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The home-made in-situ passive flux sampler for the measurement of monoterpenes emission flux: preliminary studies

Mariusz Marć[1], Jacek Namieśnik[1], Bożena Zabiegała[1]*

[1] *Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, Gdańsk, Poland*

[*] *Address for correspondence: Bożena Zabiegała, Department of Analytical Chemistry, Gdańsk University of Technology, ul. Narutowicza 11/12, PL 80-233, Gdansk, Poland.*
e-mail: bozena.zabiegala@pg.gda.pl

Abstract

The paper presents the construction and metrological characteristics of the home-made in-situ passive flux sampler, an analytical tool representing small-scale emission chambers working in-situ and passively sampling analytes from the gaseous phase. The sorption element was a cylindrical container made of stainless steel net, packed with a carbon sorbent bed – graphitised charcoal *Carbograph 4* 35/50 mesh. The recommended working/exposure time of the constructed passive device was determined by carrying out model tests in the laboratory. In addition, a preliminary study was conducted to determine the rate of the emission flux of selected monoterpenes released from the surface of wood-based indoor materials (laminated chipboard) used in residential areas.

Key words: passive flux sampler, emission flux, monoteprenes, indoor materials, in-situ measurements

1. Introduction

The scientific literature published over the last decade shows the emission of various types of organic compounds (from VOCs and SVOCs group) from furnishings and finishing materials, and this is one of the main indoor processes having a significant impact on the quality of indoor air. VOC and SVOC chemical compounds present in the indoor air may negatively affect the health and comfort of the inhabitants [1-3].

An overview of literature data indicates that emission rates and emission profiles are usually analysed with stationary environmental chambers (small or large scale). Despite the fact that their application in analytical laboratories is costly, time consuming and requires transportation of the tested material into the laboratory, their great advantage is the ability to obtain accurate and reliable analytical information about the type and amount of organic compounds released from the tested material used indoors [4].

However, for the individual users of residential areas the transportation of furnishings to the analytical laboratory is an inconvenient and unacceptable option. Moreover, in most cases, the emission measurements requires partial destruction or damage of furnishing material (through grinding or trimming it) to fit it to the size of the stationary environmental chamber. The optimal solution may be a portable device working in a nondestructive pattern for the studied object and that can be used in-situ in the residential area. An additional advantage of such devices would be the ability to work in a passive mode of sampling. Moreover, from an economic point of view, it is important that this type of device does not require an external power supply and is easy to use and cheap in operation. For this reason, an increasing number of analytical laboratories design and construct different types of small-sized portable emission chambers combining the classic features of the miniature emission chamber with the advantages of passive sampling of analytes from the gaseous phase [5]. This type of passive analytical device allows the obtaining of preliminary analytical information on the total amount of organic compounds (TVOC) emitted from the surface of a studied material, or rate of the emission flux of individual compounds, or groups of organic compounds such as formaldehyde [6, 7], toluene, ethylebenzene, xylenes, styrene [8], acetaldehyde, acetone, n-hexanal [9], organophosphate flame retardants [10], phthalate esters [11] and monoterpenes [12]. The general operating principle of small-sized portable emission chambers passively sampling analytes from the gaseous phase is based on the Fick's first law of diffusion. The emission flux largely depends on the organic compound diffusion coefficient in the gaseous phase, the surface area of the studied material, defined by the device's inner dimensions and the passive flux sampler exposure time [4, 5, 13]. To estimate the emission flux of organic compounds from solid indoor materials the transport of organic compounds is mostly described based on the macroscopic scale of the emission process. In a such case the indoor material is considered as a solid body, in which the organic compounds are present in gaseous phase, in pores of the of indoor material [12]. Solid-phase diffusion (organic compounds in adsorbed phase) is negligible compared with the much faster diffusion through pore.

The paper presents the characteristic of the new type of analytical equipment for in-situ emission measurements - the home-made in-situ passive flux sampler (PFS) representing a small-scale emission chambers passively sampling analytes from the gaseous phase. The recommended working/exposure time of the constructed analytical device was determined by conducting preliminary model studies in the laboratory for α-Pinene. The selection of α-pinene as a representative monoterpene was based on two factors: the common presence of the α-pinene in wood-based furnishing materials and its relatively low reactivity with other compounds present indoors as compared to the reactivity of other monoterpenes, e.g. D-Limonene [12, 14].

Thus, the obtained information allowed for on-site (indoor) preliminary studies to obtain analytical data about the rate of the emission flux of selected monoterpenes (α-pinene, 3-carene and D-limonene) released from the surface of wood-based indoor materials (chipboard laminated on both sides) used in residential areas.

2. Materials and Methods

2.1 Design of in-situ passive flux sampler

The in-situ PFS used in screening studies to estimate the emissions flux of monoterpenes was constructed from the following components:

- a cover and a body made of polished stainless steel with a total weight of approx. 0.40 kg,
- seal made of polytetrafluoroethylene (PTFE), providing passive flux sampler tightness during the measurement and to preventing damage to the sorption tube,
- a commercially available sorption tube (length - approx. 60 mm, external diameter - 4.8 mm) made of stainless steel net filled with graphitised charcoal (*Carbograph 4* - mass 300 ± 10 mg of 35/50 mesh).

The tube filled with a sorbent bed was installed inside the home-made in-situ PFS at a height of approx. 2.5 cm from the surface of studied material. The use of the home-made in-situ PFS in the screening study allows the estimation of the rate of the emissions flux of selected monoterpenes from a flat surface of 25.5 cm^2. The height of the described device is 3.5 cm. Figure 1 shows a general view of the designed and constructed home-made in-situ PFS.

2.2 Determination of working parameters of home-made in-situ passive flux sampler

The recommended exposure time of the home-made in-situ PFS was defined based on the relationship between the mass of the analyte trapped on a sorbent bed *Carbograph 4*, and the exposure/working time of the passive device. The recommended working time means the time needed to collect (by home made in-situ PFS) the whole amount of the analyte being in the gaseous phase inside the device.

1 μl of freshly prepared standard solution containing 858 ng of α-pinene was applied onto the watch glass placed on a ∅100 mm glass Petri dish. Then, the home-made in-situ PFS with a clean sorption tube was placed on a Petri dish. This experiment was repeated several times for different time periods. Each time the amount of α-pinene retained on a sorbent bed was determined chromatographically using the TD-GC-MS system.

Model studies allowing to determine the home-made in-situ PFS exposure/working time were carried out in two periods of time: in short intervals, i.e. 15, 30, 45, 60 minutes, and long intervals, i.e.: 120, 180, 240, 300 minutes. Three independent replicates of the experiment were performed for each time interval. Each time before carrying out the experiment, the surface of Petri dishes and the inside of home-made in-situ PFS was washed with distilled water and detergent to eliminate the wall memory effect. Additionally the sorption tube with *Carbograph 4* was conditioned for 30 minutes at 300°C

2.3 Thermal desorption and gas chromatography/mass spectrometry analysis parameters

The tubes filled with *Carbograph 4* were subsequently thermally desorbed (*Unity Markes International, Limited Version 2.00, South Queensferry, UK*) for 20 min at 280^{o}C with a high purity helium flow rate of 55 ml/min. As a cold trap (cooled down to 0^{o}C) the quartz tube filled with *Tenax TA* and *Carbotrap* dedicated for collecting VOCs samples in the $C_{4/5}$ to $C_{30/32}$ range was applied. Thermal desorption of the cold trap was performed at 280^{o}C for 5 min with a high purity helium flow rate of 1.0 ml/min. The injection split ratio was set to 1:7. The transfer line temperature was kept at 150^{o}C. Desorbed analytes were analyzed using a gas chromatograph (*Agilent Technologies 6890*) coupled with a mass spectrometer (*5873 Network Mass Selective Detector, working mode - SCAN*). The following gas chromatography parameters were selected: capillary column (*J&W Scientific, Folsom, CA, USA*) DB-5ms (30 m × 0.25 mm × 0.25 µm), carrier gas – high purity helium with a flow rate of 1.0 ml/min, GC oven programme: 50°C for 5 min, raised at a rate of 7°C/min up to 150°C, increased at the rate 15^{o}C/min up to 250^{o}C, and finally maintained for 10 min at 250°C. The mass spectrometer ionization source temperature was set to 250^{o}C and the quadrupole temperature was 150^{o}C.

2.4 Chemical standards and calibration of TD-GC-MS system

External standard calibration was carried out with the following monoterpene compounds: (−)-alpha-Pinene (≥99%, δ= 0.858 g/ml), (+)-3-Carene (≥99%, δ = 0.864 g/ml), (S)-(−)-Limonene (≥99%, δ= 0.844 g/ml), Sigma Aldrich, Germany. The liquid solutions were prepared in 10 ml volume glass flasks in two concentration ranges: from 10 to 300 µg/ml and from 300 to 3000 µg/ml. Standard liquid solutions were freshly prepared before the calibration process. Two five-point calibration curves for selected compounds were created: for concentration range from 10 to 300 µg/ml (the coefficient of determination was from 0.969 to 0.992); for concentration range from 300 to 3000 µg/ml (the coefficient of determination was from 0.998 to 0.999). Further information on the calibration procedure can be found elsewhere [12, 15]. The limit of detection (LOD) values were form 1.6 ng for α-Pinene to 1.9 ng for D-Limonene.

2.5 Preliminary field studies

The surfaces of two chipboards (with dimensions 45 cm x 30 cm) laminated on both sides were the subject of screening research (field studies) to estimate the rate of the emission flux of selected monoterpenes using the home-made in-situ passive flux sampler. Two chipboards were wood-based construction materials installed in a residential area, and differed from each other significantly in terms of the usage time in the indoor environment. A chipboard covered with a layer of dark laminate was used in the residential area for 30 months from the date of purchase and installation to the beginning of the research. In contrast, a chipboard covered with a light laminate layer was used for one week from the date of purchase and installation. During the preliminary field studies two ready to use home-made in-situ PFS were placed on the surface of each wood-based indoor material. After a pre-defined time of exposure, tubes filled with a sorbent bed were removed from PFS and transferred to a glass container, sealed by a polyethylene plug. Subsequently, containers with the sorbent bed were transported to the laboratory and subjected to liberation, separation, identification and final determination of analytes by the TD-GC-MS system.

During the studies (14 days), temperature (22 ± 2°C) and relative humidity (RH. 50 ± 5%) readings were performed. The total number of analyte samples collected during the measurement (14 days) was 28 for each studied laminated chipboard.

3. Results and discussion

3.1 Determination of working time and the sampling rate characteristics of the home-made in-situ passive flux sampler

The model study was carried out in the laboratory to determine the best (recommended) working time and the usefulness of the home-made in-situ PFS for the on-site screening study. The aim of this study was to determine the performance characteristics of the constructed passive device. Figure 2A shows the results of a laboratory test model, illustrating the relationship between the mass of α-pinene retained on the sorbent bed (*Carbograph 4*) of the home-made in-situ PFS and the exposure time of the constructed passive device.

As shown in Figure 2A, during 120 minutes of passive device exposure time, approx. 95% of α-pinene applied onto a watch glass and released into the gaseous phase was adsorbed on the sorbent bed. Moreover, data presented in Figure 2A indicate that from 0 to 60 minutes after the installation of the sampler on a glass surface (Petri dish, ∅ = 100 mm) the amount of α-pinene retained on a sorbent bed is proportional (dependent) to the exposure time of the home-made in-situ PFS. In contrast, after 120 minutes, the organic compound contained in the gaseous phase defined by the dimensions of the passive device (internal volume of approx. 64 cm^3) was completely adsorbed and retained on the sorbent bed.

The recommended working time of the constructed device, which is 120 minutes, was determined by taking into account parameters such as: the very small internal volume of the home-made in-situ PFS, and the specific characteristics of the sorption bed (adsorbing surface ca. 200 $m^2 \cdot g^{-1}$) applied inside the passive device. In the case of the home-made in-situ PFS, the sampling rate of the analyte from the gaseous phase depends on two factors: the diffusion coefficient of the analyte in the gaseous phase, and the analyte concentration gradient inside the PFS: concentration gradient between the surface of the studied material and the surface of the sorption element (driving force for the analyte sampling from the gaseous phase).

To illustrate the changes in the uptake rate of the analyte (α-pinene) from the gaseous phase inside the home-made in-situ PFS, the relationship between the exposure time of the home-made passive device and the sampling rate of the analyte from the gaseous phase was determined (Figure 2B). The analyte sampling rate was calculated based on the following equation (1):

$$S_{gp} = \frac{m}{x_{gp} \cdot t} \qquad (1)$$

where:

S_{gp} – the uptake rate of the analyte from the gaseous phase [ml/min]

m –the amount of the analyte retained on a sorbent bed [ng]

t - exposure time [min]

x_{gp} - the amount of analyte in the gaseous phase inside the home-made in-situ PFS [ng/cm^3]

Increase in the exposure time of the home-made in-situ PFS was associated with a decrease in the uptake rate of the analyte from the gaseous phase (from 2.3 ml/min for 15 minutes exposure to 0.50 ml/min for 120 minutes exposure) (Figure 2B).

3.2 The emission flux of selected monoterpenes determined using the home-made in-situ passive flux sampler

The emission flux of organic compounds depends mainly on the age of the indoor material and its indoor usage time. The newer the indoor material (delivered to the enclosed facility directly or after a short storage at the manufacturer), the higher the amount of organic compounds released into the indoor air. With storage/usage time of indoor furnishings, the amount of organic compounds released from the indoor material to indoor environment decreased [12].

The results of the preliminary screening studies aimed to estimate the emissions flux of selected monoterpenes (α-pinene, 3- carene and D-limonene) from two types of chipboards laminated on both sides, which differ of indoor storage/usage time are presented in Table 1. The initial screening study was performed using the home-made in-situ PFS. The emission flux of monoterpenes released from the surface of a wood-based indoor materials was determined using the following equation (2)[12, 13]:

$$E_f = \frac{m}{A \cdot t} \qquad (2)$$

where:

E_f – the emissions flux of the determined monoterpenes [$\mu g/m^2 \cdot h^{-1}$],

m –the mass of the monoterpene retained on a sorbent bed [μg]

t - the working time of the in-situ PFS [h]

A – the area defined by the dimensions of passive device [m^2].

The average value of emission flux of α-pinene and 3-carene, released from the tested chipboard surface covered with black laminate, determined for the entire measuring period (two weeks) was 11.0 ± 5.4 $\mu g/m^2 \cdot h^{-1}$ and 6.1 ± 3.2 $\mu g/m^2 \cdot h^{-1}$ respectively.

In the initial screening tests, where the object of the study was chipboard covered with dark laminate, the D-limonene emission flux could be determined in only 4 cases. In other measurement series, the amount of D-limonene retained on the sorbent bed was below the limit of detection (<LOD). Therefore, the average value was not determined for the entire measurement period (14 days). Estimation of the mean value for the entire 14-day measurement period, based on 4 results did not provide reliable analytical information reflecting the actual D-limonene emission flux. Measurements summarized in Table 1 indicate that despite the passage of considerable time (30 months) chipboard covered with black laminate, can still be a source of monoterpenes emissions, especially α-pinene and 3-carene, to indoor air.

In the case of chipboard covered with a light laminate and stored/used indoors for a very short time (1 week), the average value of emission flux of α-pinene, 3- carene and D-limonene estimated for the entire measurement period (2 weeks) was 35 ± 16 $\mu g/m^2 \cdot h^{-1}$, 4.3 ± 3.6 $\mu g/m^2 \cdot h^{-1}$ and 2.2 ± 1.8 $\mu g/m^2 \cdot h^{-1}$, respectively. Data summarized in Table 1 also show that the tested chipboard surface covered with a light laminate stored/used indoors for 1 week can be a relevant source of monoterpenes emission, especially α-pinene.

4. Conclusions

The obtained results of preliminary screening studies carried out using the home-made in-situ PFS indicate that this device could be used in the future for screening studies to determine the rate of emission flux of selected volatile organic compounds, e.g. BTEX (benzene, toluene, ethylbenzene, xylenes) and aliphatic hydrocarbons (from n-heptane to n- undecane), released from the surface of various indoor materials.

Preliminary screening studies carried out on laminated chipboards stored/used for different periods of time demonstrated the suitability of the in-situ PFS in measuring the emission flux of monoterpenes released from the tested wood-based materials. Preliminary findings from screening suggest that laminated wood-based materials used indoors for shorter periods of time release greater amounts of monoterpenes than materials used indoors for long periods of time.

5. Acknowledgements

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6. Conflict of Interest

The authors declare that they have no conflict of interest

7. References

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Figure captions

Figure 1. The overall view of the designed and constructed home made in-situ PFS.

Figure 2. A graphical representation of the relationship between: A - the amount of α-pinene retained on a sorbent bed of the sorption tube, and the working/exposure time of the home-

made in-situ PFS; B - the uptake rate of α-pinene from the gaseous phase and the working/exposure time of the home-made in-situ PFS.

Table 1. The results of the determination of the emission flux of selected monoterpenes using home-made in-situ PFS.

The emissions flux of selected monoterpenes released from the surface of the wood-based element covered on both sides by dark laminate, used in residential area for 30 months

Parameter	first week of research (n = 14)			second week of research (n = 14)		
	α-Pinene	3-Carene	D-Limonene	α-Pinene	3-Carene	D-Limonene
Average [μg/m^2·h^{-1}]	17.8	7.0	<LOD	8.3	4.9	<LOD
Standard deviation [μg/m^2·h^{-1}]	1.9	1.3	<LOD	6.5	3.6	<LOD
Median [μg/m^2·h^{-1}]	14.7	6.8	<LOD	7.2	4.3	<LOD
Min [μg/m^2·h^{-1}]	10.1	5.5	<LOD	0.41	1.4	<LOD
Max [μg/m^2·h^{-1}]	15.3	9.2	<LOD	16.5	9.4	<LOD

The emissions flux of selected monoterpenes released from the surface of the wood-based element covered on both sides by a light laminate, used in residential area for one week.

Parameter	first week of research (n = 14)			second week of research (n = 14)		
	α-Pinene	3-Carene	D-Limonene	α-Pinene	3-Carene	D-Limonene
Average [μg/m^2·h^{-1}]	42	5.1	2.4	29	3.4	2.1
Standard deviation [μg/m^2·h^{-1}]	19	4.4	1.6	11	2.8	2.0
Median [μg/m^2·h^{-1}]	31	2.7	2.5	28	2.7	1.0
Min [μg/m^2·h^{-1}]	23	0.72	0.68	17	0.62	0.49
Max [μg/m^2·h^{-1}]	67	10.9	3.7	47	7.5	5.8

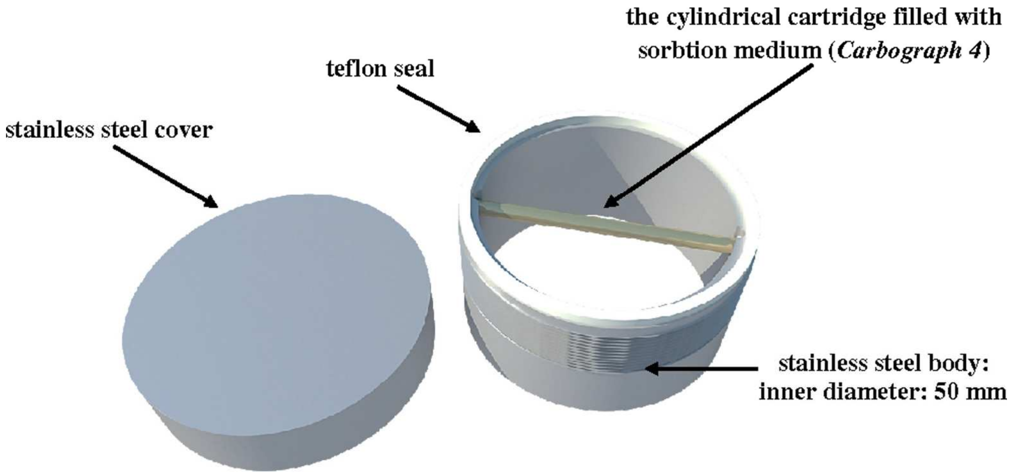

Figure 1. The overall view of the designed and constructed home made in-situ PFS
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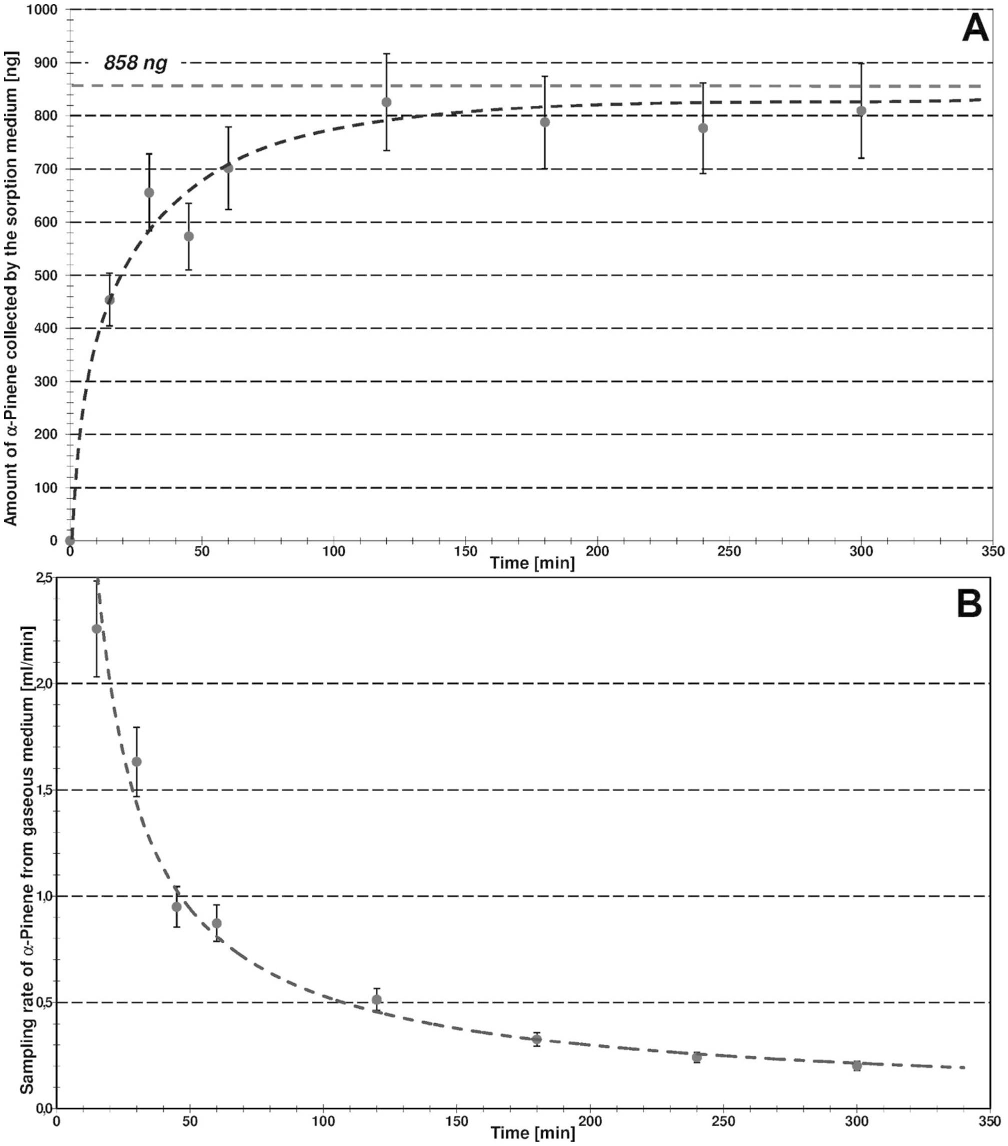

Figure 2. A graphical representation of the relationship between: A - the amount of α-pinene retained on a sorbent bed of the sorption tube, and the working/exposure time of the home-made in-situ PFS; B - the uptake rate of α-pinene from the gaseous phase and the working/exposure time of the home-made in-situ PFS.
191x218mm (300 x 300 DPI)