buildings. Mean indoor concentrations for chlorinated hydrocarbons were highest for the existing office buildings. Presumably, indoor concentrations resulted from the use of solvent-based office materials. Elevated levels of chlorinated hydrocarbons were also found during the third trip to the hospital.

There appeared to be no discernable trends either for building type or age of building for the oxygenated compounds.

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THE USE OF A PASSIVE SAMPLER FOR THE SIMULTANEOUS DETERMINATION OF LONG-TERM VENTILATION RATES AND VOC CONCENTRATIONS

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Abstract

When interpreting seasonal variations of indoor concentrations of volatile organic compounds (VOC), the ventilation rate must be known. Therefore, a method has been developed which permits the simultaneous determination of the average ventilation rate and the concentration of VOC in a room over an integration period of 2 weeks with the same passive sampler. Hexafluorobenzene (HFB), a non-toxic substance, was chosen as the tracer not to interfere in the gas chromatographic analysis of VOC in indoor air. Emission rates of HFB sources were determined at various temperatures from 15 to 30 °C. After a test of the procedure for sampling periods of 1 and 2 weeks in an experimental chamber at ventilation rates between 0.5 and 2 h^{-1}, it was successfully applied under field conditions.

Introduction

The concentrations of VOC in indoor air depend on the emission rates of pollutant sources, but are also determined by the ventilation rate which changes over the year due to changing climatic conditions. Therefore, the ventilation rate should be known for interpreting variations in indoor VOC concentrations.

In the context of a current study in which we followed the VOC concentrations of 12 households in Berlin over 1 year (1), a need arose for the simultaneous determination of the ventilation rate. Although the perfluorocarbon technique according to Dietz and Cote (2) is well-established, this technique is cumbersome since it needs a separate passive sampler to collect the tracer components. It was the aim of our work to develop a method for the simultaneous determination of both VOC and ventilation rates with only one passive sampler.

Experimental

Choice of the tracer compound

The tracer should be a volatile, non-toxic compound not occurring in households under normal conditions. Perfluorinated methylcyclohexane, dimethylcyclohexane and dimethylcyclobutane which have been successfully used as tracer compounds for the determination of ventilation rates (2,3), were not well separated in the gas chromatographic procedure used to determine VOC in indoor air. In contrast, we found that hexafluorobenzene (HFB) did not interfere with other halogenated organic compounds in our GC/ECD method.

Toxic effects have not been observed at HFB concentrations several thousand times higher than those arising from the emissions of our tracer sources (4). Bioaccumulation did not occur in feeding experiments with mice (5). The Ames test for mutagenicity gave negative results. (We are indebted to Dr. Moriske, Institute of Hygiene, Free University, Berlin, for the respective experiments).

Preparation and test of tracer sources

The sources were Pasteur pipettes closed at one end by melting. They were filled with 2 ml of HFB. A short PTFE tubing was placed over the open end of the pipette. The other end of the tubing was stoppered with a glass rod. Two types of sources were prepared with different PTFE permeation surfaces. Their emission rate, S, was about 80 and 400 $\mu g/h$, respectively (Figures 1a and 1b). The emission rate was determined by weighing at intervals of several days until equilibrium was reached. The emission rate of 5 low-emitting sources was determined at temperatures from 15 to 30 °C at steps of 3 °C to check the influence of room temperature on the emission rate. Setting S ($\mu g/h$) at 100 % for 21 °C, the following equation was found to describe the long-term behaviour of the relative source emission rate, S_T/S_{21}, as a function of the temperature T (°K):

$$S_T/S_{21} = \exp[-5070(1/T - 1/294)] \qquad (1)$$

Between 15 and 30 °C, S_T/S_{21} varied from 70 to 167 % (Figure 2). Dropping a CS_2 standard solution of HFB on charcoal pads of OVM-3500 passive samplers gave a mean recovery of 70 % even after 4 days of storage. Dropping the HFB standard into NIOSH charcoal tubes gave analogous results. HFB was eluted from the charcoal using CS_2 and analysed by gas chromatography. The quantification limit was found to be about 1 μg per sampler, which is about 1.5 $\mu g/m^3$ for a sampling period of 2 weeks. For more detailed information about sample preparation and gas chromatographic analysis see Seifert et al. (1).

Chamber and field experiments

The applicability of the method was tested in a 12 m^3 chamber with adjustable air exchange rate. A source emitting 384 μg HFB/h was placed at a height of 0.5 m, and four OVM-3500 passive samplers (3M Company) were hung at a height of 2 m and a distance of 2.5 m from the source. Air convection was forced with a fan. Two samplers were removed after 1 week, the remaining samplers after 2 weeks. One sampler of each sampling period was analysed immediately after removal, the other after several weeks of storage. The experiments were performed at air exchange rates of n = 0.5, 1.0 and 2.0 h^{-1}.

For the field study, one source was brought to each test family 3 days before the sampling period started and placed in the same room as the passive sampler at a distance of several meters. No restrictions regarding living and ventilation habits were made to the test families (1). In 2 households, measurements of the ventilation rates were started in September 1986. Measurements in 8 more households were started in December 1986. Households having "1" as the first code number are located in new buildings (after 1950), whereas those with a "2" are in old buildings. In household 202 which has large open connected rooms, the HFB concentration reached a detectable quantity only after the addition of 2 more sources to give a total emission rate of 1.1 mg HFB/h.

Results and discussion

In Table 1, theoretical and measured concentrations c ($\mu g/m^3$) of HFB are compared. The theoretical concentrations were calculated using Equation 2, in which a steady-state HFB concentration is assumed (V is the room volume in m^3). This is reasonable in view of the sampling periods of several hundred hours.

$$c = S/(n \cdot V) \qquad (2)$$

$$n = S/(c \cdot V) \qquad (3)$$

Using Equation 3, the air exchange rates were calculated from the measured HFB concentrations (Table 1). As can be seen, the relative standard deviations for the air exchange rate are in the order of or even lower than those to be expected for the determination of VOC (6). However, they would probably be higher at the HFB concentration levels below 10 $\mu g/m^3$, which usually occur under field conditions. For a normal range of room temperatures (18 to 24°C), the emission rate of the sources varies within $\pm$ 20 % (cf. Figure 2).

Table 1: Results of chamber experiments

Given air exchange rate (h⁻¹)	Exposure time of passive sampler (days)	HFB concentration Theoretical ($\mu g/m^3$)	HFB concentration Measured ($\mu g/m^3$)	Air exchange rate Measured (h^{-1})	Air exchange rate Average (h^{-1})	Relative standard deviation (%)
0.5	7		59.7	0.54		
	7	64.0	65.4	0.49	0.5	$\pm$ 4
	14		64.3	0.50		
	14		60.0	0.53		
1.0	7		35.7	0.9		
	7	32.0	30.5	1.1	1.0	$\pm$ 7
	14		30.9	1.0		
	14		33.9	1.0		
2.0	8		16.0	2.0		
	8	16.0	16.0	2.0	2.0	$\pm$ 7
	13		17.0	1.9		
	13		14.4	2.2		

Since the passive sampler is a long-term integration sampler, intermittent high concentrations of VOC cannot be detected. Similarly, a detection of rapid changes in the ventilation rate, e.g., resulting from the opening of windows and doors, also is not possible. Therefore, only the average ventilation rate will be obtained from the HFB tracer method, while short-term measurements, e.g., with N_2O or SF_6 as tracer gases, permit to obtain the "effective" ventilation rate from stepwise varying ventilation rates (7). Although the effective ventilation rate has been shown to be smaller than the average ventilation rate (7), it can be demonstrated that the difference will generally be well below 20 % and can be neglected in most cases, making the average ventilation rate an appropriate parameter to correlate the concentrations of VOC with seasonal and individual ventilation habits.

Table 2 shows the air exchange rates as measured in field experiments. Except in one case, ventilation rates exceeded 1.0 h^{-1} in households located

in old buildings (last 4 households), whereas in the new buildings ventilation rates were both below and above 1.0 h^{-1}.

Although the winter was severe in the sampling periods 20 and 21, no significant changes in the ventilation rates could be observed. A period of good weather in October 1986 resulted in higher ventilation rates (Table 2; Figure 3).

In the cold season with ambient temperatures between +5 and -10 °C or below, the ventilation rates did not vary within large ranges. Since the study of VOC concentrations in selected homes was not yet terminated at the time of delivery of this manuscript (February 1987), more interesting results could be expected at the more moderate ambient temperatures likely to occur in spring time.

Table 2: Mean air exchange rates [h^{-1}] under field conditions

Household No.	13 *)	14	15	16	17	18	19	20	21	22	23
101						2.2	0.7	0.4	0.6	0.7	0.5
102						1.7	1.7	1.6	1.3	1.6	1.6
103	0.8	1.1	0.4	0.5	0.5	0.5	0.6	0.5	0.4	0.4	0.5
111						n.d.	1.7	1.9	1.8	2.0	1.8
112						0.7	0.9	0.7	0.9	1.0	0.8
113						1.6	1.8	1.4	1.8	1.4	1.3
201	1.4	2.1	1.9	1.2	1.1	1.1	1.1	1.3	1.3	1.4	1.6
202						n.d.	n.d.	n.d.	3.6	2.5	2.0
211						1.1	0.6	2.0	2.0	2.0	1.8
213						1.7	1.6	1.4	1.5	1.4	1.8

*) Period 13 is from 22 September to 5 October 1986

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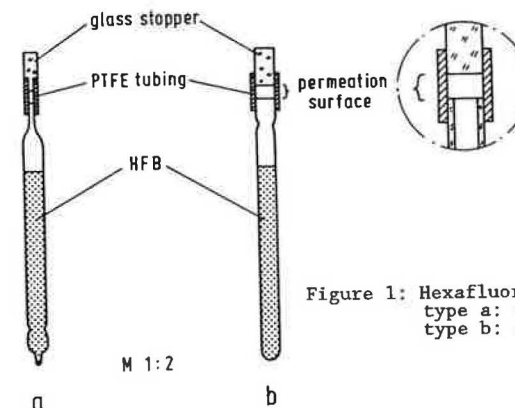
Figure 1: Hexafluorobenzene tracer sources
type a: emitting about 80 µg HFB/h
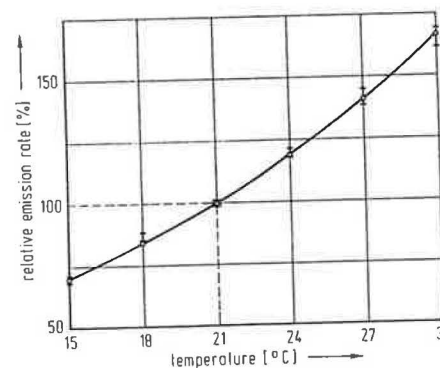type b: emitting about 400 µg HFB/h

Figure 2: Relative source emission rate as a function of the temperature,
(o) = theoretical value according to Equation 1
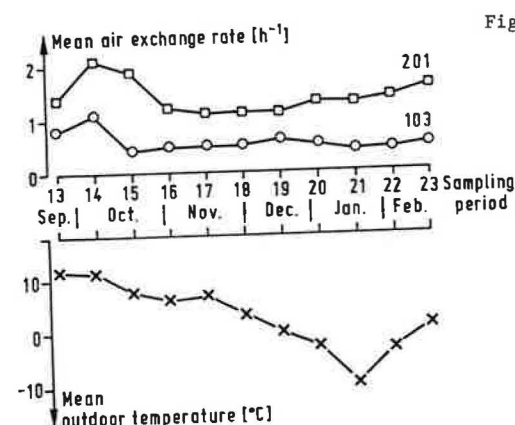(I) = range of measured values

Figure 3: Mean air exchange rates in 2 households and the corresponding mean outdoor temperature