081, TSI, USA) was used for particle size analysis and a condensation particle counter (CPC Model 3775, TSI, USA) for number concentration. All instruments were set to a sampling time of 135 s, which is the scan time of the SMPS for a single run.

### 3.2 Field tests

For additional details on these field tests, refer to [36].

#### 3.2.1 Sugar cane burning

Emissions from a sugar cane burn at Umhlali on the KwaZulu-Natal North Coast, South Africa, were sampled using the silicone rubber trap denuder system incorporating quartz fibre filters which had been punched to the correct size (6 mm o.d.), washed with methanol followed by dichloromethane, and then oven dried at 100 °C for 30 min. A Gilair portable sampling pump equipped with a low flow module was used to sample air in the emission plume for 10 min at 0.5 L min$^{-1}$.

#### 3.2.2 Diesel exhaust emissions
Sampling of the exhaust of an idling diesel vehicle (2006 Citroen C3, 1.4L) was performed under cold start conditions for 11 min, by means of battery-operated portable Gilair sampling pumps. The following three sampling configurations and sampling flow rates were employed:

i) Trap-filter-trap (0.43 L min$^{-1}$)

ii) Tube-filter-trap (0.44 L min$^{-1}$)

iii) Trap-trap (0.37 L min$^{-1}$).

Teflon tubing connections were used in each case. Tube refers to an empty glass tube without PDMS. After sampling, the filters were transferred to sealed 2 mL amber vials and the traps were end-capped and wrapped in aluminium foil. Samples were then refrigerated prior to analysis by Thermal Desorption – Gas Chromatography – Mass Spectrometry (TD-GC-MS), as described in [28].

4. RESULTS AND DISCUSSION

4.1 Laboratory tests

The transmission efficiency was determined from the ratio between the denuder and bypass particle concentrations. From the three data sets displayed in Fig. 5, an average transmission efficiency of $0.92 \pm 0.04$ was determined. The ratio was constant during the sampling period except for the first seconds of sample 1 which may have been due to a valve switching effect.

Size resolved number concentration data averaged for the three sets of measurements are displayed in Fig. 6 with respect to transfer through denuder, and in Fig. 7 for transfer through the bypass line. In both cases a lognormal distribution was fitted to
the data using the Hatch-Choate-Conversion constraints \[23\], with a particle median diameter of 64 nm and a $\sigma_g$ (geometric standard deviation) of 1.98 in the case of the denuder and a particle median diameter of 59 nm and a $\sigma_g$ of 1.91 for the bypass.

Both size distributions are very similar and seem to be shifted to smaller particle sizes, compared to the fit line. This is likely due to losses through the sampling lines between the nebulizer and analyzer, which is very dependent on the retention time for ultrafine and nano-particles.

In Fig. 8 both size distributions are plotted together. For particle sizes above 100 nm, both graphs show nearly identical concentrations, whilst the transmission efficiency of the denuder decreases for particles < 80 nm. The size resolved transmission efficiency was found to be < 60 % for particles below 20 nm and 100 % for particles larger than 200 nm. It should be noted that loss of particles could result from the presence of electrostatic fields inside the denuder, generated for example by the triboelectric effect, especially for particles < 40 nm in diameter and for operation at low flow rates, as the generated particles were not neutralised prior to introduction into the denuder \[30,34\].

4.2 Sugar cane burning

Visual inspection of the traps after sampling clearly showed that the fine particles had passed through the first silicone trap, and were present on the filter, as shown in Fig. 9). Any analytes which entered the gas phase after impacting on the filter would have been trapped by the second silicone rubber trap, as were any gas phase analytes which broke through the first trap.

4.3 Diesel vehicle emissions
The results of the diesel vehicle emission monitoring experiments are summarized in Table 1. The primary trap of the trap-filter-trap sampling configuration contained significantly more naphthalene than any of the other traps, probably due to the positioning of this sampling system, which placed the trap closer to the emission source than the other two sampling configurations, as well as due to the gusty wind conditions experienced during sampling. The same amount of naphthalene was collected in the primary trap of the trap-trap configuration and in the trap of the tube-filter-trap configuration, which confirmed that no gas phase naphthalene was adsorbed onto the filters during sampling. Although the filter was blackened due to particle loading, no particle-associated naphthalene was found at the sampling temperature (28 °C), as would be expected. Visual inspection of the filters and traps showed that particles had been successfully collected on the filters and had not been lost in the primary trap. No breakthrough of naphthalene was evident in the secondary traps at the low sample volumes employed, and phenanthrene fluoranthene and pyrene were not detected in any of the samples as a result of the low sample volumes.

5. CONCLUSIONS

From a theoretical perspective, the multi-channel silicone rubber traps meet the requirements to effectively serve as denuders for semi-volatile compounds, specifically PAHs. Laminar flow through the traps was confirmed, and linear velocity arising from longitudinal diffusion was found to be negligible. Removal efficiencies of gas phase analytes depends on breakthrough volumes, which can be readily determined. The calculated particle transmission efficiency through the denuder was found to be essentially 100 % for particles > 50 nm at a flow rate of 0.5 L min⁻¹.
The experimental particle transmission efficiency was determined by CPC and SMPS measurements by switching three times between the denuder and a bypass line and averaging these data sets. The overall particle transmission efficiency was thus found to be $92 \pm 4\%$ from CPC data at a flow rate of $0.5 \text{ L min}^{-1}$. The size resolved transmission efficiency was $< 60\%$ for particles below 20 nm and 100\% for particles larger than 200 nm. The loss of small particles could have been due to diffusional as well as electrostatic effects inside the silicone tubes. Sedimentation loss was not expected, as the denuder was mounted vertically. Reduced particle transmission efficiencies are commonly reported for particles below 20 nm, even at higher flow rates, for example in an eight-channel annular denuder operating at $17 \text{ L min}^{-1}$ [34].

Loss of small particles by diffusion may be reduced by decreasing the residence time in the denuder, for example by increasing the flow rate or decreasing the length of the denuder. Such changes would, however, result in a decrease in gaseous analyte collection efficiency and would therefore negatively impact on the sensitivity of the method. It is likely that losses in our silicone denuder may occur primarily in the inter-tube spaces inside the denuder, where the flow rate would be lower. It is also possible that losses occurred due to slight kinks or twists in the PDMS channels induced during manufacture. Slight variations between the particle transmission efficiencies between traps may therefore be expected.

It has been reported, however, that $> 95\%$ of particle bound PAHs are associated with the particle size fraction ranging from 0.1 to 8 $\mu$m in diameter [34]. We found that
particle transmission of this size fraction through the silicone rubber trap was good
therefore our denuder appears to be suitable for PAH monitoring.

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 reported here allows for pre-concentration of the gaseous
analyte in the PDMS. The silicone rubber traps can be thermally desorbed using
commercially available equipment, thus 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. Total transfer and detection of
collected analyte is possible with by TD-GC-MS, which enhances detection limits and
allows for lower sampling flow rates and shorter sampling times, which are
advantageous for studies requiring high temporal resolution. The denuder is small
and only requires a battery operated portable personal sampling pump for operation.
References


Acknowledgements

Funding provided by the CSIR, NLC and NRF is acknowledged. Andreas Trüe is thanked for his assistance with TD-GC-MS analyses.
Figure captions

Figure 1: Schematic diagram of the multi-channel silicone rubber traps and a quartz fibre filter employed in the denuder configuration (Courtesy of WIT Press from WIT Transactions on Ecology and the Environment Volume 136, 2010, page 369).

Figure 2: Laminar flow conditions inside an open tube.

Figure 3: Particle transport efficiency through a silicone rubber trap with respect to diffusive losses.

Figure 4: Schematic diagram of the experimental setup used for the determination of the denuder particle transmission efficiency.

Figure 5: Temporal variability of particle transmission efficiency from CPC data.

Figure 6: Averaged size distribution of sulfate particles through denuder.

Figure 7: Averaged size distribution of sulphate particles through the bypass line.

Figure 8: Averaged size distributions of denuder and bypass transmission of sulphate particles.
Figure 9: Dismantled silicone trap system after sugar cane burn sampling, with no particles evident on the trap, whilst the filter which was downstream of the trap is heavily loaded with particles.
Table 1: Naphthalene concentrations ($\mu g \ m^{-3}$) in diesel vehicle emissions sampled onto multi-channel silicone rubber traps and quartz fibre filters with TD-GC-MS analysis (Courtesy of WIT Press from WIT Transactions on Ecology and the Environment Volume 136, 2010, page 372).
### Table 1

<table>
<thead>
<tr>
<th>SAMPLING CONFIGURATION</th>
<th>PRIMARY TRAP (ng)</th>
<th>FILTER</th>
<th>SECONDARY TRAP</th>
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<td>nd</td>
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<td>ii) Tube-filter-trap</td>
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<td>iii) Trap-trap</td>
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<sup>a</sup> na = not applicable
<sup>b</sup> nd = not detected (<1 ng)
Figure 1
Figure 2
Figure 3

Click here to download Figure: Fig 3.xls
Figure 5

The graph shows the ratio of total number concentration over experiment time. Three samples (sample 1, sample 2, and sample 3) are plotted with different line styles. Sample 1 is represented by a solid black line, sample 2 by a dashed line, and sample 3 by a dotted line. The y-axis represents the ratio of total number concentration ranging from 0.0 to 1.2, while the x-axis represents experiment time ranging from 0 to 125 seconds.

The right side of the graph contains a box plot indicating the median (n=388), with the interquartile range and outliers shown. The median value for sample 3 is 0.92 ± 0.04.
Figure 6

Size distribution (nm) (Stokes Diameter; \(\rho=1\text{g/cm}^3\); CF=1.03; RC=1)

- **Modal diameter**
- **Median diameter**
- **HCFit**
- **FitMedian**
Figure

Click here to download Figure: Fig 9 (Colour for web use).ppt

Figure 9
Supporting documentation

Table S1: Neutral particle transport efficiencies for different particle sizes.

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<th>(d_p) ((\mu)m)</th>
<th>(C_c)</th>
<th>(D_p) (m(^2).s(^{-1}))</th>
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<th>Transport efficiency (%)</th>
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