

Design factors affecting the passive release of tracer gas for ventilation measurements

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Abstract. The ventilation rate is an important parameter for assessing indoor air quality and energy efficiency. In occupied buildings, ventilation measurements utilising passive methods are preferable to active methods due to their simplicity and less intrusive nature. The perfluorocarbon tracer method can be used to measure long-term ventilation rates for this purpose. This method requires the passive release of a tracer gas which is often a liquid chemical diffusing out of a vial. The tracer gas emission rate is a key parameter of the vial design as if it is too low, the sampler will not be able to detect the tracer gas. If the emission rate is too high, the sampler can become saturated. Both scenarios will lead to inaccurate ventilation results. There is wide variability in vial design but little information about the relative impact of each design factor. Thus, the aim of this study was to compare the emission rate of a common tracer gas, perfluoromethylcyclohexane, using different vials designs i.e. capping styles, septa materials, and fill levels. Samples were kept in an incubator and gravimetric analysis was carried out using a semi-microbalance (resolution: 0.01 mg). The results demonstrate that the emission rate is significantly affected by capping style but not by fill level.

1 Introduction

Air exchange between the indoors and outdoors can affect indoor air quality and energy consumption. The rate of air exchange can be measured using tracer gas techniques which involve injecting a tracer gas into a space and measuring its concentration change. One such technique is the perfluorocarbon tracer (PFT) method which is based on the constant injection principle. Tracer gas is passively emitted into a space using a source, and its concentration is measured using passive samplers. The samplers are analysed by gas chromatography coupled with mass spectrometry or electronic capture detection to determine the mass of adsorbed tracer gas. An advantage of the PFT method is that both the emission and sampling of tracer gas can be carried out by passive means, meaning the approach is less intrusive for occupants. In addition, the method allows for long-term measurements of room-specific air change rates which other methods (e.g. tracer gas decay) are not suited towards. This is important as ventilation rates constantly vary both spatially and temporally according to building characteristics, occupant activity, weather conditions, and ventilation equipment.

The air change rate is calculated using the following equation [1]:

$$q = \frac{G}{V C_s} \quad (1)$$

where q is the air changes per hour (h^{-1}), G is the tracer gas emission rate ($\mu\text{g h}^{-1}$), V is the space volume (m^3), and C_s is the steady-state tracer concentration ($\mu\text{g m}^{-3}$). The steady-state tracer concentration is calculated based on the tracer gas mass, uptake rate of tracer gas onto adsorbent, and sampling duration.

An important parameter in Equation 1 is the tracer gas emission rate, G . This can be determined by gravimetric analysis in a lab by measuring the mass of a tracer source before and after experimental use. However, there will be emissions during storage if sources are prepared in batches in advance of deployment, and during transport to and from the study site. These emissions cannot be easily accounted for. In addition, manual weighing of sources can be time-consuming in large-scale studies or when multiple sources are deployed per zone, as recommended by Dodson *et al.* [2]. In practice, researchers experimentally derive relationships between temperature and the emission rate of their sources, and then estimate the emission rate in a field study using monitored temperature data. Therefore, there is an advantage for a researcher to adopt a single source design, characterise the temperature-emission rate relationship, and then replicate the source design. Sateri *et al.* [3] recommend that it is sufficient to characterise one emission rate for each manufacturing lot of sources. If sources of different

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designs are made, the temperature-emission relationship would have to be derived for every unique design.

1.1 Tracer gas vessel design

A basic design of a tracer gas source is a hollow vessel (with one end closed) in which liquid chemical of a tracer compound is injected. The open end of the vessel is then covered with a permeable material which could be a simple plug or a septum as part of a capping system. The tracer liquid volatises into a gas internally and diffuses out through the permeable material.

Several studies describe their source design and have characterised emission rates [1,4,5]. Whilst dimensions are often stated, replicating a source design can be difficult as not all the required materials may be available commercially. In addition, some materials are more expensive than others or the design requires additional equipment. Nonetheless, basing a source design on literature is a starting point. This is useful because if emission rates are too low then, depending on the duration of sampling, not enough tracer gas may be adsorbed for the gas chromatographer to analyse. If the tracer gas concentration is too high, then the adsorbers could become saturated. Therefore, there is a need to understand which design factors affect the emission rate.

Vessels have included aluminium shells [6], crimp top glass vials [1,7] and screw top glass vials [4]. The advantage of the glass vials is that they are common lab equipment and commercially available in standard sizes. They also allow the researcher to visually verify when the tracer liquid has been fully volatised. Whilst the screw top vials can be assembled by hand, the crimp top vials require the additional purchase of a crimper. In both cases, there can be experimenter variability with how tightly crimped or screwed the vials are. There also exists a third capping style, the snap top vial, which has not been investigated for tracer gas source design before. Thus, the performance of glass vials with different capping styles will be compared in this study.

In terms of permeable material, silicone rubber is commonly cited as being used in source design, but the type of silicone is not always mentioned e.g. vinyl methyl silicone (VMQ), polydimethylsiloxane (PDMS), etc. It is not clear how these different types of silicone can impact emission rates. However, the impact of material thickness has been investigated by Jong *et al.* [6] who developed perfluoromethylcyclohexane (PMCH) sources using aluminium cylinders and VMQ silicone plugs. The plug thicknesses were varied between 0.635 and 1.905 cm, and it was found that the emission rate was indirectly proportional to the plug thickness. Lunden *et al.* [4] prepared tracer sources using screw cap vials of different sizes: 4-dram, 2-dram and ½-dram. The vials required septa of different diameters: 22 mm, 13 mm and 8 mm, respectively. The emission rate of three PFT gases were found to increase with increasing vial size.

As the tracer liquid volatises, it is expected that the length of the diffusion path (i.e. headspace above the liquid surface) will increase, and thus the tracer level could affect the emission rate. Paralovo *et al.* [1]

developed decane-D₂₂ sources using crimp top vials, and found that weight loss of sources were almost perfectly linear with time, suggesting that tracer level reduction did not affect the emission rate over a period of 10 days. Jong *et al.* [6] tested the impact of different initial fill levels (0.1 to 0.6 mL) and found that fill level had an insignificant impact on emission rate.

Thus, the aims of this paper are to examine the impact of different capping styles, septa materials and fill levels on the emission rate of a selected tracer gas.

2 Methods and materials

Tracer gas sources were prepared using different septa materials (natural rubber/TEF, VMQ, PDMS, natural rubber), fill levels (0.2 mL, 0.4 mL, 0.6 mL), and capping styles (crimp, screw, snap). PMCH (CAS: 355-02-2, purity: 99.1%) was selected as has been well-researched and validated for use in ventilation measurements. PMCH was pipetted into each vial before being capped. The sources were placed in an incubator set to 25°C (fluctuation: ± 0.1°C, uniformity: ± 0.2°C) and then periodically taken out to be weighed using a semi-microbalance (resolution: 0.01 mg). The results of each investigation informed the design of subsequent tests.



Fig. 1. Snap cap, crimp cap and screw cap vials. Left: Uncapped. Right: Capped.

The caps were only compatible with vials that had specific head designs (Fig. 1), so the same vial could not be used with every cap. Three types of vials were selected which had similar internal dimensions (Fig. 2 and Table 2). This was to ensure the diffusion path was similar for every vial. The exception to this was that the external head diameter of the screw cap vial only came as 9 mm instead of 11 mm wide. This meant the screw cap vials would require septa with a smaller diameter than the crimp and snap cap vials. However, as shown by Table 3, it was ensured that the caps had same centre hole diameter and septa thickness.

Table 2. Dimensions of selected vials provided by manufacturer.

Vial type	Screw top	Snap top	Crimp top
Height [H] (mm)	32	32	32
External body diameter [EBD] (mm)	12	12	12
Internal neck diameter [IND] (mm)	6.25	6.3	6.25
External head diameter [EHD] (mm)	9	11	11
Total volume (mL)	2	2	2
Usable volume (mL)	1.5	1.5	1.5

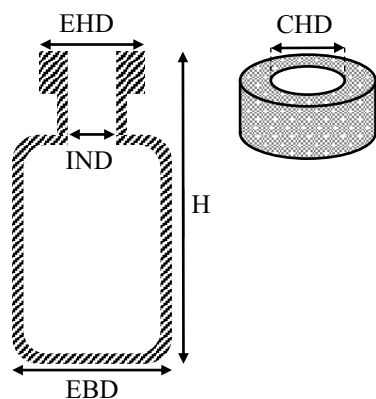


Fig. 2. Schematic of vial and cap dimensions. EHD = external head diameter, IND = internal neck diameter, EBD = external body diameter, H = height, CHD = centre hole diameter.

Table 3. Dimensions of selected caps provided by manufacturer.

Cap type	Screw cap	Snap cap	Crimp cap
Centre hole diameter [CHD] (mm)	6	6	6
Thickness of septa (mm)	1	1	1
Septa diameter (mm)	9	11	11

The vial caps came with a 1 mm thick natural rubber/TEF (NR/TEF) septum as the default. Other septa were made by purchasing sheets of materials and using a hollow punch tool to stamp 9 mm or 11 mm circles. The materials were selected based on literature, cost, and availability of the correct thickness (Table 4). VMQ and PDMS were selected as they have been previously used in tracer gas sources. Other candidates included fluorosilicone and natural rubber, which have been identified as having a lower oxygen permeability than PDMS [8]. However, fluorosilicone was discarded as it was too costly at 15x price of VMQ. For the material tests, the same initial PMCH volume (0.4 mL) was used. As the crimp top vials were equal in size, the height of the tracer liquid was also equal. Thus, the diffusion length between the surface of the liquid and the septum remained the same.

Table 4. Selected septa materials and price relative to VMQ.

Septa material	Relative price
Natural rubber/TEF (NR/TEF)	N/A
Vinyl methyl silicone (VMQ)	1
Polydimethylsiloxane (PDMS)	3
Natural rubber (NR)	0.08

3 Results

3.1 Impact of materials

The emission rate was calculated by measuring the mass change of each vial at the beginning and end of the experiment. The results in Table 5 show that the NR/TEF and NR sources had low to negligible emission rates compared to the VMQ and PDMS sources. This can also

be seen in Fig. 3 which shows the average change in mass over 600 hours. The VMQ and PDMS had fully volatilised in this experiment, but the NR/TEF and NR had not even after more than 700 hours. As the VMQ and PDMS options had relatively similar emission rates, it was not deemed worthy to increase the sample size for statistical purposes.

Table 5. Average emission rate of sources with different materials.

Septa material	Sample size	Elapsed time (hrs)	Average emission rate ($\mu\text{g/hr}$)
NR/TEF	3	763	0.232
VMQ	3	599	572
PDMS	3	541	598
NR	3	1390	1.92

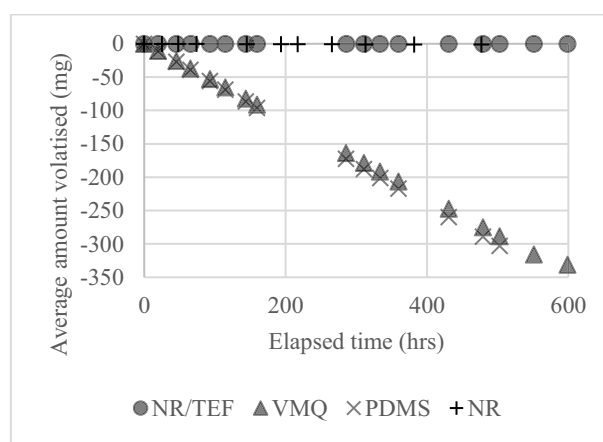


Fig. 3. Average amount of PMCH volatised for each material over 600 hours.

3.2 Impact of fill level

Crimp top vials were prepared with PDMS and 0.2, 0.4 or 0.6 mL of PMCH. Each volume had six replicates. As the subsequent experiment on capping styles included six additional 0.4 mL crimp top vials, these six results were retrospectively added to this section for analysis. Results are presented in Fig. 4 and Table 6 which show relatively similar emission rates for different initial fill levels. Determining the distribution of the data was important for choosing an appropriate statistical method. A Shapiro-Wilk test was performed on the 0.4 mL data as this was the largest group, and the results suggest the distribution departed significantly from normality ($W = 0.83$, $p\text{-value} = 0.024$). Based on this, the non-parametric Kruskal-Wallis test was used to examine whether the fill level had a significant impact on emission rate. The results suggest that the initial fill levels tested did not have a significant impact on emission rate ($H(2) = 3.69$, $p = 0.158$).

Table 6. Average emission rate of sources with different initial fill levels. RSD = relative standard deviation.

Initial fill level (mL)	Sample size	Average emission rate ($\mu\text{g/hr}$)	RSD (%)
0.2	6	607	1.6
0.4	12	616	2.7
0.6	6	621	1.9

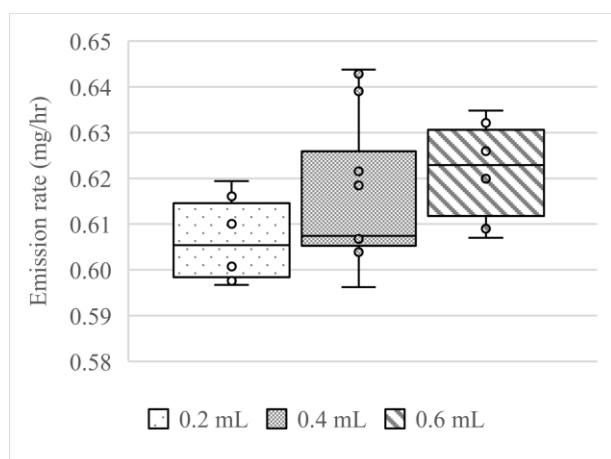


Fig. 4. Boxplot of emission rates by fill level.

As PMCH volatises, the tracer level in the vial reduces. To examine whether this reduction in tracer level impacts the emission rate, the linearity of the mass loss over time for each vial was modelled with the y-intercept set as 0. For all 48 PDMS and 3 VMQ vials, the loss in mass over time was almost perfectly linear ($R^2 > 0.999$). This suggests that the tracer level lowering due to volatisation did not impact the source's emission rate.

3.3 Capping style

The differently capped vials were prepared with PDMS and 0.4 mL of PMCH. Given the results of the fill level experiment, the 0.2 and 0.6 mL crimp vials from the previous section were added to the analysis. Results are presented in Fig.5 and Table 7. Snap cap vials had the highest emission rates whereas the screw cap vials had the lowest. The relative standard deviation (RSD) of the screw cap vials was greater than the crimp and snap cap vials. A Kruskal-Wallis test indicated there was a significant difference in emission rates between the different groups ($H(2) = 39.7$, $p < .001$). To examine where the differences lie, a pairwise comparison using Dunn's test ($\alpha = 0.05$) was carried out. The test indicated the emission rates observed are significantly different between each group ($p < .001$ for crimp-screw, crimp-snap and screw-snap comparisons).

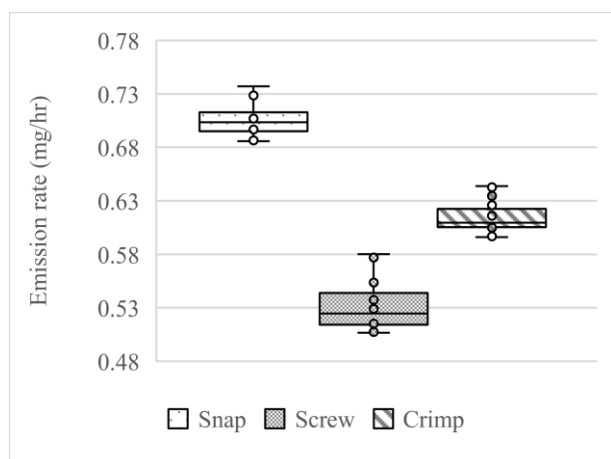


Fig. 5. Boxplot of emission rates by capping style.

Table 7. Average emission rate of sources with different capping styles. RSD = relative standard deviation.

Capping style	Sample size	Average emission rate ($\mu\text{g/hr}$)	RSD (%)
Crimp	24	615	2.4
Screw	12	533	4.8
Snap	12	706	2.5

4 Discussion

According to Batterman *et al.* [9], the emission rate of a tracer source can be predicted using a simple Fickian diffusion model from its geometry as follows:

$$F = 3600 A D C / L \quad (2)$$

where F is the source emission rate (mg h^{-1}), A is the diffusion path cross-sectional area (cm^2), D is the diffusion coefficient in air ($\text{cm}^2 \text{s}^{-1}$), C is the saturated vapour concentration of the tracer (mg cm^{-3}), L is the diffusion path length (cm), and 3600 converts from seconds to hours. As Paralovo *et al.* [1] also noted when using similar glass vials, the value of A is not homogenous along the length of L as the internal diameter of the vial varies. To overcome this, an intermediate value of A could be used. However, the diffusion path imposed by the septum must also be included which requires knowledge of the permeability of the material. This information is not always available from manufacturers, which highlights the difficulty in predicting tracer gas emission rates.

The difference in emission rates between the VMQ and PDMS sources were small enough to not warrant further investigation. As VMQ is commercially more common and cheaper than PDMS, it is the preferred material if a 1 mm thick septum is needed. The availability of thinner materials was not examined, but PDMS as thin as 0.13 mm has been used before [5]. The NR/TEF sources had a negligible loss of PMCH which is expected given that these vials are intended to seal samples and allow for injections through the septa. The NR alone appeared to be slightly more permeable than NR/TEF but the emission rate was too low to be practically useful.

As also found by previous research [1,6], the initial fill level and lowering tracer level due to volatisation do not appear to significantly impact the emission rate. This is useful as it means the initial fill level can be tailored for the duration of a particular experiment which can help reduce potential wastage of tracer gas.

In terms of capping styles, the repeatability of the crimp and snap cap vials were similar (RSDs = 2.4% and 2.5%, respectively). The process of manual crimping can lead to variable results as crimpers often allow changes to the crimping pressure and height. However, once the appropriate pressure and height has been identified for a particular type of vial, further changes are not needed. In this study, it was ensured that the vials were not under-crimped by hand-checking whether the seal was loose, nor over-crimped by observing whether the septum had an upward or downward bulge. However, as Ovardia *et al.*

[10] report, it is challenging to characterise the effectiveness of a crimp seal in a quantitative and non-subjective manner. For the snap caps, there is minimal experimenter variability in cap placement as an audible 'click' sound indicates the cap is correctly aligned and a seal has been formed.

The screw cap vials had slightly worse repeatability (RSD = 4.8%). Screwing appeared to be a more variable process as there was no procedure to ensure each vial was tightened by the same amount. The twist effect when applying the screw lid to the glass vial may cause distortion to the septum if not perfectly applied, increasing the chance of leakage. A loose cap is an easy identifier of an under-screwed vial, whilst a bulging septum indicates an over-screwed cap. Thus, in-between these two states, a wide range of tightness levels exists. However, it was observed that the RSD was strongly affected by two vials which had emission rates that exceeded 0.57 µg/hr, which can be seen in Fig. 5. If these 'outliers' are removed, the RSD reduces to 3% which is closer to the other capping styles. Thus, as Sateri *et al.* [3] advise, checking the emission rate of every source at the start would allow outliers to be identified early and remedied.

The emission rate of the snap cap vials was higher than the crimp cap vials (706 and 615 µg/hr, respectively). The seal of the crimp cap appeared to be good, given as the NR/TEF septum had a negligible loss of PMCH. As both vials had the same internal dimensions and septa diameters, the higher emission rate of the snap cap was likely due to the seal being leakier. The effect of a NR/TEF septum with the snap cap was not tested, but this would indicate whether there was significant loss of PMCH through means other than diffusion through the septum i.e. general leakiness.

The screw cap vials had a lower emission rate than the crimp cap vials (533 and 615 µg/hr, respectively). The main difference between these vials was that the screw cap vial required a 9 mm wide septa instead of 11 mm. If it is assumed that the crimp cap seal was good such that PMCH diffusion through the septum was the primary means of emission, then the higher emission rate of the crimp cap vial could be attributed to its greater septum surface area. For both vials, the theoretical septum surface area exposed to the internal neck of the vial (30.7 mm²) and to the centre hole of the cap (28.3 mm²) is the same. However, the crimp cap vial has an additional 31.4 mm² of septum material. There may be lateral diffusion through the material or air gaps between the septum and vial, which increases the septum area exposed to PMCH, contributing to an increased emission rate.

5 Conclusion

This study has investigated the impact of different septa materials, fill levels and capping styles on the emission rate of PMCH. At 1 mm thickness, there was little difference between the emission performance of VMQ and PDMS septa. In addition, emission rates did not appear to be significantly impacted by the initial fill level

or volatisation loss of PMCH. There are differences in emission rates when using different capping styles, some of which are likely attributed to the sealing of the caps and others to the diameter of the septa. The repeatability of crimp and snap cap vials are better than screw cap vials, likely as screwing produces more variable levels of tightness. However, the variability could be reduced by checking emission rates at least once and then adjusting the seal of outliers.

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