

Ventilation Measurement Using Spot Sampling of Sulphur Hexafluoride on a Solid Adsorbent

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A technique for measuring the ventilation rate using spot sampling of sulphur hexafluoride (SF₆) on a solid adsorbent for subsequent thermal desorption and gas chromatographic analysis has been developed. This paper describes the mathematical model used, the analytical details of the technique, as well as results from a validation test using an experimental chamber. The mathematical model assumes an exponential decay of the tracer gas concentration. The precision of the analytical procedure was estimated to be better than 9% whilst the error of the measured ventilation rate of the test chamber was 5%.

INTRODUCTION

MONITORING of the environment is becoming increasingly important and proper control of ventilation in buildings is necessary to maintain an acceptable indoor climate. A convenient method for a field study of ventilation is the tracer gas technique [1] and interzone airflows in a building can be measured using multiple tracer gases [2]. Usually the tracer gas is sampled and analysed on site using sophisticated sampling and measurement instrumentation which generally require a skilled technical operator. In the present study, a method is described for measuring the ventilation rate by spot sampling of a tracer gas, sulphur hexafluoride (SF₆) on a reusable solid adsorbent for subsequent analysis in the laboratory. By using a solid adsorbent for the sampling, the tracer gas is preconcentrated. This requires less injection of tracer gas compared to the usual on-line analysis. Other advantages are the portability and the simplicity of the equipment that is required on site. The lack of an immediate indication of gas concentration and the possible deterioration of the trapped sample during transit are two of its main disadvantages. Solid adsorbents have been used previously in ventilation studies for measuring re-entrainment [3] of exhaust contaminants into fresh-air inlets (Freon-114 as the tracer trapped on charcoal) and for infiltration [4] measurements in homes (Perfluorocarbon as the tracer trapped on XE-347 Amborsorb), but so far no method of trapping SF₆ on a solid adsorbent has been reported.

THEORY

Consider a room with volume V , a ventilation airflow rate of Q and an initial concentration C_0 of a tracer gas.

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Ventilation rate, N , is equal to Q/V and assuming no supply of tracer gas to the room and assuming the decay of the tracer is due to ventilation only, under well mixed conditions the concentration $C(t)$ at time t is described as

$$C(t) = C_0 e^{-Nt}. \quad (1)$$

If two samples of the tracer gas are taken with a 100% trapping efficiency during the time periods of $t_0 - t_1$ and $t_2 - t_3$ at sampling rates of q_1 and q_2 respectively, the collected masses of the tracer gas are given by

$$M_1 = C_0 \int_{t_0}^{t_1} q_1 e^{-Nt} dt \quad (2)$$

$$M_2 = C_0 \int_{t_2}^{t_3} q_2 e^{-Nt} dt. \quad (3)$$

If $t_0 = t_2 = 0$ and constant sampling rates $q_1 = q_2 = q$, the collected masses can then be calculated as

$$M_1 = -\frac{C_0 q}{A} (e^{-Nt_1} - 1) \quad (4)$$

$$M_2 = -\frac{C_0 q}{A} (e^{-Nt_3} - 1). \quad (5)$$

If $k = t_3 - t_1/t_1 > 0$, equations (4) and (5) give

$$\frac{M_1}{M_2} = \frac{e^{-Nt_1} - 1}{e^{-kNt_1} e^{-Nt_1} - 1} \quad (6)$$

from which the ventilation rate N can be evaluated.

If k is an integer, equation (6) can be rewritten [5] as

$$\frac{M_2 - M_1}{M_1} = e^{-Nt_1} + e^{-2Nt_1} + \dots + e^{-kNt_1}. \quad (7)$$

If m is the integer portion when $k (> 1)$ is a non-integer, equation (6) can be written [5] as

$$\frac{M_2}{M_1} = e^{-kNt_1} + e^{-(k-1)Nt_1} + \dots + e^{-(k-m)Nt_1} + (e^{-(k-m)Nt_1} - 1)/(e^{-Nt_1} - 1). \quad (8)$$

Assuming in equations (2) and (3) that $t_2 \neq 0$ but $t_1 - t_0 = t_3 - t_2$ and $t_0 = 0$, it can be shown [5] that the ventilation rate is

$$N = \frac{1}{t_2} \ln \left(\frac{M_1}{M_2} \right) \quad (9)$$

Standard techniques of error analysis can be used to estimate the errors involved in determining the ventilation rate. As an example let $k = 1$ and $M = M_2 - M_1$ in equation (7). Then

$$\frac{\Delta T}{T} = \frac{\Delta t_1}{t_1} - \frac{T}{t_1} \left(\frac{\Delta M_1}{M_1} - \frac{\Delta M}{M} \right) \quad (10)$$

where $T = 1/N$ and the prefix Δ indicates the absolute standard error.

METHOD

Analysis

The gas chromatograph used (gc) in this study was an Analytical Instrument Development Model 511 equipped with a 200 mCi tritium foil parallel-plate type electron capture detector. This is designed to operate under pulsed mode with 5% CH_4 in Ar as carrier gas. The 1.8 m by 3 mm gc-column (all tubing was stainless steel) contained Molecular Sieve 13X 40/60 mesh, and the column was conditioned overnight at 150°C. The gc was run at 100°C and a carrier gas flow of 30 $\text{cm}^3 \text{min}^{-1}$. It is common practice to relate the area under a peak to the concentration of the substance under test. However, an integrator was not available at the time of this study and instead the peak heights were calibrated using gas mixtures. These were prepared in sampling bags with polyethylene on the inner surface as the mixtures can then be kept for a long period without deterioration in air quality [8]. The samples were injected using a 2 cm^3 gas sample valve.

The solid adsorbent used for trapping SF_6 was thermally desorbed by preheating at 325°C for 5 min and then flushed for 4 min with carrier gas at a flow of 20 $\text{cm}^3 \text{min}^{-1}$. The effluent was collected in a 100 cm^3 gastight syringe and analysed by injection via the gas sample valve on the gc.

Solid adsorbent

Trapping weakly adsorbed low boiling substances like SF_6 (BP = -68°C) requires a large bed of a strong adsorbent and in the present study charcoal and Spherocharb were investigated as adsorbents. The adsorbent was packed in a stainless steel tube 89 mm long by 6 mm o.d. and the charcoal (550 mg, 40/50 mesh) was held in place by inert glass wool plugs. The Spherocharb (500 mg, 60/80 mesh) was held in place by sintered stainless steel discs. Air was pulled through the tubes at a regulated flow rate using a calibrated pump. Before and after sampling the tubes were sealed with polythene end caps and were then stored in airtight 500 cm^3 polyethylene bottles filled with pure nitrogen.

The breakthrough volume of an adsorbent bed is the volume that can be sampled before the gas breaks through the bed. This volume is defined [6] as the amount of air

which is just enough to produce an effluent concentration equivalent to 1% of the input concentration. When breakthrough was about to occur, samples of the effluent of the adsorbent bed were analysed at time intervals which correspond to increases of less than 100 cm^3 in the sampled volumes. The adsorbent beds were exposed to gas mixtures prepared in sampling bags and the air temperature and the relative humidity of the mixtures were kept at 18–25°C and 42–55% respectively. Using Spherocharb as the adsorbent, the breakthrough volume was measured at SF_6 concentrations of 33, 100 and 300 ppm and sampling rates of 20, 50 and 100 $\text{cm}^3 \text{min}^{-1}$ in a 3 × 3 factorial design experiment with five replications. Using charcoal as the adsorbent resulted in a low breakthrough volume and this volume was only measured at a concentration of 300 ppb at a sampling rate of 20 $\text{cm}^3 \text{min}^{-1}$. Due to the low breakthrough volume, charcoal as an adsorbent was excluded from further studies.

The effect of storing the exposed tubes at different temperatures and time intervals on the recovery of the gas from the adsorbent was investigated in a 2 × 4 factorial design experiment with five replications. Storage temperatures at 4°C and 15–20°C at storage intervals of 1, 2, 3 and 4 days were used. Before storage, a known mass (10–15 ng) of SF_6 was deposited on the adsorbent bed by pulling the gas mixture through the tubes. The effect on the recovery of depositing different amounts of SF_6 on the adsorbent was investigated by putting down 10, 15, 20, 30, 40 and 50 ng of the gas on the adsorbent and carrying out the analysis within an hour.

Field study

The application of Spherocharb as a solid adsorbent for measuring the ventilation rate was validated in a simulated field study using a test chamber with a volume of 7.83 m^3 , from which air was extracted at a constant rate. The air in the chamber was mixed continuously using a desk fan. The ventilation rate of the chamber was obtained by the following techniques:

(A) Using a calibrated orifice plate [10] in the outlet duct to measure the extracted volume of air.

(B) Using an infrared analyser to measure the decay rate from an initial concentration of 50 ppm SF_6 .

(C) Measuring the decay rate using a syringe for sampling and the gc for the analysis and starting with an initial SF_6 concentration of 30 ppb.

(D) Calculating the ventilation rate from equation (7), for $t_1 = 20$ min and $k = 1$, using the adsorption tubes for sampling the SF_6 tracer at an initial ($t = 0$) concentration of 20 ppb. The adsorption tubes were analysed on the same day they were used for sampling.

RESULTS

Calibration

The gc was calibrated in the range of 0.3–80 ppb SF_6 and showed a linear response (corr. coeff. 0.998). At concentrations approx. > 80 ppb, the detector gradually became saturated to give a non-linear response. As reported elsewhere [9], the calibration can be extended down to concentrations of 0.002 ppb by modifying the gc.

Table 1. Breakthrough volumes

Conc. of SF ₆ (ppb)	Sampling rate (cm ³ min ⁻¹)	Breakthrough volume (l. *)
33	20	1.18 ± 0.12
33	50	1.19 ± 0.11
33	100	1.16 ± 0.09
100	20	1.31 ± 0.10
100	50	1.32 ± 0.15
100	100	1.18 ± 0.06
300	20	1.27 ± 0.15
300	50	1.29 ± 0.12
300	100	1.33 ± 0.12

* Arithmetic mean and standard deviation of one measurement on five different adsorption tubes.

Breakthrough volume

Table 1 shows the breakthrough volumes obtained for the tubes containing Spherocarb. In a two-way analysis of variance, the concentration level was found to have a significant effect on the breakthrough volume at an $\alpha = 0.05$ but not at $\alpha = 0.01$. Neither the effect of the sampling rate on its own nor the combined interaction between concentration level and the sampling rate was found to be significant ($\alpha = 0.05$). The Tukey HSD-test [7] showed that the breakthrough volume at 33 ppb was significantly lower ($\alpha = 0.05$) than at the higher concentration levels. For the tubes containing charcoal, the obtained breakthrough volume was 0.24 ± 0.03 l for five replications.

Recovery

Table 2 shows the percentage of tracer recovered after the exposed adsorption tubes had been stored at different temperatures for different time intervals. In a two-way analysis of variance, the temperature, time and the interaction between temperature and the time were found to have significant ($\alpha = 0.05$) effect on the recovery. Storing the tubes at room temperature compared to a temperature of 4°C results in a lower percentage recovery. Recovery also decreases with the time of storage. Table 3 shows the obtained percentage recoveries after depositing different amounts of SF₆ on the adsorption tubes and in a one-way analysis of variance the deposited amount was found to have a significant ($\alpha = 0.01$) effect on the recovery. The

Table 2. Recovery for the adsorption tubes stored at different time intervals and temperatures

Storage interval (h)	Storage temp. (°C)	Recovery (%*)
24	4	94.1 ± 4.7
	15–20	92.9 ± 4.4
48	4	81.2 ± 2.9
	15–20	83.2 ± 5.0
72	4	78.1 ± 1.3
	15–20	73.0 ± 1.7
96	4	77.2 ± 1.8
	15–20	70.5 ± 1.4

* Arithmetic mean and standard deviation of one measurement on five different adsorption tubes.

Table 3. Recovery from adsorption tubes with different amounts of SF₆ deposited

SF ₆ deposited (ng)	Recovery (%*)
10	100.0 ± 4.2
15	89.8 ± 2.1
20	88.1 ± 3.4
30	86.0 ± 1.2
40	83.8 ± 0.7
50	83.2 ± 0.9

* Arithmetic mean and standard deviation of one measurement on four different adsorption tubes.

more SF₆ was deposited on the adsorbent bed the less was recovered during the analysis.

Field study

Table 4 shows the values of ventilation rate for the test chamber obtained using the four different measuring techniques. For comparison, the ventilation rates were given to two decimal places. Compared with the orifice plate results, the values obtained from adsorption tube measurements deviate by 8%.

DISCUSSION

The breakthrough volume is dependent [11] upon many factors, mainly the surface area and activity of the adsorbent, its mesh size, and dimensions of the bed and the temperature. It is independent of flow rate between certain limits (typically 5–80 cm³ min⁻¹ through a 6 mm diameter tube) and is also independent of humidity up to a value near the saturation point. The gas concentrations affects breakthrough volume for some adsorbents more than others and generally the breakthrough volume is decreased as the gas concentration is increased, provided that the saturation capacity of the adsorbent is not reached. Using Spherocarb as the adsorbent, it was found in the present study that the breakthrough volume at the $\alpha = 0.05$ level was decreased as the gas concentration was decreased. This effect however was not significant at the $\alpha = 0.01$ level. The breakthrough volume was independent of flow rate between 20 and 100 cm³ min⁻¹. Using charcoal as the adsorbent, a breakthrough volume of 0.24 l. was obtained. Breakthrough volume for tracer gases other than SF₆ have been reported [6]. Porapak Q (200 mg, 50/80 mesh) has given a breakthrough volume of 0.5–0.6 l. when trapping Freon 11 whilst values of 0.8–1.0 l. have been obtained from Freon 12 trapped on an adsorbent made from charcoal (100 mg, 20/40 mesh) and molecular

Table 4. Ventilation rate of the test chamber

Measuring technique	Ventilation rate (h ⁻¹)
Orifice plate	1.59
Infrared analyser	2.68
Syringe/gc-analysis	2.42
Adsorption tubes/gc-analysis	2.80

sieve 3A (500 mg, 20/40 mesh). In practice it is preferable to work at a safety margin of 60–70% of a listed breakthrough volume in order to allow variability of the adsorption tubes [12].

Adsorption tubes can be stored after sampling provided they are sealed effectively. The effect of storage on the recovery is mainly dependent on the adsorbent, the length of the storage period, temperature and the volatility and reactivity of the sampled gas [13]. In the present study, a continuous decline in the recovery of SF₆ from the stored tubes was found and storage at low temperature reduced this rate of decline. As reported elsewhere [13] similar effects might occur when storing other adsorbents used for trapping contaminants. The recovery of SF₆ from the Sphero carb was found to depend on the deposited amount of SF₆, and a similar dependence has been reported for other substances trapped on solid adsorbents [13, 14]. Because the SF₆ is not fully recovered from the Sphero carb in the analytical procedure, the value *M* of the recovered quantity must be corrected so as to obtain the true amount of SF₆ originally deposited. The recovery factor, *R* consists of two multiplicative terms

$$R = R(st) \times R(am)$$

where *R*(st) is the correction due to the storage (Table 2) and *R*(am) is the correction due to the effect from the deposited amount of SF₆ (Table 3). The true amount, *Z*, collected of SF₆ is calculated as $Z = M/R$. In the range investigated, the precision of the analytical procedure is estimated to be better than 9% for tubes containing 10 ng SF₆ and better than 6% for tubes containing 50 ng of SF₆.

In the simulated field study, the measured ventilation rate using adsorption tubes agreed well with results obtained by other techniques. From equation (10), the error in the measured ventilation rate using the adsorption tubes is calculated to be 5%. Equation (10) shows that this error can be reduced by increasing the sampling period provided the analytical errors are not affected.

CONCLUSIONS

The solid adsorbent technique developed here for measuring ventilation rates by spot sampling of a tracer gas (SF₆) was validated using a test chamber and was found to agree well with other measuring techniques. It was found that Sphero carb was a better adsorbent for SF₆ than the more common charcoal packing used in adsorbent tubes. The precision of the analytical procedure for the applied adsorbent was estimated to be less than 9%. Using the spot sampling technique, the error of the measured ventilation rate of the chamber was found to be 5%.

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