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Performance of two different types of passive samplers for the GC/ECD-FID determination of environmental VOC levels in air

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Abstract Two types of passive samplers differing in their geometry (OVM 3500 by 3M, ORSA 5 by Dräger) were compared with respect to their suitability for typical environmental indoor and outdoor VOC concentrations. Benzene, toluene, o-, m-, p-xylene, ethylbenzene, tetrachloroethene, trichloroethene, nonane and ethyl acetate were representatively analyzed by dual-column capillary gas chromatography with tandem ECD-FID detection. There was a good correlation between the results obtained with OVM 3500 and ORSA 5 monitors indicating that both monitors can be used for this kind of application. The ratio between the results for indoor air sampling with OVM 3500 and ORSA 5 monitors was between 0.89 and 1.14 showing no systematic variation. For outdoor air sampling the ratio was between 1.06 and 1.26 indicating that the results obtained with OVM 3500 monitors were slightly higher. Reproducibility was slightly better when using ORSA 5 monitors. But, due to the higher sampling rates which are a result of the larger cross-sectional area, signal-to-noise ratios obtained with OVM 3500 monitors were between six to nine times higher than those of ORSA 5 samplers. Blank values of the unexposed samplers were comparable for both sampler types. As a consequence, detection limits were by a factor of 1.5 to 4 better for OVM 3500 monitors.

Introduction

Interest in sampling volatile organic compounds (VOCs) with inexpensive and easy to operate passive devices instead of active techniques using a pump and a solid sorbent tube has been growing in the past decade. Throughout exposure the passive samplers collect VOCs from their nearest surrounding onto an adsorbent. Depending on the kind of application, various adsorbents such as charcoal, silica gel and porous polymers such as Tenax, XAD, Porapak and molecular sieves can be used as collection media for active as well as for passive sampling [1, 2]. The mass transport is controlled by permeation and/or diffusion and depends upon the length and diameter of the cavity and the properties of the analyte [3]. Commercially available passive samplers mainly fall into two categories differing in their geometry: badge-type and tube-type devices. Tube-type samplers are characterized by a long axial diffusion path length and a low cross-sectional area resulting in relatively low sampling rates. Badge-type samplers which have a shorter diffusion path length and a greater cross-sectional area typically exhibit higher uptake rates.

Passive sampling have been proven as a reliable, simple and inexpensive screening tool for measuring indoor and outdoor VOC concentrations in the occupationally as well as in the environmentally relevant concentration range [4–8]. Especially in large-scale field studies their superiority to active sampling techniques is out of question. In contrast to active sampling techniques, passive samplers are inexpensive, light-weight and need no associated sampling equipment and less maintainance. A comparison of results obtained with active and passive sampling using OVM 3500 monitors is given in a former paper [4] indicating that active and passive sampling techniques give equivalent results.

Due to its excellent adsorption properties for hydrocarbons and its high adsorption capacity, charcoal is the most frequently used adsorbent in passive sampling. Different types of passive samplers equipped with charcoal as adsorbent are commercially available and have been used for the collection of environmental VOC concentrations in indoor and outdoor air such as OVM 3500 (by 3M) [4–7, 9–12], ORSA 5 (by Drägerwerk) [10], PRO-TEK G-AA (by Dupont) [3], PRO-TEK G-BB (Dupont) and Gasbadge (National Mine Service) [13, 14].

Experimental laboratory studies have been carried out to compare various types of passive monitors to active sampling techniques mainly under laboratory conditions

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in a test atmosphere [3, 6]. A systematic comparison of different types of commercially available passive monitors under typical field conditions for the sampling of indoor and outdoor air has to our knowledge not been published yet. Field evaluation is a further test for method validation since conditions existing in the field are difficult to reproduce in the laboratory. It also allows the analyst to estimate the ruggedness of the analytical procedure [15].

In this paper results are presented on the detailed comparison of a tube-type and a batch-type passive sampler device being exposed in the field (indoor and outdoor) under real-life conditions. Benzene, toluene, o-, m-, p-xylene, ethylbenzene, tetrachloroethene, trichloroethene, nonane and ethyl acetate were investigated as representatives for the aromatic, aliphatic and halogenated classes of volatile organic compounds.

Experimental

Description of the passive samplers

The OVM 3500 (by 3M, Neuss, Germany) is a batch-type permeation passive sampler consisting of a permeable membrane and an activated charcoal pad (180 mg) assembled in a disk-shaped plastic holder. The cross sectional area through which diffusion occurs is ≅ 7.07 cm^2, the diffusion distance (length) is ≅ 1 cm.

The ORSA 5 (by Drägerwerk, Lübeck, Germany) is a tube-type diffusive passive sampler containing 400 mg of activated charcoal. The cross-sectional area is 0.88 cm^2 with a diffusion distance of 0.5 cm.

Sample collection

For indoor sampling, OVM 3500 passive samplers and ORSA 5 passive samplers were placed in the room where the volunteers spent their most time (in detail described in a former paper [4]) which in this case was generally the sleeping room. The monitors were exposed for four weeks under normal living conditions with a distance of about 20 cm between them. After exposure they were closed with impermeable caps and shipped to the laboratory placed in a cold-box containing cooling units and activated charcoal sheets to prevent a contamination of the monitors by car exhausts or cigarette smoking, for example. Until analysis the monitors were stored at +4 °C in a refrigerator.

For outdoor measurements the samplers were placed on the balconies of the dwellings (partially roofed) fixed to a clothes line at a distance of about 20 cm from each other. The samplers were also exposed for four weeks, closed and stored at +4 °C [4].

Sample preparation

All glass vials were washed with nitric acid (1+1) rinsed with ultrapure water and heated for 12 h at 150 °C. Plastic material was cleaned with a 3% (v/v) Extran® solution, rinsed with water and heated for 20 h at 80 °C.

ORSA 5 monitors: The activated charcoal section of the monitors was transferred to a glass vial. After addition of 2.0 mL of carbon disulfide ("low benzene" grade, by Promochem, Wesel, Germany) the VOCs were desorbed by mechanically agitating the vial for 30 min. After centrifugation (4000 rpm, 5 min) the extract was transferred into a GC autosampler vial and stored at +4 °C until GC analysis.

OVM 3500 monitors: 1.5 mL of carbon disulfide were added to the charcoal pad of the OVM 3500 monitors through the center port of the elutrication cap. The monitors were then mechanically agitated for 30 min. The extract was decanted into GC autosampler vials and stored at +4 °C until analysis.

Gas chromatographic analysis

Separation and detection of the VOCs was achieved by dual-column capillary gas chromatography with tandem ECD-FID detection. The system used has been already described in detail in a former paper [5]. In short: after injection using a cold split-splitless injector, the mobile phase was splitted via a Y-connector and let onto two capillary columns of different polarity switched in parallel. Detection was achieved by connecting the outlet of each column with a non-destructive ECD and an FID which were switched in series.

The gas chromatographic conditions are summarized in Table 1.

Calibration and calculation

Calibration was performed by analyzing a blank and a set of three standards of all analytes in three different concentrations before and after each analytical series. The means of both runs were used

Table 1 Gas chromatographic conditions for the determination of VOCs in indoor and outdoor air samples

Gas chromatograph	HRGC 5300 (Fisons Instruments) with autosampler AS 200 and PC data station with software "Maxima" (version 3.3)
Injector	Split-splitless temperature programmable multi-injector MFA 515
Detectors	2 sets of serial ECD/FID tandem detectors switched in parallel after each column
Precolumn	2.5 m methyl silicone desactivated capillary column, 0.32 mm inner diameter (Chrompack)
Capillary column 1	60 m DB-5 (5% phenyl, 95% methyl silicone, by J&W Scientific) 1 µm film thickness, 0.32 mm inner diameter
Capillary column 2	60 m DB-1701 (14% cyanopropyl phenyl silicone, by J&W Scientific) 1 µm film thickness, 0.32 mm inner diameter
Carrier gas	Helium, purity: 5.6, flow rate: 2 mL/min
Make-up gas	Nitrogen, purity: ECD grade, flowrate: 30 mL/min
Split	10 mL/min
Temperatures	
ECD1 and ECD 2	330 °C
FID1 and FID 2	330 °C
Injector	50 °C for 1 s, then ballistically heated to 250 °C
Columns	5 min at 35 °C, 4 °C/min to 150 °C, 30 min at 150 °C
Sample size	2 µL
Data evaluation	Peak area

for calibration. Standards were prepared using the highest purity which is commercially available. The stock solution which was prepared in methanol was stable at +4 °C for at least 6 months. The standards were prepared by diluting the stock solution which contained all analytes under investigation with carbon disulfide. They were freshly prepared before use. Calibration was set up in the concentration range between 7 and 60 mg/L for benzene, toluene, o-, m-, p-xylene, ethylbenzene, ethylacetate and nonane (FID detection) and between 0.3 and 1.0 mg/L for trichloroethene and tetrachloroethene (ECD detection).

When the sampling interval (t, in min), the absolute amount of each VOC adsorbed onto the sampler (m, in µg), the sampling rate (SR, in 10^{-3} min m^{-3}) and the recovery rate (r) are known, the time-weighted average concentration C_a (in mg m^{-3}) of each analyte can be calculated according to the following equation:

$$C_a = m\, t^{-1}\, r^{-1}\, SR$$

where the sampling rate is a function of the diffusion coefficient (D) of the individual analyte, the cross-sectional area of the monitor A and the length L over which diffusion occurs ($SR = D\, A\, L^{-1}$). For a given analyte the uptake rate is a constant for the same type of monitor. The sampling have been individually adopted from [17, 18], the recovery rates of each VOC have been determined according to a procedure described by Rodriguez et al. [19].

Detection limits

The limit of detection obtainable with passive samplers is a direct function of

- the sampling rate
- the sampling time
- the blank values of the unexposed samplers
- the reproducibility
- the sensitivity of the GC detector
- the selectivity of the GC column

Additional parameters effecting the analytical result are temperature, humidity and air velocity. These latter parameters are in this case negligible, because both sampler types were exposed simultaneously close to each other.

The detection limits were calculated as the three-fold standard deviation of the monitor blanks converted to a sampling interval of four weeks. For compounds with monitor blanks too low to be registered by the integration software (see Table 4), the three-fold standard deviation of replicate measurements of monitors spiked with low amounts of the analytes in the same concentration range as the blanks (0.01 µg/sampler for halogenated compounds and 0.2 µg/sampler for non-halogenated compounds) was used. This is an appropiate procedure in chromatographic analysis. It is not always useful to define the detection limit on the basis of the instrumental signal-to-noise ratio, which is not selective for the analyte, because the chraracteristics of the analyte peaks must be the basis for calculation.

In field studies, only monitors with the same lot number were used, because former investigations with OVM 3500 sampling devices have shown, that background levels of unexposed monitors vary from lot to lot [4].

Quality control

The applied dual-column gas chromatography tandem ECD-FID configuration provides an increased resolution and selectivity. This procedure permits the determination and confirmation of the results within a single run. For internal quality control purposes a standard pooled from real samples in the environmental concentration range was analyzed within each analytical section.

The reproducibility between different monitors of the same sampler type was investigated by exposing ten OVM 3500 and ten ORSA 5 monitors simultaneously in a living room at a distance of about 20 cm from each other.

Results and discussion

The results of the simultaneous VOC determinations in indoor and outdoor air with the two different types of passive samplers are given in Table 2. Data obtained with both types of samplers corresponded well, the variation was between 1 and 13% for indoor air measurements and between 6 and 26% for outdoor air measurements. The slightly greater variation for outdoor sampling may result from differences in the sampling rates due to varying meteorological conditions (e.g. humidity, temperature, air velocity) during the sampling period. Indoor and outdoor VOC levels of this study are comparable with those reported from other studies [4, 5, 11, 16] indicating that the monitors were tested under representative environmental conditions.

The ratios of the signal intensities of OVM 3500 vs. ORSA 5 monitors and the detection limits refering to a sampling period of four weeks are summarized in Table 3. Signal intensities corrected for the analytical blank were between a factor of 6 and 9 higher when using OVM 3500 monitors. Our finding may be explained by the fact that the cross-sectional area through which diffusion occurs is

Table 2 Results of the simultaneous determination of VOCs in indoor air and in outdoor air using OVM 3500 and ORSA 5 monitors (µg/m^3)

Compound	Indoor			Outdoor		
	OVM 3500 (*n* = 7) AM[a] ± SD[b]	ORSA 5 (*n* = 7) AM[a] ± SD[b]	Ratio OVM/ ORSA	OVM 3500 (*n* = 7) AM[a] ± SD[b]	ORSA 5 (*n* = 7) AM[a] ± SD[b]	Ratio OVM/ ORSA
Benzene	4.3 ± 0.1	3.9 ± 0.03	1.10	4.0 ± 0.1	3.2 ± 0.2	1.25
Toluene	46.9 ± 1.5	43.8 ± 0.3	1.07	12.3 ± 0.2	9.9 ± 0.5	1.24
m-, p-Xylene	7.1 ± 0.2	7.2 ± 0.1	0.99	5.4 ± 0.4	5.1 ± 0.3	1.06
o-Xylene	2.2 ± 0.1	2.3 ± 0.2	0.96	1.8 ± 0.1	1.5 ± 0.03	1.2
Ethylbenzene	5.3 ± 0.3	4.7 ± 0.02	1.13	2.9 ± 0.1	2.3 ± 0.1	1.26
Trichloroethene	0.76 ± 0.1	0.85 ± 0.05	0.89	0.37 ± 0.02	0.32 ± 0.02	1.16
Tetrachloroethene	0.83 ± 0.02	0.73 ± 0.04	1.14	0.37 ± 0.01	0.30 ± 0.01	1.23
Ethyl acetate	14.8 ± 0.4	15.5 ± 0.2	0.95	1.0 ± 0.1	0.9 ± 0.1	1.11
Nonane	2.0 ± 0.2	1.9 ± 0.2	1.04	0.34	0.19 ± 0.03	1.08

[a] AM = arithmetic mean
[b] SD = standard deviation

Table 3 Ratio of signal intensities (corrected for the blank value) for OVM 3500 and ORSA 5 monitors and detection limits for a sampling interval of 4 weeks

Analyte	Empirical mean signal ratio OVM/ ORSA	DL (µg/m^3) OVM 3500 (n = 10)	DL (µg/m^3) ORSA 5 (n = 6)
Benzene	7	0.1	0.2
Toluene	7	0.2	0.7
m-, p-Xylene	6	0.4	0.6
o-Xylene	7	0.1	0.4
Ethylbenzene	6	0.2	0.3
Trichloroethene	9	0.01	0.02
Tetrachloroethene	6	0.01	0.02
Ethyl acetate	6	0.2	0.6
Nonane	7	0.1	0.3

7.07 cm^2 for OVM 3500 and only 0.88 cm^2 for ORSA 5 monitors with the consequence that the total amount of substance collected per time unit is distinctly higher for OVM 3500 monitors. For illustration, Fig. 1 shows two chromatograms of typical indoor air samples obtained by exposing an OVM 3500 (a) and an ORSA 5 monitor (b) simultaneously in a distance of a few centimeters from each other. All peaks which are not named are unknown compounds.

In spite of the lower signal intensities, reproducibility was slightly better with ORSA 5 monitors (see Table 2). This explains why detection limits were only by a factor of 1.5 to 4 better with OVM 3500 than with ORSA 5 monitors. Nevertheless precision ranging between 0.7 and 8.0% for ORSA 5 and between 2.4 and 7.3% in case of OVM 3500 was satisfactory for both types of samplers. Precision of the OVM 3500 monitors was nevertheless

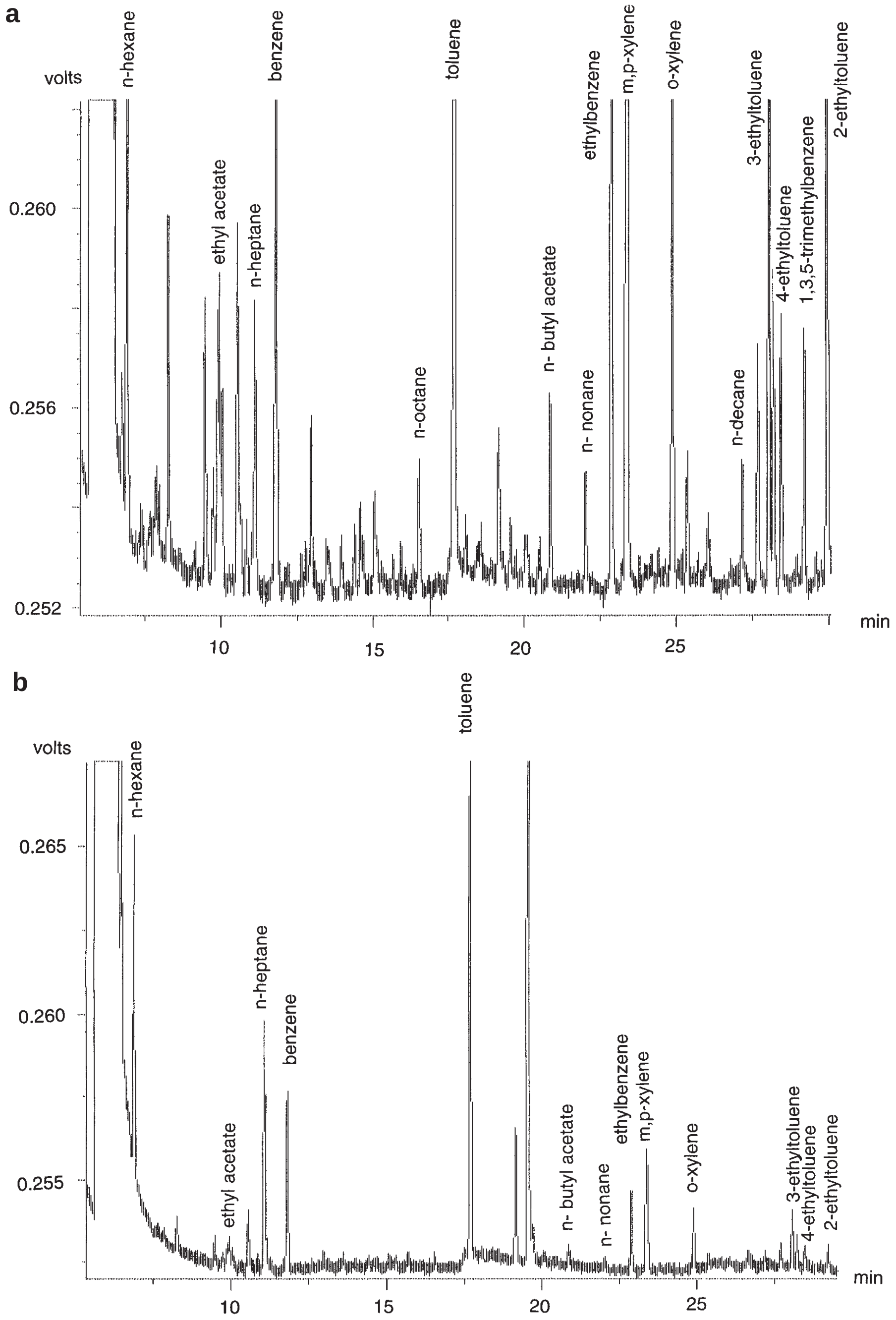

Fig. 1 a, b Gas chromatograms of indoor air samples (DB 1701 column, FID detection, sampling interval: 4 weeks) under identical GC conditions: **a** OVM 3500 monitor, **b** ORSA 5 monitor. Both types of monitors were exposed simultaneously at a distance of a few centimeters from each other. The differences in the chromatograms are a result of the different sampling rates for the individual VOCs

Table 4 Blank values of OVM 3500 and ORSA 5 monitors (*n* = 3, DB 5 column, in μg absolute) (n.d. = not determined, DL = detection limit)

Compound	OVM 3500	ORSA 5
Benzene	< DL	0.019 ± 0.07
Toluene	0.057 ± 0.034	0.042 ± 0.025
m-, p-Xylene	0.126 ± 0.039	< DL
o-Xylene	0.032 ± 0.010	< DL
Ethylbenzene	0.021 ± 0.014	< DL
Trichloroethene	0.002 ± 0.001	0.008 ± 0.006
Tetrachloroethene	0.003 ± 0.002	0.005 ± 0.003
Ethyl acetate	n.d.	n.d.
Nonane	n.d.	n.d.

better than those described by Shields and Weschler [7] who exposed two sets of three OVM 3500 monitors indoors for 31 and 53 days, respectively. In their study reproducibility averaged about 13% of the mean value.

Blank values of unexposed OVM 3500 and ORSA 5 samplers (given in Table 4) were in the same very low concentration range. A further reduction of the blanks of unexposed OVM 3500 samplers is possible by agitating them first with 2 mL carbon disulfide and then with acetone. Before sampling, residues of the solvents can be removed by treating the samplers at 80 °C under vacuum [20]. A likewise cleaning of ORSA 5 monitors is not possible. This is especially important for short-term sampling intervals (less than 24 h).

Conclusions

OVM 3500 and ORSA 5 are both effective and reliable collectors of indoor as well as outdoor VOC concentrations under real-life conditions. They are both capable of sampling low (environmental) VOC concentrations over extended periods of time, e.g. several weeks.

In conclusion, if environmetally caused VOC concentrations are to be collected, OVM 3500 samplers are preferable to ORSA 5 monitors. This is a consequence of their larger cross-sectional area and their shorter diffusion path-length of the OVM 3500 resulting in higher uptake rates and lower detection limits. Another advantage of OVM 3500 monitors is, that they can be more easily preconditioned to remove blanks. This may become important for shorter sampling periods and for the determination of environmental VOC concentrations, e.g. about 1 μg m^{-3} [20]. On the other hand, ORSA 5 monitors are the sampling device of choice if microwave-induced thermodesorption is used, because only tube-type devices such as the ORSA 5 are compatible with this technique.

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