

Principles and calibration of solid phase microextraction fibre (passive sampler) for measurements of airflow and air infiltration in domestic houses

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Abstract

Tracer gas techniques have been the most appropriate experimental method of determining airflows and ventilation rates in houses, however, current trends to reduce greenhouse gas effects have prompted the need for alternative techniques, such as passive sampling. In this research Passive sampling techniques have the potential to fulfil these requirements by using solutions of volatile organic compounds (VOCs) and solid phase microextraction (SPME) fibres. Passive sampling techniques have been calibrated against tracer gas decay techniques and measurements from a standard orifice plate. Two constant sources of volatile organic compounds were diffused into two sections of a humidity chamber and sampled using SPME fibres. From a total of four SPME fibres (two in each section), reproducible results were obtained. Emission rates and air movement from one section to the other were predicted using developed algorithms. Comparison of the SPME fibre technique, to that of the tracer gas technique and measurements from an orifice plate showed similar results, with good precision and accuracy. With these fibres, infiltration rates can be measured over grab samples in a time weighted averaged period lasting from 10 minutes up to several days.

Keywords: Passive Samplers, Solid Phase Microextraction fibre, tracer gas techniques airflow and air infiltration.

1. Introduction

Air infiltration and inter-zonal air movement have been recognised as a major factor for determining energy efficiency, indoor air quality and condensation formation risk in buildings. Existing methods (tracer gas techniques, computer modelling and pressure tests) have limitations (Sanders, 1982; Essah et al., 2006) for determining and predicting airflows in buildings. The most established techniques uses tracer gas and in some instances computer simulations (simple cases) (Mundt, 1996).

The appropriate experimental method of determining air movement and ventilation rates in houses have been tracer gas techniques (Sanders, 1982). It provides the only direct measure of total flow rates (including infiltration) of outdoor air to buildings under actual living conditions (Dietz and Cote, 1982). However, this technique is becoming more and more difficult to sustain, since such techniques uses tubes, pumps, filters and light-scattering devices (Koziel et al. 1999) all of which makes the sampling equipment: expensive, bulky to

carry around, and requiring lengthy sampling periods. Also, some of the gases used have adverse effects on the climate, such as ozone depletion (Essah, 2009). Consequently, there have been growing demands for simple, cost-effective sampling and analytical methods, capable of achieving very low detection limits in near real-time (Koziel et al. 1999).

1.1 Importance of this Research

One of the issues that were considered during the Kyoto Protocol was the impending ban of all fluorine gases, one of which is currently used as a tracer gas (i.e. Sulphur hexafluoride-SF₆) was considered. This raised concerns for a possible alternative, in case tracer gas techniques are eventually abolished (Essah, 2009). It is therefore essential that alternative techniques are extensively researched.

The introduction and current use of passive samplers shows that such devices have the potential to be possible alternative or replacement for tracer gas techniques, however, this has to be developed. Passive samplers are used to assess the quality of various environmental components (air, water, soil). Probably

the most common of its application is the evaluation of indoor air quality (IAQ) (Zabiegała et al., 2002). So far all measurements and analyses performed using these devices have concentrated in only one volume (zone); either by grab samples or time weighted averages (TWA) (Zabiegała et al., 2002; Górecki and Namieśnik, 2002; Namieśnik et al., 2005). None of these measurements involved monitoring the mass transport (such as water vapour, contaminants, etc) from one volume to the other.

In this paper, the concept and potential of a passive sampler to be used in monitoring air infiltration and inter-zonal air movement in houses have been investigated using a Solid-Phase Microextraction (SPME) fibre. The procedures of using the SPME Fibre have been demonstrated. In addition, a comparison is made with standard techniques (i.e. tracer gas techniques and flow rates through orifice plates) to calibrate and validate measurements of the fibre for air movements in houses.

2. General Theory of Passive Samplers

The theory of passive samplers and hence SPME fibres are well documented by previous researchers in environmental and chemical analyses (Khaled and Pawliszyn, 2000; Martos and Pawliszyn, 1999). However, its use in houses to monitor air movement has been documented in only a few instances. One of such instance involved Perfluorocarbon Tracers (PFT) (Dietz and Cote, 1982) to analyse ventilation rates in one zone or volume but not for inter-zonal air movement determinations.

By definition, passive sampling is a technique based on free flow (according to the Fick's first law of diffusion) of tracer molecules from the source to a collecting medium due to the difference in chemical potential. The device use is usually based on diffusion through a well-defined diffusion barrier or permeation through a membrane. This technique is particularly suited to determine time-weighted averages (TWA) of concentrations (Zabiegała et al. 2002; Namieśnik et al. 2005) as well as transitory (grab) concentration levels in an environment.

2.1 Existing Applications

Passive samplers have been used for numerous applications since its introduction in 1927 (Górecki and Namieśnik, 2002). The sampling mode is normally selected based on the goals of the actual measurements (Zabiegała et al. 2002). Most of its application are summarised in Table 1. The choice of an ideal sampler is decided depending on the sampling matrix (i.e. gas, liquid or solid). Nevertheless, it is by no means limited to these sampling categories.

2.2 Principles and Choice of a Passive Sampler

The net flow of analyte (tracer) molecules from a medium to the sampler continues till equilibrium is established in the sampling system or until the sampling session is terminated by the user (Górecki and Namieśnik, 2002). In these two approaches, two main conditions must be met:

- Firstly, the sampler should act as a *zero sink*. That is, it should not allow the trapped molecules to be released even if the concentration of the analyte around the sampler decreases to zero (Górecki and Namieśnik, 2002), or in other terms the mass

Table 1. Summary of the main application categories of passive samplers

Matrix	Sample Category	Measurement Objectives
Gaseous	Atmospheric air	Determination of TWA (time weighted average) concentrations over long periods of time
	Indoor air	Determination of TWA concentration Determination of transitory concentration (grab sampling by SPME)
	Workplace air	Determination of 8 hours TWA concentration Determination of personal exposure (personal sampling badges)
Liquid	Surface water	Determination of TWA concentrations over long periods of time Determination of transitory concentration (grab sampling by SPME)
Solid	Soil	Determination of volatile organic compounds

Source: Górecki and Namieśnik, 2002

loading rate is not affected by the amount of analyte already absorbed (Khaled and Pawliszyn, 2000).

- Secondly, the sampling rate (i.e. the amount of analyte collected by the sampler per unit time at constant concentration in a surrounding medium) must remain constant throughout the sampling session (Górecki and Namieśnik, 2002).

Based on these conditions, a general theory of passive samplers was deduced using Fick's first law of diffusion. By Fick's first law:

$$J = -D_B \frac{\Delta C}{\Delta x} \quad (1)$$

where

J is the diffusion flux, $\text{mol m}^2\text{s}^{-1}$

D_B is the diffusion coefficient or diffusivity (say of gaseous substance B), m^2s^{-1}

ΔC is the difference between the average ambient concentration (C_F) and the concentration at the reactive surface (C_S) (i.e. $\Delta C = C_S - C_F$), mol m^{-3}

Δx is the total length of the diffusion path, m

Depending on the materials used, the gas to be monitored, and the availability of a chemical laboratory for analysis, there are different types of passive samplers. Namieśnik et al. (2005) in their studies cited more than ten types, some of which are listed below:

- Liquid passive sampler (LIPS)
- Personal aldehydes and ketones sampler (PAKS)
- Passive diffusion bag samplers (PDMS)
- Passive integrative mercury sampler (PIMS)
- Passive air samplers (PAS)
- Solid-phase microextraction (SPME) fibre

Other notable samplers cited on the health and safety site (<http://www.hse.gov.uk>) are:

- Charcoal/solvent desorption tubes
- Thermal desorption tubes (for instance, Tenax tubes).

In this research, the SPME fibre was the most appropriate technique (for reasons further discussed in section 3). Volatile organic compounds (VOCs) were considered as possible tracer molecules. This is because most applications of VOCs contribute significantly to compounds in air as it is used in paints, varnishes amongst others. These compounds which are available, suitable and compatible for these applications are normally present in air at levels above $0.1\mu\text{g/l}$ (Khaled and Pawliszyn, 2000).

Two of the well known VOCs selected were:

- Toluene C_7H_8
- Xylene C_8H_{10} {ortho(o)-, meta(m)-, para(p)- isomers}

Toluene: Toluene, also known as methylbenzene or phenylmethane, is a clear, water-insoluble liquid with the typical smell of paint thinners. It occurs naturally at low levels in crude oil, usually produced in the processes of making gasoline via a catalytic reformer. It is a common solvent, able to dissolve paints, paint thinners, silicone sealants, many chemical reactants, rubber, printing ink, adhesives, lacquers, leather tanners, and disinfectants (Atkins, 1989; www.smarterhomes.org.nz).

Xylene: The term xylene refers to a mixture of three benzene derivatives which is also used as a solvent in the printing, rubber, and leather industries. Xylene is a colorless, sweet-smelling liquid (Atkins, 1989; www.smarterhomes.org.nz). It has three isomers; ortho(o)-, meta(m)-, para(p)- isomers

After a sensitivity analysis (Section 4.1) *ortho*-xylene was selected as the most suitable isomer. Appropriate SPME fibres were also selected based on fibre sensitivity (Table 2).

2.3 Properties of Fibre Coating

Polydimethylsiloxane (PDMS): is the most widely used silicon-based organic polymer, and is particularly known for its unusual rheological (or flow) properties. Its applications range from contact lenses and medical devices. PDMS is optically clear, and is generally considered to be inert, non-toxic and non-flammable (www.scribd.com).

Table 2. Specification of suitable SPME fibres for extracting analytes

Analyte	Molecular Weight	Boiling Point (°C)	1 st Choice Fibre	2 nd Choice Fibre
Toluene	92.1	≈ 111.1	CAR/PDMS	DVB/CAR
Xylene	106.2	≈ 144.4	DVB/ CAR	CAR/PDMS

* PDMS- Polydimethylsiloxane * DVB – Divinylbenzene * CAR – Carboxen

Source: SPME newsletter, 1999/2000

Divinylbenzene (DVB): consists of a benzene ring bonded to two vinyl groups. It is related to styrene (vinylbenzene) by the addition of a second vinyl group. Divinylbenzene is a 2:1 mixture of *m*- and *p*-divinylbenzene, containing also the corresponding ethylvinylbenzene isomers (Essah, 2009).

Carboxen (CAR): it is a carbon molecular compound with a relatively low affinity for water (Essah, 2009; <http://www.sisweb.com>)

The chemical composition of Carboxen and polydimethylsiloxane (i.e. CAR/PDMS) is ideal for gaseous/volatile analytes which has a high retention for tracer analysis. Divinylbenzene/Carboxen (DVB/CAR) on polydimethylsiloxane coating is suitable for sampling a broad range of analyte (with carbon chains from C3-C20). These selected SPME fibres can be used to analyse both VOCs, however, their sensitivities are different (Table2) hence

different sampling rates for the different compounds (SPME newsletter, 1999/2000).

3. Passive Sampling: the solid phase microextraction (SPME) fibre

SPME fibres are designed and manufactured to use a re-useable syringe-like fibre coated with a liquid (polymer), a solid (sorbent) or a combination of both (Supelco, Bulletin 929). When the concentrations of tracer compounds in an environment are too low to be measured by conventional means, the SPME fibre is capable to detect these low concentrations (for instance in order of parts per billion - *ppb*). It also allows for direct transfer into a standard gas chromatography (GC), where the results are analysed. Figure 1 illustrates a typical SPME fibre. The stainless steel casing (Figure 2) was designed and manufactured for field measurements, to withstand environmental conditions.

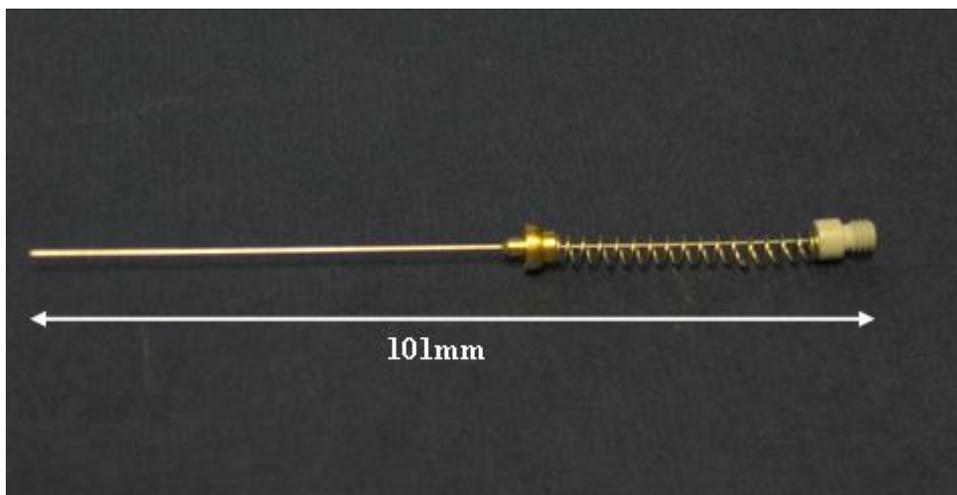


Figure 1. A picture of a SPME fibre without a holder



Figure 2. Diagram illustrating a plunged SPME showing its fibre

The SPME fibre is occasionally used by exposing the fibre to the sample matrix, until equilibrium is reached (Koziel et al., 1999). The amount of analyte absorbed onto the fibre is proportional to the concentrations in the matrix. It can be used to sample very low concentrations as well as high concentrations (Martos and Pawliszyn, 1999). In addition, it is also used for TWAs. This is achieved by retracting the coated fibre a known distance into its needle housing. The amount of analytes accumulated gives the measurement of the average concentration to which the device was exposed (Martos and Pawliszyn, 1999). Depending on the approach used, the equilibrium time varies from minutes to days (Koziel et al., 1999).

The time weighted average concentrations of several grab sampled analytes, over a series of time intervals are computed using Equation 2

$$\bar{C}_{t_n} = \frac{C_1 t_1 + C_2 t_2 + C_3 t_3 + \dots + C_n t_n}{t_1 + t_2 + t_3 + \dots + t_n} \quad (2)$$

Where C_t is the concentration of the time-weighted averages, C_I is the analyte concentration observed at time t_I , until time t_n .

Alternatively, it is obtained with only one sampler, where $t_I = t_n$ (Equation 2). In this, the sampler absorbs the analyte in direct proportion to the bulk analyte concentration for a specific sampling period (Martos and Pawliszyn, 1999). This approach can be achieved as follows:

- Figure 3 illustrates the concentration gradient of an analyte produced between the opening of the needle and the position of the fibre coating. The sampler which consists of a sorbent is positioned at a distance “Z” from the opening, of a fixed surface area, “A”.

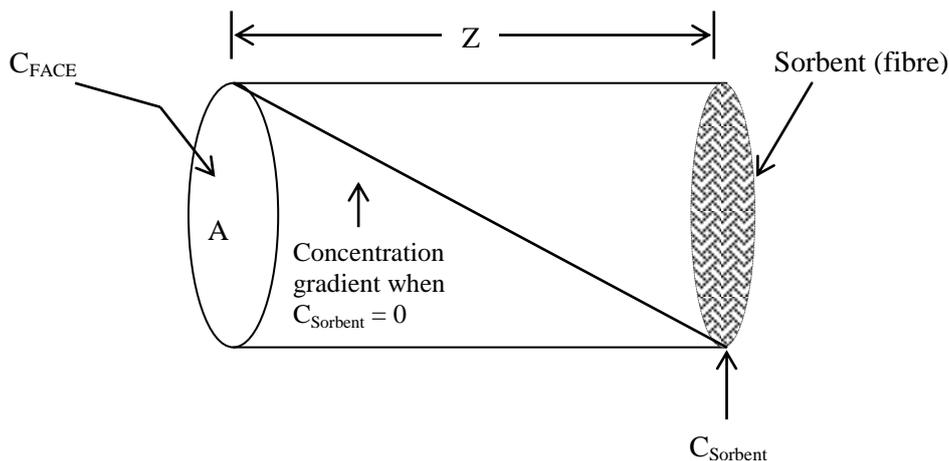


Figure 3. A typical open-faced diffusive sampler at a fixed length (Z)

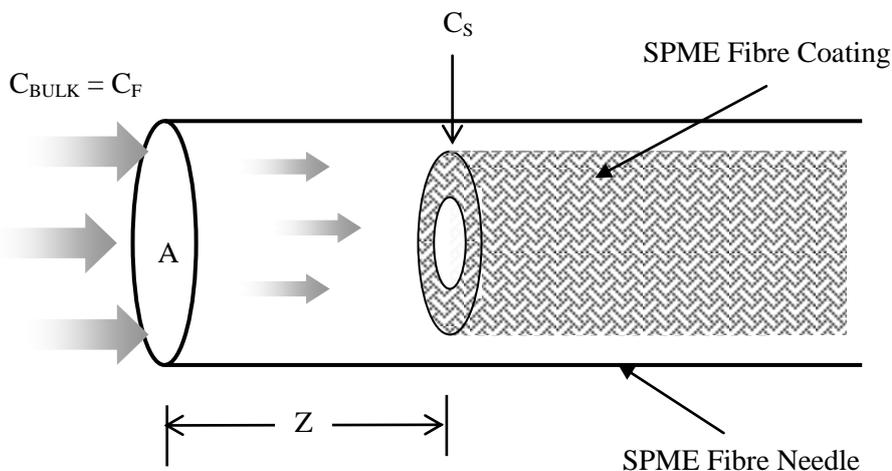


Figure 4. SPME diffusive fibre in the retracted mode for TWA Sampling

- By Fick's law of diffusion, it is possible to determine the amount of analyte that is loaded onto the fibre (Khaled and Pawliszyn, 2000; Martos and Pawliszyn, 1999).

Assumptions

To accomplish using the fibre effectively, three basic assumptions were considered;

- ❖ The analyte concentration in the bulk gas system, C_{BULK} , must be equal to the analyte concentration at the face of the sampling device, C_F (Figure 4).
- ❖ The sampling device must respond in proportion to the changing analyte concentration at the face of the device.
- ❖ The fibre should act as a "zero sink" for the target analytes.

Since the SPME diffusive fibre obeys Fick's first law, Equation 1 is applicable. Studies conducted by Martos and Pawliszyn (1999) and Khaled and Pawliszyn (2000) developed relations for monitoring a single volume. These have been used extensively for TWA sampling.

In their key findings, they concluded that, the mass load of the substance accumulated on the sampler (M) is a function of time (t), the effective cross sectional area open to diffusion (A), and the flux (J). A simplified expression identifies $M/S_R t$ to be an average sampling rate, which is directly proportional to the average bulk tracer concentration (C_F) over time from t_1 to t_2 (with $t_1 = 0$ and $C_S = 0$).

$$C_F = \left(\frac{M}{S_R t} \right) \quad (3)$$

This indicates that the mass loading of analyte onto the diffusive sampler (M/t) is dependent on the sampling rate of the device (S_R) which is directly proportional to the bulk analyte concentration (i.e. $C_F = C_B$). For a constant analyte concentration, S_R can be empirically determined using Equation 4.

$$S_R = \left(\frac{M}{C_B t} \right) \quad (4)$$

Once S_R is determined, it can be used to quantify unknown concentration by simply measuring the amount of analyte loaded (M), on the fibre for a given sampling time t . (Khaled and Pawliszyn, 2000; Martos and Pawliszyn, 1999). One of the main advantages of using SPME fibres as TWA samplers is that, the path length, Z , as illustrated in Figure 4 can be increased or decreased. This

accommodates higher concentrations or longer sampling times when increased, or lower concentrations or shorter sampling times when decreased.

The above theory is applicable for sampling from a single volume. As a result during this research, further algorithms were developed to ensure good understanding of inter-zonal air movement (section 4.3).

3.1 Potential for using SPME fibres (why and how)

In recent times the use of SPME fibre technique have become predominant in monitoring indoor air pollution and its mass transport because they are simple in design and use, and are relatively cheap. They do not require any power supply and they are able to simultaneously detect the presence of different compounds in their vapour form. SPME fibre technique is used in many applications where very sensitive yet simple air sampling and analysis are required. This is because it is easy to monitor and has the potential of replacing labour and cost intensive methods (such as tracer gas techniques) which are currently used by regulatory agencies, research or academic institutions, and contract laboratories (Namieśnik, 2001).

The fibre can be re-used 50-100 times, and disposed of when the fibre is no longer usable. (Supelco, Bulletin 929). In this research, the fibres have been re-used at least 50 times.

4. Measurements and calibration

4.1 Sensitivity analysis of the isomers of xylene-using head space

A series of sensitivity analyses to select one suitable isomer of xylene was performed. Head space of the pure liquids were taken and plunged into the GC. Retention times (R_T) of *ortho*-, *meta*-, *para*- xylene obtained from the GC (Figure 5) are summarised in Table 3. It was impossible to distinguish between the isomers of *para*- and *meta*- xylene. As a result *ortho*- was the most practical isomer selected.

Definitions

Head Space: Head space analysis is basically a technique where the vapour in the gas above, and in equilibrium with a solid or liquid is sampled, instead of sampling, solely, the solid or the liquid themselves (<http://www.chromatography-online.org>).

Retention Time (R_T): Retention time of an analyte as defined on the site of the Journal of Chromatographic science is considered as the elapsed time between the time of injection of an analyte into a detection device (i.e. GC) and the time of elution of the maximum peak

of that analyte. It is a unique characteristic of the analyte and can be used for its identification purpose (<http://www.chromatography-online.org>).

4.2 Calibration Curves

5µl of liquid toluene and o-xylene were injected into a 5 litre tedlar bag (here after referred to as bag). The bag is made from polystyrene, designed with two valves; one fitted

with a septum (necessary for injecting the liquid) and an adjustable valve that opens and shuts to allow the injection of air. The bag was half filled (2.5L) with air after which 5µl of the required VOC was injected into the bag through the septum. It was then filled by air. This method (i.e. in two stages), was adapted to ensure good mixer of the VOC. Calculations and dilutions were made after equilibrium was attained.

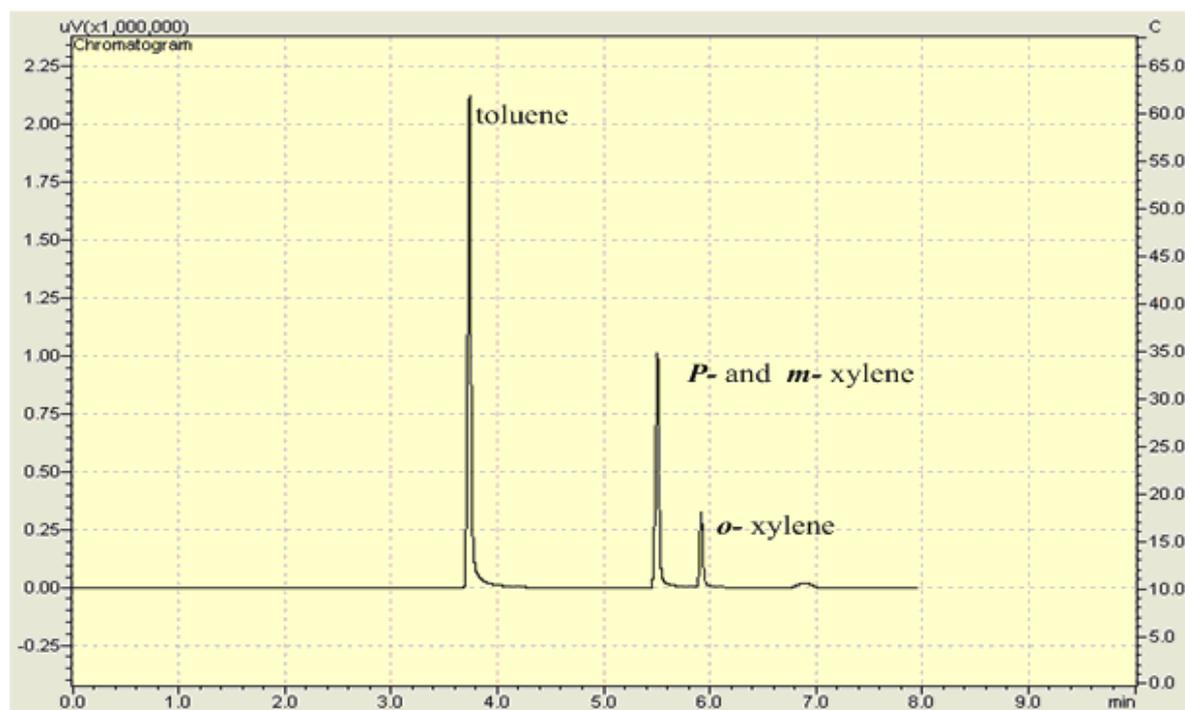


Figure 5. Retention times of each compound as analysed in the gas chromatography

Table 3. Retention times of the VOCs obtained from a sensitivity analysis

Compounds	R _T (A) min	R _T (B) min	R _T (C) min	R _T (Av) min
Toluene	3.731	3.728	3.730	3.730
Para-xylene	5.509	5.509	5.509	5.509
Meta- xylene	5.508	5.509	5.509	5.509
Ortho-xylene	5.924	5.927	5.925	5.925

Calculations and method of diluting concentrations

Recommendations by Occupational Safety and Health (OSHA) and National Institute for Occupational Safety and Health (NIOSH) specify that in any given workplace, the limit of exposure to concentrations levels of VOCs for a maximum of 15 minutes must not exceed 50 ppm or 191mgm⁻³ (McCammon, 1995). These levels are significantly lower than the 332 mg/m³ recommended by WHO (WHO, 2007).

For simplification, assuming that 5mg (liquid) ≈ 5µl (liquid), Essah (2009) assumed that every 5 mg of the liquid solution was the maximum possible concentration that is in a 5 litre container (in this case the bag).

Hence, if 5mg of liquid toluene or o-xylene was injected separately into the 5 L bag, the concentration generated in the bag in mg/m³ was obtained using Equation 5. From this relation, diluted concentrations were generated by taking known concentrations in

micro-litres (μl) of head space from the bag into vials (Table 4).

$$\text{Conc. in bag} \left(\frac{\text{mg}}{\text{m}^3} \right) = \frac{\text{mass of liquid (mg)}}{\text{vol.occupied (m}^3)} \quad (5)$$

That is

$$\text{Diluted Conc.} \left(\frac{\text{mg}}{\text{m}^3} \right) = \frac{\text{vol. of sampled gas (ml)}}{\text{vol. of vial used (ml)}} \times \text{Conc. generated (mg/m}^3) \quad (6)$$

$$\text{Conc. in bag} \left(\frac{\text{mg}}{\text{m}^3} \right) = \frac{5 \text{ mg}}{0.005 \text{ m}^3}$$

$$\text{Conc. generated in bag (mg/m}^3) = 1000 \text{ mg/m}^3$$

Knowing that the bag contains 1000 mg/m^3 of the VOC, other concentrations are made-up using Equation 6.

Based on exposure limits recommended by OSHA and NIOSH, made-up concentrations were restricted to a maximum of 50 mg/m^3 (i.e. 13 ppm). This ensured that the calibration values were within the accepted exposure limits. The concentration developed for calibration could determine levels of at least 1.7 ppb, lower than the safe concentrations (Table 4).

Concepts of vapour absorption

Each VOC has a maximum equilibrium concentration which was reached in the tedlar bag (Essah, 2009). This concept was verified, by monitoring the concentration levels at constant intervals. It was observed that once saturation was attained, the peak values were constant all through the experiments.

Table 4. Made-up concentrations from the tedlar bag

Number	Concentration (mg/m^3)	Concentration (ppm)	Mode of dilution from tedlar bag
1	250	65.4	500 μl into a 2ml vial
2	50	13.0	1000 μl into a 20ml vial
3	25	6.5	500 μl into a 20ml vial
4	5	1.3	100 μl into a 20ml vial
5	1	0.26	20 μl into a 20ml vial
6	0.5	0.13	200 μl of Conc. No.2 into a 20ml vial
7	0.25	17 (ppb)	100 μl of Conc. No.2 into a 20ml vial
8	0.125	8.6 (ppb)	100 μl of Conc. No.3 into a 20ml vial
9	0.025	1.7 (ppb)	100 μl of Conc. No.4 into a 20ml vial

Analysis and results

Two sets of SPME fibres were used to sample head space from each vial for 10mins, (5mins less the recommended exposure limit). Using the GC, the sampled analytes were analysed as tabulated in Tables 5 and 6

Data obtained after sampling toluene (C_7H_8) from the vials

At this stage the vials contained only toluene. Two fibres of each type were used to reduce errors and ensure accuracy. Comparing both fibres there is a very good correlation (R^2), and the theory of the manufacturer is confirmed, that is DVB/CAR is less sensitive to toluene compared to CAR/PDMS

(Table 5). Repeated results obtained from the GC analysis were identical, within $\pm 3\%$ of each other.

Data obtained after sampling o-xylene (C_8H_{10}) from the vials

In this analysis the vials used contained only o-xylene, a very good correlation was obtained from the calibration curves. Table 6 illustrates the sensitivity of each SPME fibre to o-xylene. As above, two fibres were used to reduce errors and ensure accuracy. This shows that the SPME fibre is consistent in its measurements as the sampled results obtained from the GC analysis varied within $\pm 3\%$ of each other

Table 5. Results obtained from varying concentrations of toluene

Concentration mg/m ³	AREA UNDER PEAKS (μV)					
	CAR/PDMS Fibre 75μm			DVB/CAR Fibre 50/30μm		
	1 st Run	2 nd Run	Av	1 st Run	2 nd Run	Av
50	711858	711900	711879	352391	365000	358696
25	285014	273322	279168	195953	194200	195077
5	63563	74578	69071	43774	50001	46888
1	34798	31059	32929	5468	6453	5961
0.5	10022	9822	9922	1399	1508	1454
0.25	6476	5788	6132	1235	1354	1295
0.125	5902	5586	5744	650	823	737
0.025	5390	5001	5196	0	0	0

Table 6. Results obtained from varying concentrations of o-xylene

Concentration mg/m ³	AREA UNDER PEAKS (μV)					
	CAR/PDMS Fibre 75μm			DVB/CAR Fibre 50/30μm		
	1 st Run	2 nd Run	Av	1 st Run	2 nd Run	Av
50	711858	711900	711879	352391	365000	358696
25	285014	273322	279168	195953	194200	195077
5	63563	74578	69071	43774	50001	46888
1	34798	31059	32929	5468	6453	5961
0.5	10022	9822	9922	1399	1508	1454
0.25	6476	5788	6132	1235	1354	1295
0.125	5902	5586	5744	650	823	737
0.025	5390	5001	5196	0	0	0

Table 7. Summary of equations obtained from the calibration curves

Calibration Equations			Relations		
VOC	Fibre	Equation	m	c	R ²
Toluene	CAR/PDMS - 75 μm	y = 13624x + 316.97	13624.0	317.0	0.9882
Toluene	DVB/CAR - 50/30 μm	y = 7266.8x + 1868.9	7266.8	1868.9	0.9976
O-xylene	CAR/PDMS - 75 μm	y = 5954.8x + 2565.1	5954.8	2565.1	0.9972
O-xylene	DVB/CAR - 50/30 μm	y = 9692.6x + 7707.2	9692.6	7707.2	0.9939

From Tables 5 and 6, calibration curves were plotted. Table 7 shows a summary of the equations obtained from the curves which are based on standard linear notations ($y = mx + c$)

where

y is the Peak Area, μV; m is the slope; x is the concentration, mg/m³; c is the intercept.

4.3 Calibrating the SPME fibre with established techniques

Figure 6 shows a sketch of the wire frame mode of the humidity chamber as used for the experiment.

The chamber was partitioned into two sections with a 0.5 m thick insulation material. The internal dimensions of the two sections, labelled as “1” (i.e. representing a cold section) and “2” (i.e. representing a warm section) measure 2.2 m x 2.4 m x 2.5 m and 3.9 m x 2.4 m x 2.5 m respectively. For the purpose of this experiment, the chamber was designed to simulate conditions in a house and its roof.

The section labelled “1” was kept at lower temperatures (considered as the roof - below 10 °C) than the other labelled “2” (considered as the house i.e 20 °C). This principle originates from previous research work by Essah et al. (2006) and Essah and Sanders (2006).

An outlet vent was created through the cold section with an extractor fan connected to the outlet to ensure air movement through it. Flow directions are as illustrated in Figure 6. It is assumed that there are no reverse flows. Figure 7 illustrates the location of all the parameters used for measurements. Table 8 gives a brief description of these parameters.

Experiments performed in the humidity chamber involved two other techniques (i.e. tracer gas technique and an orifice plate) to compare, calibrate and validate the airflow rates obtained between the two sections using the SPME fibre.

The orifice plate was fitted through a hole created between the two sections (labelled O_p in Figure 6), measuring 51mm (2 inches) in diameter (i.e. the size of the tube connecting the orifice plate).

This was to ensure that the orifice plate remained the only source through which air was exchanged between the two sections, assuming other infiltration sources were thoroughly sealed.

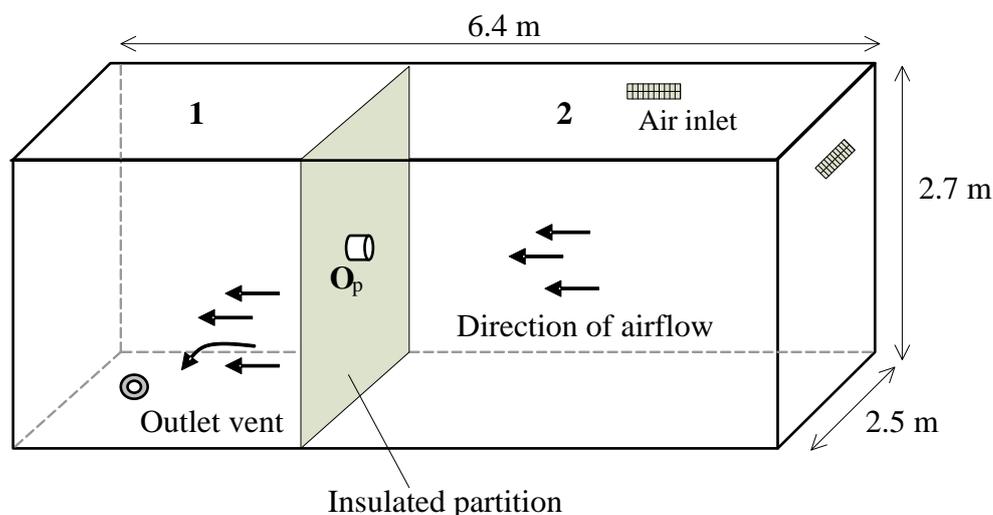


Figure 6. A wire-frame view of the partitioned humidity chamber

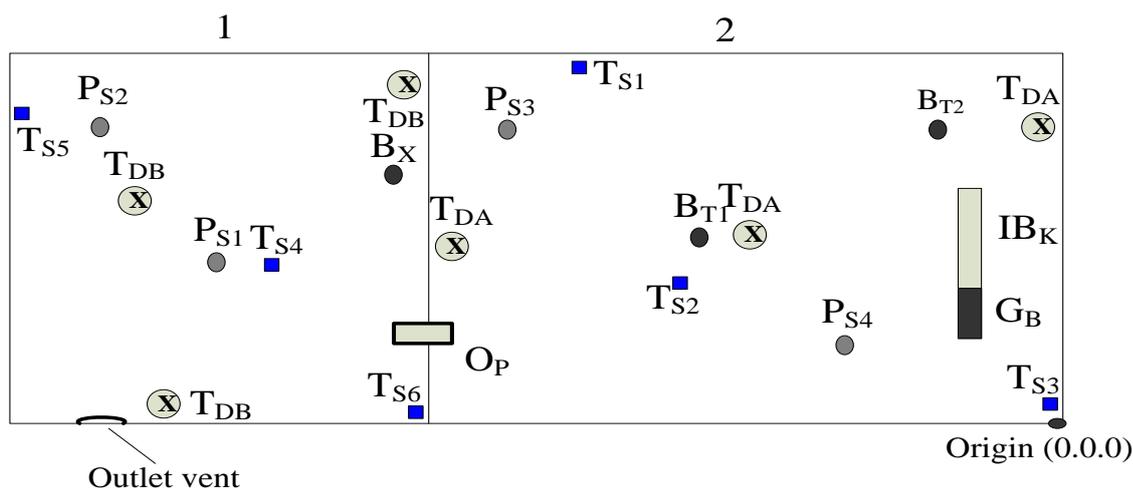


Figure 7. Spatial distribution of passive samplers ($P_{...}$), sources of analyte ($B_{...}$), tracer gas sampling ($T_{s...}$) and dosing ($T_{d...}$) tubes and Bruel & Kjaer dosing and analysing units

Table 8. Summary of description and location of parameters listed in Figure 7

Parameters	Descriptions	Location in Chamber (L x B x H) m
P _{S1}	Passive sampler (SPME fibre) suspended in the middle of the volume	5.3 x 1.3 x 2.0
P _{S2}	Passive sampler (SPME fibre) at position 2	5.9 x 2.0 x 0.3
P _{S3}	Passive sampler (SPME fibre) at position 2	3.5 x 1.9 x 2.0
P _{S4}	Passive sampler (SPME fibre) suspended in the middle of the volume	0.5 x 0.8 x 0.8
B _X	Two 20ml beakers containing o-xylene placed side by side	5.0 x 1.8 x 1.1
B _{T1}	20ml beakers containing toluene at position 1	2.1 x 1.3 x 0.7
B _{T2}	20ml beakers containing toluene at position 2	0.5 x 2.0 x 0.7
IB _K	Innova Bruel & Kjaer analyser and doser units	-
G _B	Location of gas bottle for tracer gases CO ₂ and SF ₆	-
T _{S (1-6)}	Tracer gas sampling tubes	-
O _P	Orifice plate	4.3 x 0.7 x 1.1
T _{DA}	Tracer gas dosing tubes at 3 different locations in zone 2	4.3 x 1.5 x 2.0 2.0 x 1.6 x 2.6 0.0 x 2.0 x 0.5
T _{DB}	Tracer gas dosing tubes at 3 different locations in zone 1	5.0 x 2.2 x 1.8 5.1 x 1.3 x 2.0 5.7 x 0.0 x 1.1

The chamber was designed to be practically air tight, therefore the only sources of air inlet were through air infiltration sources around; the insulation material used to split the volumes, the door and narrow openings for air inlet.

This was verified by Essah (2009) when a study of the decay characteristics of tracer gases was performed using the chamber with the same configuration.

Attached to the outlet vent was an extractor fan which regulated flow out of the chamber.

4.4 Results and discussion

The results were analysed based on the concept and principles of the three techniques which were performed simultaneously, at the same internal conditions.

Orifice plate

Monitoring known flow rates through the orifice plate was essential to complement the tracer gas techniques and hence calibrate the results obtained from the SPME fibre. The orifice plate was set up as in Figure 8. Figure 9 illustrates the calibration curve of the orifice plate which was generated using the relation in Equation 7.

For effective analysis, air flows through the orifice plate for each set of experiments was controlled at a constant pressure difference. This was to enable a fairly constant flow through the orifice plate with less variation.

$$\text{Airflows (m}^3/\text{h)} = 3.536 * \sqrt{\Delta P} \quad (7)$$

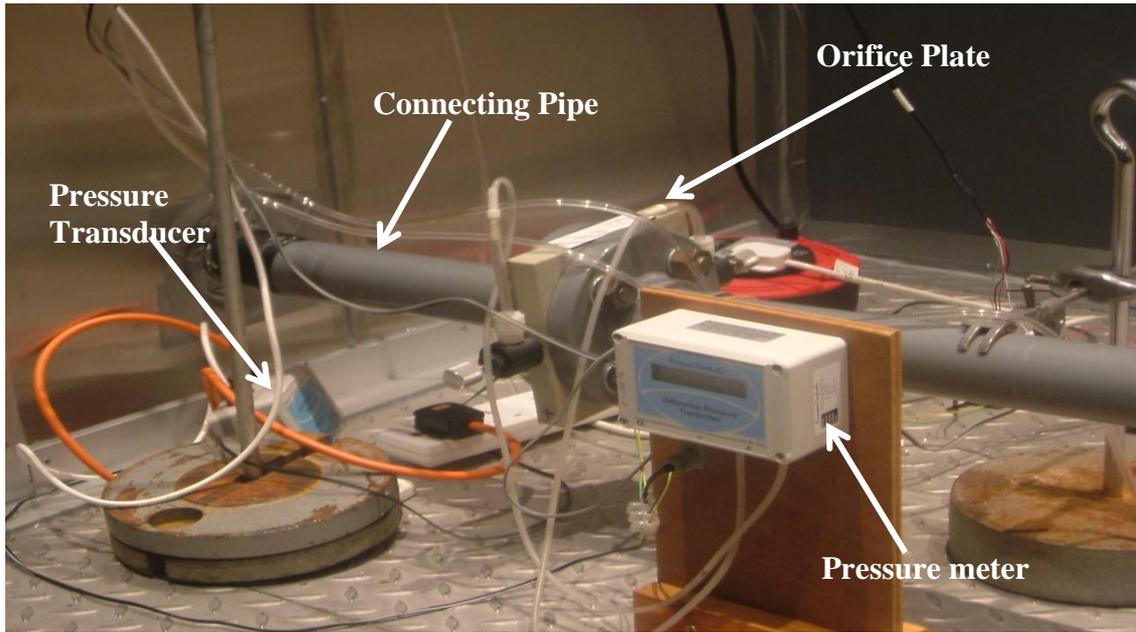


Figure 8. The set-up of the orifice plate within the environmental chamber

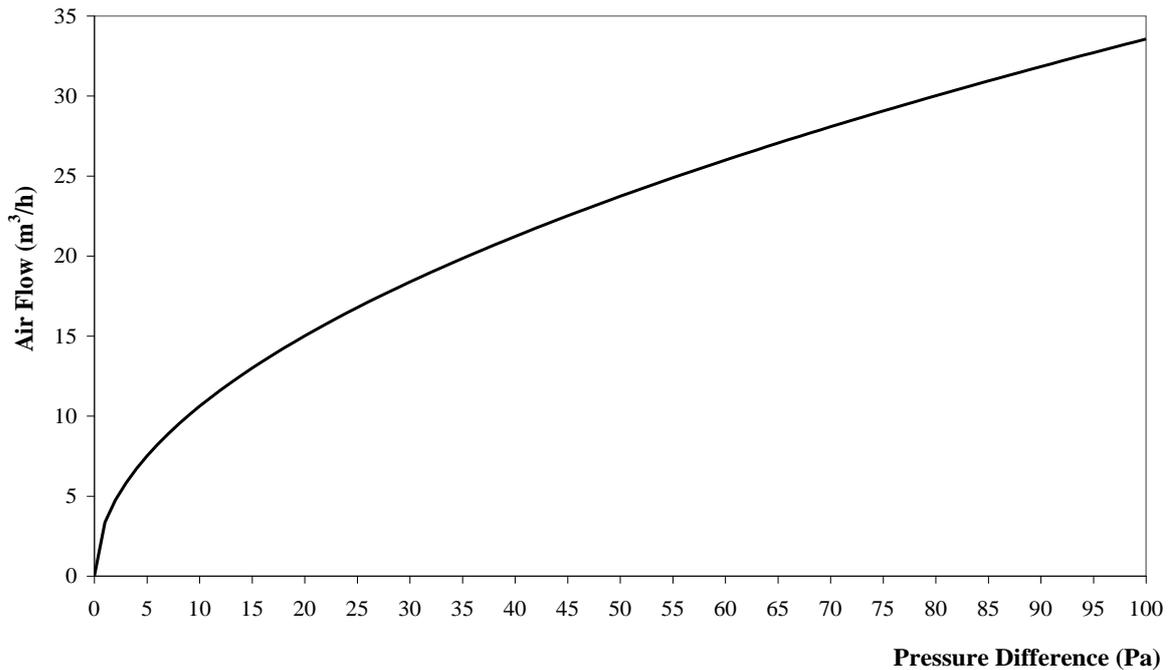


Figure 9. Calibration curve generated from the orifice plate

Tracer gas technique

Using a verified tracer gas decay technique (Sanders, 1982; Essah and Sanders, 2006 and Essah et al, 2006), two gases (CO_2 and SF_6) were injected into the section *1* to compare the ventilation rates that would be obtained from each gas.

Sampling was performed from three different locations within the section. The ventilation rate obtained for both gases were within 10% deviation (i.e. $0.6 \pm 0.06 \text{ h}^{-1}$), which verified that the tracer gas technique was a good enough measure to validate the SPME fibre.

Relations for air movement from one section to the other generated by Sanders (1982) was adapted with CO₂ injected in section 1 and SF₆ injected in section 2. The airflows were calculated using Equation 8 which have been verified and validated in other research work by Essah et al (2006), Essah and Sanders (2006) and Essah (2009). The set-up of the tracer gas technique is as illustrated in Figure 10. Sampling was performed from three different locations within each section (Figure 7).

$$X_{21} = \frac{\sum [C_1(t)A] - \sum (AB)}{\sum A^2} \quad (8)$$

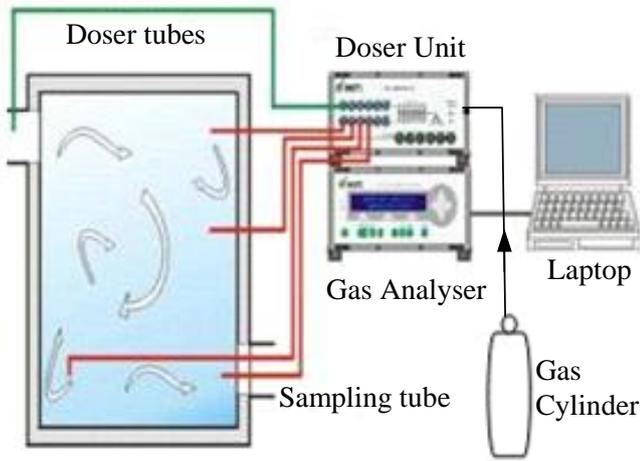


Figure 10. Diagram of the computer-controlled tracer gas measurement system

SPME fibre technique

Considering the concept of the tracer gas technique above, liquid toluene was poured in the beaker and introduced into the warm section of the chamber. Similarly, liquid o-xylene was introduced into the cold section. The airflows from the warm to the cold section were calculated using Equation 10.

The ventilation rate (β) of a zone is calculated using Equation 9 where V is the volume in m³ of the zone, G is the diffusion rate and C is the concentration in mg/m³.

$$\beta = \frac{G}{VC} \quad (1/h) \quad (9)$$

Although both fibres (CAR/PDMS and DVB/CAR) were calibrated only the 75 μ m CAR/PDMS SPME fibre was used during this research. Four SPME

fibres were used each retracted 9 mm within the needle housing to obtain longer sampling periods of at least 48 hrs. These fibres which are designed to sample both VOC's (Table 2) were all introduced from the outside to ensure the internal environment was not affected.

Two main scenarios (i.e. either it is well mixed or not) were adopted to understand the effectiveness of the fibre. The experiments showed that the chamber was well mixed which was due to the extractor fan, aided by the position of the analytes (tracer gases) and the sampling time.

In the first scenario the fibres were introduced at least 30 mins (note, the time difference is dependent on the volume under investigation) after the VOCs were introduced (i.e. to ensure it is well mixed) into the environment, while in the second; the fibre was introduced simultaneously with the VOCs (i.e. not well mixed). The airflows were calculated using Equation 10 (Essah, 2009). The results obtained are summarised in Table 9

$$X_{21} = \frac{X_{o1}(C_{a2} - C_{ao})}{(C_{a2} - C_{a1})} \quad (10)$$

Where

X_{o1} is the airflows from outside to zone 1 in m³/s, given

by the relation $\frac{NV}{3600}$ (N is the number of air

changes per hour (ach) and V is the volume of the zone.

C_{a2} concentration of VOC a in section 2, g/m³

C_{a1} concentration of VOC a in section 1, g/m³

C_{ao} outside concentration of VOC a (usually zero), g/m³

N was obtained from Equation 9 and used to calculate X_{o1} . Based on this and concentrations of VOC "a" (toluene) in zone 1 and 2, X_{21} was calculated (Equation 10).

From a simple analysis of the data using the statistical package SPSS, the results obtained from the three techniques are summarised in Table 9. During the sampling process, the extractor fan was set a high and low flow rate to ensure that the SPME fibre was capable at both rates. For the low flow rates, only one sample analysis was achieved with values of 3.3, 3.5 and 3.6 m³/h for SPME fibre, Orifice plate and Tracer gas respectively. As a result no error analysis is presented.

Table 9. Summary of the results obtained from the three different techniques

Parameter	Well Mixed environment		Not well mixed environment	
	Analysis	X_{21} (m ³ /h)	Analysis	X_{21} (m ³ /h)
SPME	Mean	7.9099	Mean	6.4185
	Std.Error	0.4591	Std.Error	0.1577
Orifice Plate	Mean	8.2449	Mean	7.8423
	Std.Error	0.4785	Std.Error	0.1926
Tracer gas	Mean	7.5578	Mean	5.6300
	Std.Error	0.2351	Std.Error	0.2828

From the results in Table 9, the standard error for both the SPME fibre and the Orifice plate were similar for separate mixture conditions while that of the tracer gas remained almost the same.

From Table 9, the estimated distributions of airflows, X_{21} between sections 2 and 1, from the three methods were plotted using box blots.

All calculated error bands are 95% confidence intervals for mean.

In Figure 11 and 12, the solid bar shows the median of the data, the box, the inter-quartile range and the vertical lines of the overall range of the data. From the length of the boxes in Figure 11, there is a larger spread of data compared to that of Figure 12.

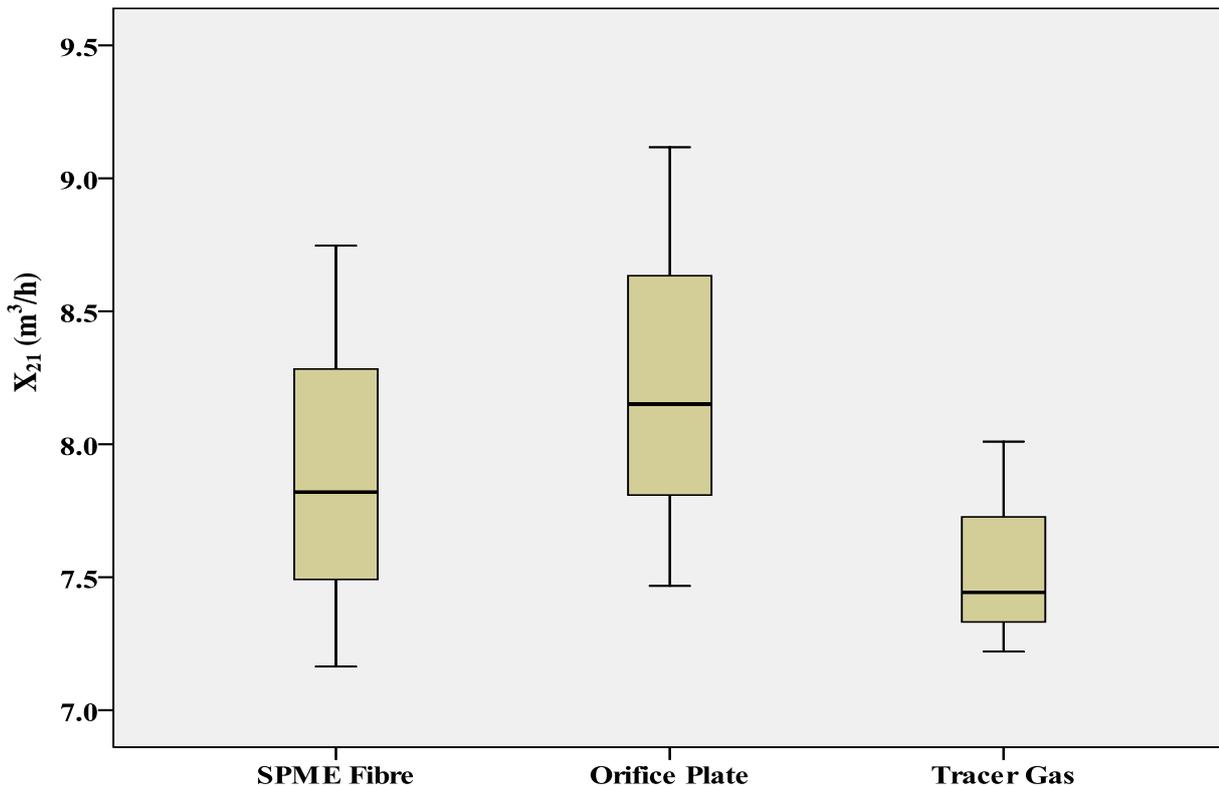


Figure 10 Distribution of analysed airflow rates when the tracer gases were well mixed

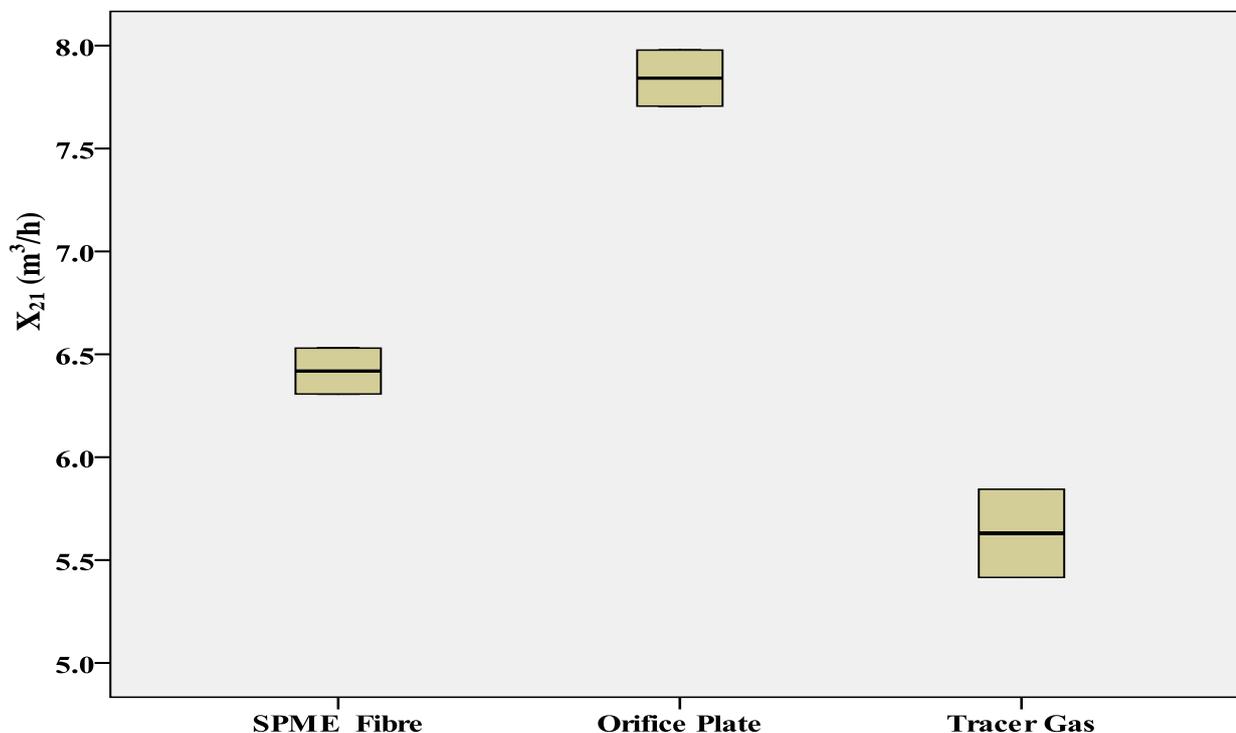


Figure 11 Distribution of analysed airflow rates when the tracer gases were not well mixed

4.5 Conclusions

Simple steps have been taken to calibrate and validate a Solid Phase Microextraction (SPME) fibre (a passive sampler) to monitor air movements between two volumes. This calibration was performed using two established techniques (i.e. tracer gas techniques and orifice plate measurements). The key findings are as follows:

- The experiments using the same and/or different SPME fibres were reproducible within experimental precision, similar results to within $\pm 3\%$.
- The two scenarios employed in the humidity chamber illustrates that the fibre is most effective within a well mixed environment.
- Comparison of the SPME fibre technique with the other two within a well mixed environment, illustrates a deviation between 3%-7%.
- This study confirms the use of SPME fibres as a potential technique to monitor air movement from one volume to the other.

This research paper has demonstrated how to extend the potential of existing passive sampling techniques for measuring air movements between two volumes. It shows that SPME fibres can be used as an alternative to tracer gas techniques but unlike the latter, which provides several results,

TWAs of the SPME fibre gives only one value, unless several fibres are used simultaneously. This knowledge is essential for further development of on-going research work.

Acknowledgement

The work described in this paper was sponsored by Monier Technical Centre, Ltd, UK in collaboration with the RICH Centre of Glasgow Caledonian University, Glasgow.

References

Atkins, P.W., 1989. *General Chemistry-International Students Edition*, Oxford University. New York-USA, Scientific American Books (Publishers). P 712, 863-865.

Carboxen (CAR) - from Scientific Instrument Service, Inc (sisweb) [online]. Available from: <http://www.sisweb.com/index/referenc/car569am.htm>

[Accessed 02 June 2008]

Dietz, R.N and Cote, E.A., 1982. Air infiltration measurements in a home using a convenient Perfluorocarbon tracer technique. *Environment International*, **8**, pp 419-433.

Essah, E.A. and Sanders, C.H., 2006. Heat and moisture transport between houses and cold lofts - a combination of convection and diffusion. *International Energy*

Agency, Annex 41: Whole building Heat, Air and Moisture response MOIST-ENG, Kyoto-Japan

Essah, E.A., Sanders, C.H., Galbraith, G.H., and McLean, R.C., 2006. Airflow between houses and their roofs. Proceedings of the Third international Building Physics Conference, Concordia University, Montreal-Canada. *Research in Building Physics and Building Engineering*. ISBN 0-415-41675-2, pp. 737-744.

Essah, E.A., 2009. *Modelling and measurements of airflow and ventilation within domestic pitched roofs-PhD Thesis*. Glasgow Caledonian University, Glasgow, UK

Górecki, T. and Namieśnik, J., 2002. Passive sampling. *Journal of Atmospheric Environment. Trends in Analytical Chemistry*, **21** (4), pp. 276-291

Khaled, A. and Pawliszyn, J., 2000. Time-weighted average sampling of volatile and semi-volatile airborne organic compounds by the solid-phase microextraction device. *Journal of Chromatography A*, **892**, pp. 455-467.

Koziel, J., Mingyu, J., Khaled, A., Japheth, N., and Pawliszyn, J., 1999. Field air analysis with SPME devices. *Journal of Analytical Chemistry Acta*, **400**, pp.153-162

Library 4 Science-Gas Chromatography, *Journal of Chromatographic science* [online]. Available from: <http://www.chromatography-online.org/topics/retention/time.html> [Accessed 20 September 2007]

Library 4 Science-Head Space analysis, *Journal of Chromatographic science* [online]. Available from: <http://www.chromatography-online.org/topics/head/space/analysis.html> [Accessed 20 September 2007]

Martos, P.A. and Pawliszyn, J., 1999. Time-weighted average sampling of with solid-phase microextraction device: Implications for enhanced personal exposure monitoring to airborne pollutants. *Journal of Analytical Chemistry*, **71**, pp. 1513-1520

Methods for the determination of hazardous substances: *Health and Safety laboratory*, 1997. Sorbent tube standards-Preparation by the syringe injection technique. **33** (2) [online]. Available from: <http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs33-2.pdf> [Accessed 16 May 2007]

McCammon, C., 1995. Department of Health Services . Fact Sheet, Legal exposure limits -

Hazard Evaluation System and Information Service [online]. Available from: <http://www.osha.gov/SLTC/autobody/docs/cdc001.html> [Accessed 13 October 2006]

Mundt, E., 1996. The Performance of Displacement ventilation systems. PhD Thesis, Royal Institute of Technology Building Services Engineering, Stockholm.

Namieśnik, J. 2001. Modern trends in monitoring and analysis of environmental pollutants. *Polish Journal of Environment studies*, **10** (3), 127-140.

Namieśnik, J., Kot-Wasik, A., Zabiegaa, B. and Partyka, M., Wasik, A., 2005. Passive sampling and/or extraction techniques in environmental analysis: a review. *Journal of Analytical and Bio-analytical Chemistry*, **381** (2), pp. 279-301

Polydimethylsiloxane (PDMS) Available at: <http://www.scribd.com/doc/6667501/Polydimethylsiloxane> [Accessed June 2008].

Sanders, C.H., 1982. Air movement in houses: a new approach. *Building Research and practice*, CI/SFB **81** (57), pp. 160-175.

SPME newsletter, 1999/2000 (winter). Sample Prep Made Easy-“SPME”. How to choose the proper SPME fibre. A continuation of reports discussing SPME parameters [online]. Available from: <http://www.sigmaaldrich.com/Graphics/Supelco/objects/6800/6727.pdf> [Accessed 20 August 2006]

Supelco Bulletin 929. A practical guide to quantitation with Solid Phase Microextraction [online]. Available from: <http://www.sigmaaldrich.com/Graphics/Supelco/objects/11200/11143.pdf> [Accessed 10 October 2006]

Smarter Homes, Glossary- Toluene and Xylene [online]. Available from: <http://www.smarterhomes.org.nz/help/glossary/> [Accessed November 2008].

WHO, 2000. Air Quality Guidance for Europe, v91: Copenhagen, WHO Regional Publications European series, pp. 273

Zabiegala, B., Gorecki, T., Przyk, E. and Namiesnik, J., 2002. Permeation passive sampling as a tool for the evaluation of indoor air quality. Passive sampling. *Journal of Atmospheric Environment. Trends in Analytical Chemistry*, **36**, pp. 2907-2916