

The miniaturised emission chamber system and home-made passive flux sampler studies of monoaromatic hydrocarbons emissions from selected commercially-available floor coverings

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Abstract

The estimation of the emission rate of organic compounds released from various types of indoor materials can be performed using stationary environmental test chambers (ETC) classified as ex-situ methods or small-scale portable analytical devices based on the use of passive technique at the stage of analytes sampling from the gaseous phase (in-situ methods).

The paper presents results of emissions of selected organic compounds from the monoaromatic hydrocarbons group (benzene, toluene, ethylbenzene, p,m-xylene and styrene) emitted from the surfaces of various types of commercially-available floor coverings and the underlay made of polyurethane foam which might be installed indoors under floor coverings. The research were conducted simultaneously using a new type of miniature emission chambers system μ -CTE™ 250 and a new type of home-made passive flux sampler (PFS). The interpretation and comparison of the obtained results allowed for determination of main factors that significantly affect the result of analysis and, ultimately, on the reliability of emission assessments, which included: the operation mode of the analytical device, the duration of studies and metrological and morphological characteristics of the studied samples. It was observed that in a case of floor coverings with synthetic fibres, the emission rate is influenced by factors such as: the fleece/pile weight (g/m^2), the type of synthetic material used for fibre production, the colour of fibres and the applied underlay type (felt or synthetic jute). In a case of flexible floor coverings made of poly(vinyl chloride), the thickness of the abrasive layer influenced the quantity of released organic compounds.

Keywords:

μ -CTE™ 250

Floor coverings

Passive flux sampler

Emission rate Monoaromatic hydrocarbons

1. Introduction

The average adult, depending on numerous behavioural and climatic factors, spends from 70 to even 90% of his/her life in various types of residential and public utility indoor environments. One of the most significant factors shaping the quality of indoor air, which, as a result, influences the comfort of persons staying in a given residential area includes emissions of chemical compounds from all kinds of equipment, finishing, building and constructing materials as well as materials used to cover flat surfaces (ceilings, walls, floors) [1–3]. Furnishing materials that are most commonly

purchased and installed in newly-constructed buildings and apartments include various types of floor coverings. Information from the literature can be the basis to conclude that, on average, in a standard residential apartment (e.g. living room) floors take up the surface of approx. 7–8 m^2 , which, after further calculations, renders a loading factor of approx. 0.41–0.45 m^2/m^3 . This result allows for classification of floor surfaces as one of the most significant factors influencing the shape of indoor environment quality - after the walls, it is the second largest usable surface of the almost every apartment [4]. The influence of floor coverings on the indoor air quality in a residential area is mostly related to the phenomenon of the release (emissions) of chemical compounds that were added at the manufacturing and aesthetic processing of a given product. Those compounds can be released into the gaseous phase from a given indoor material as remains of solvents added at the stage of its production (production of the base materials) or colourants and

special additives that improve the visual quality of the product as well as from adhesives and resins used to connect individual elements of floor coverings into the final product suitable for its regular use [5–7]. The performance parameters of floor coverings defined by manufacturers, which are largely taken into account by potential consumers and users of residential areas include: fleece/pile weight (g/m^2), thickness of the floor covering, the type of applied underlay, synthetic material from which floor covering fibres are made, the colour and colour arrangement, the price etc.

Due to the fact that the process of releasing chemical compounds from indoor materials is sometimes the most significant and direct source of indoor air pollution, a large number of scientific laboratories and research centers use a wide range of stationary (ex-situ methods) or portable devices (in-situ methods) that are used to obtain analytical information on the type and quantity of chemical compounds released from indoor materials [8,9].

The ex-situ methods are generally based on the application of stationary environmental test chambers (ETCs) installed in scientific laboratories or research and development centers. The ETCs are mainly made of inert materials such as stainless steel or glass in order to significantly reduce the possibility of adsorption of chemical compounds on the internal surface of chambers (reduce the impact of wall-memory effect on the final results). The stationary chambers can be classified generally into two groups, taking as a classifier the internal volume of devices: (i) small-scale ETCs (mainly home-made cylindrical containers), in which the internal volume is lower than 1 m^3 ; (ii) large-scale ETCs, where the internal volume is over 1 m^3 . Mentioned stationary chambers provide the possibility to conduct studies under conditions similar (close to) to indoor environment conditions. In the case of ETCs research, the samples of chemical compounds emitted to the gaseous phase from the surface of studied indoor material (inside a chamber) are collected in a dynamic/active way (transport of a gas stream through a container filled with appropriate sorption medium e.g. Tenax TA). The primary advantage of ETCs application to the research on indoor materials emissions is a possibility to receive a reliable analytical information (mainly expressed as the emission rate [$\mu\text{g}/\text{m}^2$] or [$\mu\text{g}/\text{g}$]) about the type and the amount of chemical compounds released from the studied material. The main limitation and drawback of the use of ETCs in daily analytical practice is the fact that single analysis is expensive and time consuming. Also there is a need to transport selected indoor material into the laboratory and in some cases (especially using small-scale ETCs) divide it into pieces of appropriate dimensions (defined by internal volume of a chamber) [10–14]. However, on the other side studies performed under laboratory conditions allow evaluating the influence of environmental factors (temperature, humidity, solar radiation, presence of oxidizing substances) on the emission process [15–19].

As for the in-situ methods, the sample collection of chemical compounds emitted from the surface of studied indoor equipment is performed directly in residential area (in indoor environment) using small-scale portable analytical devices such as: (i) passive flux samplers (PFSs); (ii) small-scale passive emission chambers (SSPECs). In these types of devices the samples of chemical compounds emitted to the gaseous phase from the surface of studied indoor element are collected in a passive way - using passive sampling technique. The transport of mass of chemical compounds present in indoor material to the sorption medium is based on the Fick's laws of molecular diffusion. The cover of PFSs and SSPECs is generally made of inert materials such as: (i) polished stainless-steel; (ii) glass (tinted or transparent); (iii) high quality plastic material e.g. polytetrafluoroethylene (PTFE). In the central point of every portable passive sampling device the appropriate sorption medium (suited to analytes) is placed – the type of applied sorption

medium defines the group of chemical compounds which can be collected using selected device, for example the graphitized charcoal or activated carbon are applied as a sorption medium to collect the volatile organic compounds (VOCs) samples. The most important advantages of small-scale portable passive analytical devices are: (i) low exploitation costs; (ii) simple construction; (iii) lack of sources of energy supply; (iv) the sampling stage is performed in a non-invasive/non-destructive way for the surface of studied indoor element, and directly in indoor environment. Mentioned passive analytical devices are mainly used in screening research, for rapid identification of the potential emission sources of chemical compounds to indoor environment and the obtained analytical information is expressed as the emission flux [$\mu\text{g}/\text{m}^2 \cdot \text{h}^{-1}$] or emission rate [$\mu\text{g}/\text{m}^2$] [20–23].

In contemporary literature, information can be found about numerous design solutions in the field of portable analytical devices using passive technique at the stage of analytes sampling from the gaseous phase (chemical compounds released from the indoor material to the gaseous phase) [24]. The main limitation of all design solutions described in the literature as regards analytical devices working under in-situ conditions seems to be the doubt concerning the reliability of the information obtained on the actual quantity of chemical compounds released into the indoor environment from the surface of studied material [25]. Still there is a lack of appropriate uniform and clearly-defined tools (used to ensure the quality of analytical measurements), which would allow for conducting the validation process in a correct manner for both the instrument and the analytical procedure used (lack of suitable reference materials or standards defining the course of the procedure using portable analytical devices using passive technique at the stage of analytes sampling from the gaseous phase). There are only a few publications available that describe reference materials in the field of the emission of organic compounds into the gaseous phase developed under laboratory conditions [26–30].

From the point of view of the users of residential areas, it seems the most important to obtain clear analytical information on the main source of pollutant emissions and on what kinds of chemical compounds are released in the greatest quantities. For this reason, it seems fully justified to use such analytical devices, which allow for performing screening studies and obtaining quick general information on the type and quantity of pollutants emitted from selected indoor materials. However, one should strive after developing design solutions in the area of in-situ measurements, which would allow for obtaining reliable analytical information by those devices or proof the occurrence of similar relationships between the determined pollutants to those obtained using reference devices and techniques (stationary emission chambers). One should also consider the fact that those devices operate in different modes (passive or dynamic mode), so the data obtained will always differ and, in each case, it will be necessary to interpret the results obtained, taking into account the characteristics of the applied device, its working conditions etc. Due to this fact, it is still necessary to develop new portable analytical devices to conduct in-situ research of the emissions of chemical compounds and to carry out studies showing the usefulness of constructed devices under real/field conditions (in residential areas).

The paper presents the results of emissions of organic compounds from monoaromatic hydrocarbons group released from the surface of commercially-available floor coverings in which fibres were made of synthetic materials (polypropylene, polyamide). The individual types of floor covering differed in terms of the synthetic material from which the fibres were made, the type of the underlay that was used, the intended place and use, and the parameter defined by the manufacturer as the fleece/pile weight (g/m^2). The next subject of the research included flexible floor coverings made



of poly(vinyl chloride); here, the types of floor coverings differed in terms of the thickness of the abrasive layer included in their structure. Moreover, the assessment of the type and amount of monoaromatic hydrocarbons released from the surface of underlay (installed indoors under floor coverings), which was made of polyurethane foam with a defined thickness was conducted.

The described studies were performed using at the stage of sample seasoning and collection of analyte samples from the gaseous phase the new type of miniature emission chambers system μ -CTE™ 250 (ex-situ method) and the home-made in-situ passive flux sampler (home-made PFS). The attempt was also made to compare the obtained data by the two types of analytical devices and to investigate and identify those main factors, which might clearly influence the differences between the obtained results and on the final result of determinations in the long term.

2. Materials and methods

2.1. Samples description – commercially-available floor coverings

Floor covering samples were delivered to the analytical laboratory directly from a commercial and service company specialising in distribution of a broad range of floor coverings, carpets and various types of floor materials and accessories. It was not possible to determine precisely the time of storage of the delivered samples at the distributor's due to the fact that floor covering samples were not delivered directly by the manufacturer. However, it was established on the basis of information provided by the distributor that the storage time of floor covering bales available for retail clients at the company was no longer than 6 months.

The most popular types of floor coverings sold were selected for estimating the emissions of monoaromatic hydrocarbons: (i) floor coverings in which fibres were made of synthetic material (polypropylene, polyamide), which differ from each other by the type of the underlay (felt or synthetic jute), the colour, total thickness and the parameter specified by the manufacturer as the fleece/pile weight expressed in g/m^2 ; (ii) floor coverings made of poly(vinyl chloride) (PVC), which differed from each other in terms of the total thickness and the thickness of the abrasive layer; (iii) the single type of underlay (installed indoors under floor coverings) made of polyurethane foam of a specified thickness. Table 1 presents information that can be treated as the general characteristics of floor covering samples, which were the subject of the studies of the emissions of selected monoaromatic hydrocarbons.

From each bale of selected floor coverings available at the commercial and service company, strips were cut that were 4 m long and 15 cm wide. Next, the strips were divided into two parts, each of which was two metres long. From the first part of the floor covering, 10 randomly-selected 4 cm \times 4 cm samples were cut that corresponded to the dimensions of a single miniature emission chamber. The other part of the floor covering was cut into 10 cm \times 15 cm pieces, and 10 samples were randomly selected for further studies.

The 4 cm \times 4 cm floor covering samples were analysed in terms of the type and amount of emitted monoaromatic hydrocarbons using a new type of the miniature emission chambers system μ -CTE™ 250 (ex-situ method). For 10 cm \times 15 cm samples, home-made in-situ passive flux samplers (home-made PFS) were used at the stage of analyte sampling – monoaromatic hydrocarbons emitted to the gaseous phase.

2.2. Description of analyte sampling process using ex-situ and in-situ devices

To estimate the emission rate of selected monoaromatic

hydrocarbons emitted from floor covering samples based on ex-situ technique, a new type of stationary miniature emission chambers system was used - Markes' Micro-Chamber/Thermal Extractor™ – μ -CTE™ 250 (Markes International, Ltd.). Detailed information about the design and metrological characteristics of the μ -CTE™ 250 system (Fig. 1) was presented in previous literature [31–33]. One 4 cm \times 4 cm floor covering sample was placed inside each of 4 chambers (the internal volume of one chamber was 114 cm^3). Floor covering samples were seasoned in the chamber for 60 min at 25 ± 1 °C. The temperature value inside the chamber defined in this way was aimed at reflecting the temperature in the majority of indoor areas intended for permanent residence. The inert gas flow rate (nitrogen purity, 2.2) passing through the interior of each of the miniature emission chambers was set to 10 ml/min. Organic compounds emitted from the each of studied sample of floor covering were transported to a steel tube filled with a Tenax TA sorption bed where they were trapped. One series of measurements included the simultaneous seasoning of 4 floor covering samples placed inside miniature emission chambers system. The last measurement series (the third measurement series) involved simultaneous seasoning of 2 floor covering samples. During this time, the remaining two miniature emission chambers were empty, and they were used for the determination of the blank field for μ -CTE™ 250 system.

To study the emissions of selected monoaromatic hydrocarbons conducted with the use of portable analytical device working in the passive mode of collection of analyte samples from the gaseous phase, stainless steel home-made in-situ passive flux samplers were used (Fig. 2). Detailed information on the design and metrological characteristics of the home-made in-situ PFS was presented in previous literature report [34]. At the first stage of the studies, 10 cm \times 15 cm floor covering samples were placed on a glass board to prevent the influence of the interior material base on the final result. Next, a stainless steel home-made PFS with a commercially-available cylindrical container (made of stainless steel net) filled with the Carbograph 4 sorption bed was placed at the central point of the surface of the floor covering samples. The exposure/working time of the home-made PFS on the surface of the floor covering sample was 8 h. A home-made PFS allows for investigating the emission rate of organic compounds emitted from a surface of approx. 25.5 cm^2 of indoor material. The transport of organic compounds emitted from the surface of the studied material to the gaseous phase towards the home-made PFS took place by means of molecular diffusion in accordance with Fick's first law of diffusion [35].

While performed research using the home-made PFS, where floor covering samples made of synthetic fibres are the subject of research, it was necessary to use 1-kg weights on the surface of the devices to ensure that the device is appropriately pressed to the floor covering surface. After the completion of the phase of collecting sample analytes from the gaseous phase using the home-made PFS, the cylindrical container with the Carbograph 4 sorption bed was removed from the inside of the sampler and placed in a glass vessel, tightly closed with a polyethylene plug and wrapped in aluminium film. The air temperature in the indoor area, where studies were performed using the home-made PFS, was 24 ± 2 °C.

2.3. Instrumental analysis – TD/GC/FID conditions

To estimate the quantity of emissions of monoaromatic hydrocarbons released from the surface of floor covering samples, an analytical procedure was used in which a two-stage thermal desorption technique was applied at the stage of liberating of analytes retained on the sorption beds (Tenax TA and Carbograph 4). Conducting the analyte extraction process at a higher temperature in the inert gas flow rate allows for using analytical



Table 1

The characteristics of commercially-available floor covering samples randomly selected for the investigating the emissions of monoaromatic hydrocarbons.

Floor coverings with polypropylene fibres				
Sample name	Underlay type	Average fleece/pile weight [g/m ²]	Average total thickness [mm]	Characteristics/application
PP_1	Felt	None	3.5	Floor cover used for covering flat surfaces during renovation work characterised by low quality and a low market value.
PP_2	Felt	375	6	Its fleece is formed by thin, twisted polypropylene threads. Floor cover can be kept clean easily. An optimal solution as a temporary cover during renovations or an inexpensive corridor protection.
PP_3	Felt	500	8	Floor cover is intended for the use in the living room or in the bedroom.
PP_4	Synthetic jute	300	4	Floor cover forms thin artificial fibres twisted in small loops that thickly cover the base. It ensures good protection of the surface in rooms where the usefulness is a more important factor than comfort.
PP_5	Synthetic jute	450	5	Floor cover intended for use in living rooms, corridors and bedrooms.
PP_6	Synthetic jute	500	5	Floor cover with a fire resistance certificate for rooms characterised by low intensity of use.
PUF_1	Polyurethane foam	–	5	The product is dedicated for floor cover with very good thermal insulation properties. Resistance to biological corrosion.
Floor coverings with polyamide fibres				
Sample name	Underlay type	Average fleece/pile weight [g/m ²]	Average total thickness [mm]	Characteristics/application
PA_1	Felt	300	6.5	Floor cover intended for use in a child's room.
PA_2	Felt	560	8	Floor cover is intended for the use in the living room or in the bedroom.
Flexible floor coverings made of the poly(vinyl chloride)				
Sample name	Average abrasive layer thickness [mm]	Average total thickness [mm]	Characteristics/application	
PCV_1	None	0.55	Durable and practical flexible floor cover for residential rooms with very low traffic intensity.	
PCV_2	0.15	1.3	Durable and practical flexible floor cover for residential rooms with low traffic intensity.	
PCV_3	0.25	2.0	Durable and practical flexible floor cover for residential rooms with medium traffic intensity.	
PCV_4	0.50	3.0	Durable and practical flexible floor cover for intensively-used rooms.	

procedures consistent with the philosophy of 'green analytical chemistry', thanks to elimination of organic solvents and the nearly complete automation of the process. Detailed information on the analytical procedure used together with the conditions of the process of liberation, separation, identification and quantitative determination of analytes from the monoaromatic hydrocarbons is presented in Table 2.

2.4. Calibration of TD/GC/FID system

The determination of the quantity of aromatic hydrocarbons emitted from the surface of floor covering samples, which were retained in the sorption beds (Tenax TA or Carbograph 4) was performed using the external standard technique (ESTD). As a standard solution, a commercially-available mixture of 13 compounds from the VOCs group (in the methanol solution) in which the concentration of each organic compound was 2000 µg/ml (VOC EPA Mix 2, Supelco, USA). The calibration procedure used in studies of the TD/GC/FID system included the following stages: (i) preparation of a mixture of standard solutions containing defined concentrations of selected monoaromatic hydrocarbons in glass vessels; (ii) application 1 µl of the standard solution on a tube filled with a clean sorption bed; (iii) passing through a tube filled with a sorption bed an inert gas (helium) for 10 min with a flow rate value approx. 50 ml/min; (iv) the transfer of the tube with the standard solution into the thermal desorber oven and begin the thermal desorption process under conditions identical with those for sorption beds used for studies conducted under real condition.

As a result of the calibration process of the TD/GC/FID system, numerical parameters for the calibration curves for two different measurement ranges of standard reference substances of defined

compounds form the monoaromatic hydrocarbons were calculated: the first range of curves included values from 1 ng to 10 ng of the compound per sorption bed (the values of R² coefficient for the calibration curves of selected monoaromatic hydrocarbons were from 0.992 to 0.997); the other range of curves spanned the values of 10 ng–640 ng (the values of R² coefficient for the calibration curves of selected monoaromatic hydrocarbons were from 0.993 to 0.996). Detailed characteristics of the TD/GC/FID system calibration process with the applied devices were described in previous papers [36–38].

2.5. QA/QC protocol

To ensure the correctness and reliability of the obtained results conducted using previously-described analytical devices, a range of activities allowing for eliminating the influence of external factors (mostly connected with the use of analytical equipment and devices) on the result of analysis. In the case of the µ-CTE™ 250 system, before the sample seasoning stage, the chambers were heated at 100 °C for 1 h. Before starting the studies, the home-made in-situ PFSS were washed twice with deionized water with a detergent, dried and then heated in a furnace at 60 °C, also for 1 h. Prior conditioning of the used analytical devices at an elevated temperature was aimed at eliminating the wall memory effect on the final result of determinations and to remove possible contaminants adsorbed on their surface. These activities were repeated after each measurement phase.

Another step allowing for ensuring reliable of obtained results was the determination and adjustment of the research results by the blank field value. The determination of the blank field value for the µ-CTE™ 250 system was performed during the third



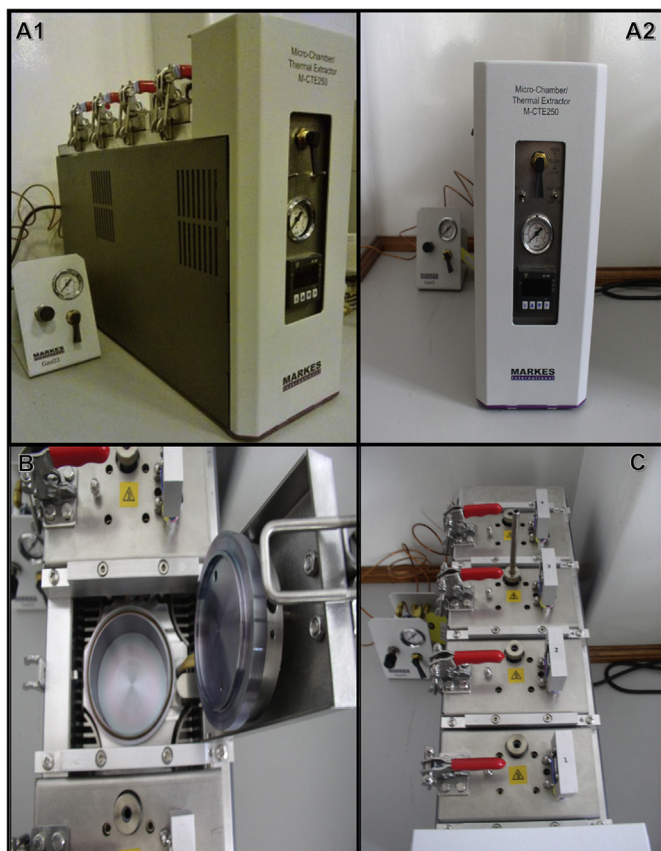


Fig. 1. The general view of applied miniature emission chambers system μ -CTE™ 250 (ex-situ method): A1, A2 – the temperature and inert gas flow rate control panel of μ -CTE™ 250 system; B – the general view of the interior of a single stainless-steel miniature chamber (internal volume - 114 cm³); C – the installation place of stainless-steel tubes filled with sorption medium (Tenax TA).

measurement series. In this measurement series, floor covering samples were seasoned inside two emission chambers, while the other two emission chambers were empty at this time. To determine the blank field value of the μ -CTE™ 250 system, two tubes containing a Tenax TA sorption bed were installed at the outlet of

two empty chambers. The conditions for the process of organic compounds present in empty miniature emission chambers were the same as for emission chambers in which samples of floor covering were placed. After the completion of the seasoning process of floor covering samples in the μ -CTE™ 250 system, the process of collection of analyte samples from empty chambers was also ended. Next, tubes with sorption bed were analysed using the same analytical procedure, which was used in the case of sorption tubes for the collection of organic compounds released from floor covering samples. Blank field values were determined each time during the last measurement series of each the group of floor covering samples. Next, the obtained results defining the amount of emitted organic compounds from floor covering samples were adjusted by the determined numerical value of the blank field.

In the case of the studies of emissions performed using the home-made in-situ PFS, the value of the blank field was obtained by placing a passive sampler using a clean sorption bed on a glass surface. The passive sampler was placed on the surface for the same time as the time of collecting organic compounds emitted from the surface of the studied floor covering samples (8 h). As in the case of the μ -CTE™ 250 system, the values of the blank field were determined each time in the last measurement series. Next, the obtained results defining the amount of emitted organic compounds from floor covering samples were adjusted by the determined numerical value of the blank field.

To determine the numerical values of parameters defining the limit of detection (LOD) and the limit of quantification (LOQ) used in the studies, the calculation method was used for TD/GC/FID, based on the determination of the numerical value of the standard deviation of the collection of signals (FID detector response) and the directional coefficient of the calibration curve. For the numerical value of the LOD parameter for the TD/GC/FID technique used in the research, the following relationships were determined (1):

$$LOD = \frac{3.3 \times S}{b} \quad (1)$$

where:

S - the standard deviation of the detector response determined on the basis of the lowest concentration of organic compound mixture from the group of monoaromatic hydrocarbons,

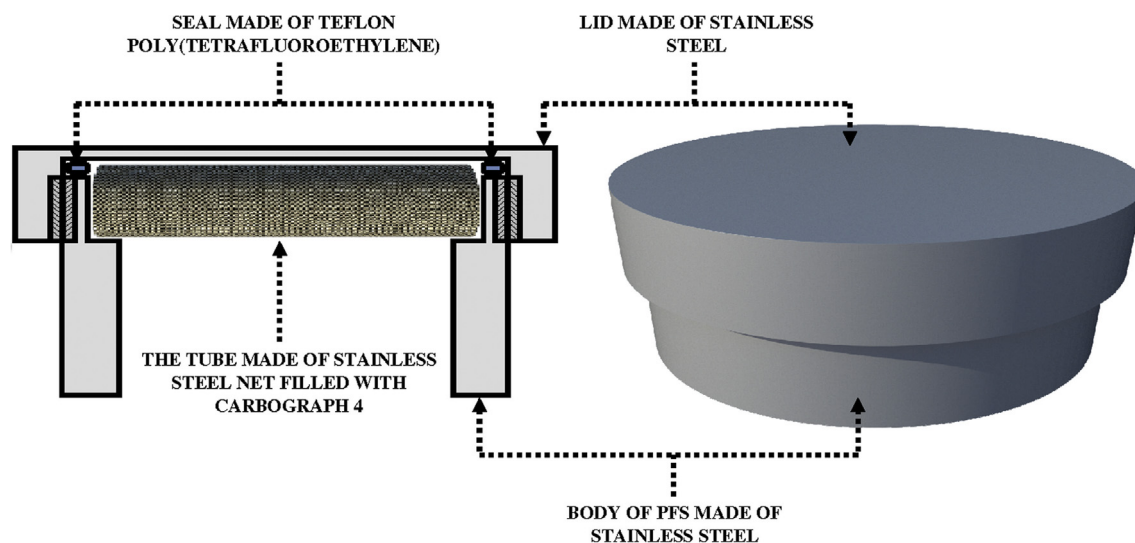


Fig. 2. The general view of home-made passive flux sampler (PFS).

Table 2
The characteristics of the analytical procedure use for the determination of selected monoaromatic hydrocarbons emitted from the surfaces of the studied floor coverings.

The stage of liberating analytes retained in the sorption medium	
The technique used for liberating analytes retained on the sorption medium	Two-stage thermal desorption (thermal desorber constructed by <i>Omnisfera S.C., Gdansk, Poland</i>)
The tool for collecting analyte samples from the gaseous phase	A steel tube filled with the sorption bed Tenax TA, 35/60 mesh (<i>Markes International Ltd.</i>) / Steel cylindrical net filled with sorption bed Carbograp 4, 35–50 mesh (<i>Supelco</i>)
Sorption bed heating temperature at the 1st stage of thermal desorption	280 °C
Sorption bed heating time	15 min / 20 min
The intensity of the inert gas flow (He) through the sorption bed	40 ml/min
Microtrap temperature (37 mg of Tenax TA and 27 mg of Carbotrap) during the 1st stage of thermal desorption	0 °C
Microtrap heating temperature at the 2nd stage of thermal desorption	300 °C
Microtrap heating time	5 min
The flow rate of the inert gas (He) through the microtrap to the chromatographic column	2.2 ml/min
Separation, identification and quantitative determination stage of analytes liberated from the sorption bed	
Gas chromatograph	Hewlett-Packard 5890 GC Series II
Detector	Flame Ionisation Detector
Detector temperature	250 °C
Transfer line temperature TD-GC	150 °C
Capillary column	DB-1 (J&W) 30 m × 0.32 mm × 5 μm
Carrier gas (flow rate)	Helium (2.2 ml/min)
Temperature programme	40 °C for 1 min; 5 °C/min to 125 °C; 10 °C/min to 220 °C 220 °C for 5 min
Data processing system	CHEMSTATION

b - the directional coefficient of the calibration curve for an individual organic compound from the group of monoaromatic hydrocarbons.

The numerical value of the LOQ parameter was calculated on the basis of the triple value of the previously-determined LOD parameter ($LOQ = 3 \times LOD$). The obtained values of the LOD parameter were verified to confirm the correctness of the determined parameter. The determined LOD parameters met the following conditions: $10 \times LOD > m_{min}$ and $LOD < m_{min}$. The determined values of the LOD parameter fell within the range from 0.25 ng for ethylbenzene to 0.35 ng for benzene.

3. Results and discussion

3.1. Organic compounds emitted from floor coverings with different types of synthetic fibres and applied underlay type

As mentioned previously in this paper, the investigate group of commonly bought and used floor coverings consisted of a product where the underlay is made of felt or synthetic jute, while fibres made of various types of synthetic material are glued directly to it. Table 3 presents the results of emissions (together with the range of minimum and maximum values) of the determined monoaromatic hydrocarbons released from surface of selected floor covering samples where the underlay was made of felt and the fibres were made of polypropylene (PP). The studied floor covering samples differed by the parameter defined by the manufacturer as the fleece/pile weight (g/m^2). Commercially-available floor covering almost completely deprived of synthetic fibres was used as the control sample (it mostly consisted of the felt underlay, no synthetic polypropylene fibres). As regards information contained in Table 3, it can be clearly noticed that, together with the increase in the parameter defined by the manufacturer as the 'fleece/pile weight', the quantity of organic compounds released into the indoor environment increases (using the example of determined

compounds from the group of monoaromatic hydrocarbons). The occurrence of this type of relationship was observed for both measurements conducted on the basis of the use of a stationary μ -CTE 250 system and the home-made PFSs. A direct comparison of the total quantity (Σ BTEX) of the determined BTEX compounds and styrene reveals significant differences between emissions of those compounds from the studied floor covering samples. The total quantity of Σ BTEX for the studied samples of polypropylene floor coverings with the felt underlay was the following: (i) floor covering without synthetic fibres (lack of fleece/pile weight) - $\Sigma BTEX_{\mu CTE} = 1.49 \pm 0.94 \mu g/m^2$, $\Sigma BTEX_{PFS} = 18 \pm 13 \mu g/m^2$; (ii) floor coverings with fleece/pale weight $375 g/m^2$ - $\Sigma BTEX_{\mu CTE} = 6.2 \pm 1.3 \mu g/m^2$, $\Sigma BTEX_{PFS} = 42 \pm 30 \mu g/m^2$; (iii) floor coverings with fleece/pale weight $500 g/m^2$ - $\Sigma BTEX_{\mu CTE} = 10.5 \pm 3.7 \mu g/m^2$, $\Sigma BTEX_{PFS} = 74 \pm 22 \mu g/m^2$. Moreover, it was clearly observed that the lack of synthetic fibres connected to the floor covering underlay caused that benzene and ethylbenzene emissions values were below the limit of detection for the used analytical procedure ($<MDL$). It was noticed, on the other hand, that floor coverings without synthetic fibres, which consists of the underlay (felt) only, can be an additional source of toluene, p m-xylene and styrene emissions into the indoor environment. In addition, it was observed that the lack of synthetic fibres in the floor covering structure (the underlay itself made of felt) allowed for obtaining more accurate results (lower standard deviation values), which may lead to the conclusion that the studied indoor material was uniform in the entire structure, and collected samples can reflect the actual state of an entire batch (bale) of the material - floor covering.

While comparing the calculated quantities of emissions on the basis of the measurements conducted using a stationary μ -CTE™ 250 system and using a home-made PFSs, it was noticed that the results obtained on the basis of the home-made PFSs were nearly 10 times higher than those obtained using the μ -CTE™ 250 system. The discussion, detailed explanation and explanation of factors influencing differences in the obtained results of measurements of



Table 3

The results of emissions of selected monoaromatic hydrocarbons from the surface of studied floor covering samples with polypropylene fibers and a felt underlay.

Floor covering with polypropylene fibers (fleece/pile weight - lack); underlay type – felt; number of samples - 10										
Parameter	Benzene (μ -CTE)	Benzene (PFS)	Toluene (μ -CTE)	Toluene (PFS)	Etylbenzene (μ -CTE)	Etylbenzene (PFS)	p,m-Xylene (μ -CTE)	p,m-Xylene (PFS)	Styrene (μ -CTE)	Styrene (PFS)
Mean [$\mu\text{g}/\text{m}^2$]	<MDL	3.8	0.50	3.9	<MDL	0.43	0.58	3.9	0.41	6.0
Stan. dev. [$\mu\text{g}/\text{m}^2$]	<MDL	2.8	0.20	1.4	<MDL	0.49	0.23	1.6	0.25	6.8
Median [$\mu\text{g}/\text{m}^2$]	<MDL	3.2	0.43	3.9	<MDL	0.23	0.52	3.4	0.29	2.0
Min value [$\mu\text{g}/\text{m}^2$]	<MDL	0.91	0.35	1.8	<MDL	0.16	0.48	2.4	0.22	0.16
Max value [$\mu\text{g}/\text{m}^2$]	<MDL	8.3	1.06	6.1	<MDL	1.72	1.25	7.4	1.00	18.0
Floor covering with polypropylene fibers (fleece/pile weight - 375 g/m^2); underlay type – felt; number of samples - 10										
Parameter	Benzene (μ -CTE)	Benzene (PFS)	Toluene (μ -CTE)	Toluene (PFS)	Etylbenzene (μ -CTE)	Etylbenzene (PFS)	p,m-Xylene (μ -CTE)	p,m-Xylene (PFS)	Styrene (μ -CTE)	Styrene (PFS)
Mean [$\mu\text{g}/\text{m}^2$]	0.110	8.6	2.13	16.7	0.52	1.8	2.67	10.8	0.76	3.8
Stan. dev. [$\mu\text{g}/\text{m}^2$]	0.035	6.9	0.76	12.5	0.12	1.9	0.23	6.0	0.12	2.3
Median [$\mu\text{g}/\text{m}^2$]	0.101	8.1	1.84	8.7	0.46	0.41	2.62	8.8	0.71	2.5
Min value [$\mu\text{g}/\text{m}^2$]	0.073	1.1	1.38	5.0	0.38	0.29	2.36	4.44	0.64	1.8
Max value [$\mu\text{g}/\text{m}^2$]	0.162	21.4	3.76	36.1	0.70	4.7	3.03	19.9	0.91	7.7
Floor covering with polypropylene fibers (fleece/pile weight - 500 g/m^2); underlay type – felt; number of samples - 10										
Parameter	Benzene (μ -CTE)	Benzene (PFS)	Toluene (μ -CTE)	Toluene (PFS)	Etylbenzene (μ -CTE)	Etylbenzene (PFS)	p,m-Xylene (μ -CTE)	p,m-Xylene (PFS)	Styrene (μ -CTE)	Styrene (PFS)
Mean [$\mu\text{g}/\text{m}^2$]	0.130	16.8	5.7	27.9	0.712	4.0	3.13	18.7	0.810	6.6
Stan. dev. [$\mu\text{g}/\text{m}^2$]	0.048	9.5	3.3	6.5	0.086	1.1	0.23	3.2	0.073	1.7
Median [$\mu\text{g}/\text{m}^2$]	0.111	17.7	3.5	26.3	0.731	3.9	3.17	19.5	0.841	6.1
Min value [$\mu\text{g}/\text{m}^2$]	0.059	6.5	2.2	20.1	0.560	2.4	2.73	14.1	0.680	4.8
Max value [$\mu\text{g}/\text{m}^2$]	0.192	36.1	10.3	38.3	0.821	5.5	3.40	24.3	0.892	10.3

MDL value – 0.032 $\mu\text{g}/\text{m}^2$; μ -CTE – results obtained using Micro-Chamber/Thermal Extractor™; PFS – results obtained using home-made emission flux sampler.

emissions of monoaromatic hydrocarbons will be presented in the further part of this paper.

Table 4 presents information on the obtained results where the subject of research included samples of floor coverings with polypropylene fibres with a synthetic jute as an underlay. It was observed that the parameter defined by the manufacturer as the fleece/pile weight does not have an unambiguous and clear influence on the quantity of individual organic compounds released into the indoor environment. This can lead to the conclusion that the appropriate quality and structure of the type and quantity of chemical compounds released into the indoor environment can be used as the underlay for synthetic fibres. Analysis of data presented in Table 4 can be the basis of the conclusion that the parameter, which is defined by the manufacturer as the fleece/pile weight influences the toluene and p, m-xylene emission rate. The higher the fleece/pile weight is, the higher the quantity of those compounds emitted from floor covering samples is. The occurrence of such relationships can lead to the conclusion that those compounds (toluene and p, m-xylene) can be used at the stage of formation of given synthetic material as solvents and next, at the regular-use stage, can be released into the indoor air in a room. It was noticed, on the other hand, that the parameter defined by the manufacturer as the fleece/pile weight influences the total amount/content of released monoaromatic hydrocarbons; a higher total value of the determined compounds was observed together with an increase in the weight. This relationship was observed both for measurements conducted using the μ -CTE™ 250 system and based on the results of measurements conducted using the home-made PFSs. The total value of the BTEX compounds and styrene released from the studied floor covering samples with polypropylene fibres with the synthetic jute as an underlay is the following: (i) floor covering with fleece/pile weight 300 g/m^2 - $\Sigma\text{BTEX}_{\mu\text{CTE}} = 37.3 \pm 28.2 \mu\text{g}/\text{m}^2$, $\Sigma\text{BTEX}_{\text{PFS}} = 23 \pm 10 \mu\text{g}/\text{m}^2$; (ii) floor coverings with fleece/pile weight 450 g/m^2 - $\Sigma\text{BTEX}_{\mu\text{CTE}} = 76.6 \pm 8.4 \mu\text{g}/\text{m}^2$, $\Sigma\text{BTEX}_{\text{PFS}} = 24.6 \pm 9.7 \mu\text{g}/\text{m}^2$; (iii) floor coverings with fleece/pile weight 500 g/m^2 -

$$\Sigma\text{BTEX}_{\mu\text{CTE}} = 100.6 \pm 9.9 \mu\text{g}/\text{m}^2, \Sigma\text{BTEX}_{\text{PFS}} = 29.7 \pm 8.6 \mu\text{g}/\text{m}^2.$$

The next subject of the research involved floor covering samples with a felt as an underlay and where fibres were made of polyamide (PA). Table 5 presents the results of emissions of selected monoaromatic hydrocarbons released from the surface of the studied floor covering samples with polyamide fibres with a varying parameter defined as the fleece/pile weight. In addition, as the subject of additional studies and supplementation of information on the covering materials used for flat surfaces, Table 5 presents data on the emissions of selected monoaromatic hydrocarbons emitted from the underlay (installed indoors under floor coverings) fully made of polyurethane foam. While interpreting data summarised in Table 5, a clear influence of the parameter defined by the manufacturer as the fleece/pile weight on the quantity of each individual emitted monoaromatic hydrocarbons. Together with an increase in the fleece/pile weight, the emissions of each of the determined compounds released from the surface of studied floor covering samples. The occurrence of such a phenomenon was also observed for the total amount of determined monoaromatic hydrocarbons released from the studied samples. The total value of the BTEX compounds and styrene released from the floor covering samples with polyamide fibres with the felt underlay is the following: (i) floor covering with fleece/pile weight 300 g/m^2 - $\Sigma\text{BTEX}_{\mu\text{CTE}} = 23.6 \pm 6.4 \mu\text{g}/\text{m}^2$, $\Sigma\text{BTEX}_{\text{PFS}} = 25.0 \pm 6.8 \mu\text{g}/\text{m}^2$; (ii) floor coverings with fleece/pile weight 560 g/m^2 - $\Sigma\text{BTEX}_{\mu\text{CTE}} = 38 \pm 13 \mu\text{g}/\text{m}^2$, $\Sigma\text{BTEX}_{\text{PFS}} = 47 \pm 20 \mu\text{g}/\text{m}^2$. The occurrence of such relationships can lead to the conclusion that in the case of floor coverings with polyamide fibres with a felt underlay, synthetic fibres have a significant influence on the quantity of organic compounds released into the indoor environment, not the underlay that was used.

While analysing the data contained in Table 5 concerning the emissions of organic compounds from the polyurethane foam single underlay, it can be noticed that such indoor material can be an additional source of pollutant emissions with high intensity, especially toluene and p, m-xylene into the indoor environment.

Table 4
The results of emissions of selected monoaromatic hydrocarbons from the surface of studied floor covering samples with polypropylene fibers and a synthetic jute underlay.

Floor covering with polypropylene fibers (fleece/pile weight - 300 g/m ²); underlay type - synthetic jute; number of samples - 10										
Parameter	Benzene (μ-CTE)	Benzene (PFS)	Toluene (μ-CTE)	Toluene (PFS)	Etylbenzene (μ-CTE)	Etylbenzene (PFS)	p,m-Xylene (μ-CTE)	p,m-Xylene (PFS)	Styrene (μ-CTE)	Styrene (PFS)
Mean [μg/m ²]	0.62	4.0	10.8	7.9	1.50	3.1	15.6	4.9	8.8	2.74
Stan. dev. [μg/m ²]	0.44	1.7	9.7	4.7	0.87	1.5	16.6	1.3	1.1	0.79
Median [μg/m ²]	0.33	3.6	3.5	6.3	0.88	2.4	2.9	4.4	8.3	2.78
Min value [μg/m ²]	0.20	1.9	3.1	4.9	0.82	1.9	2.7	3.2	7.6	1.54
Max value [μg/m ²]	1.20	6.6	24.0	20.9	2.68	6.1	37.7	6.8	10.2	4.38
Floor covering with polypropylene fibers (fleece/pile weight - 450 g/m ²); underlay type - synthetic jute; number of samples - 10										
Parameter	Benzene (μ-CTE)	Benzene (PFS)	Toluene (μ-CTE)	Toluene (PFS)	Etylbenzene (μ-CTE)	Etylbenzene (PFS)	p,m-Xylene (μ-CTE)	p,m-Xylene (PFS)	Styrene (μ-CTE)	Styrene (PFS)
Mean [μg/m ²]	1.33	3.4	27.0	11.4	2.56	2.7	35.1	4.7	10.6	2.41
Stan. dev. [μg/m ²]	0.23	1.7	3.9	2.7	0.17	2.2	1.8	2.5	2.3	0.73
Median [μg/m ²]	1.33	2.7	28.6	11.6	2.61	1.9	35.9	3.9	10.0	2.41
Min value [μg/m ²]	1.02	1.4	21.4	6.4	2.30	0.85	32.1	3.0	9.1	1.40
Max value [μg/m ²]	1.78	6.1	31.8	14.4	2.86	8.1	37.5	11.4	16.7	3.74
Floor covering with polypropylene fibers (fleece/pile weight - 500 g/m ²); underlay type - synthetic jute; number of samples - 10										
Parameter	Benzene (μ-CTE)	Benzene (PFS)	Toluene (μ-CTE)	Toluene (PFS)	Etylbenzene (μ-CTE)	Etylbenzene (PFS)	p,m-Xylene (μ-CTE)	p,m-Xylene (PFS)	Styrene (μ-CTE)	Styrene (PFS)
Mean [μg/m ²]	1.21	4.5	34.6	13.1	3.63	3.00	51.3	7.1	9.82	2.04
Stan. dev. [μg/m ²]	0.10	1.9	3.7	3.6	0.30	0.73	5.0	1.8	0.87	0.60
Median [μg/m ²]	1.18	4.5	33.5	12.1	3.50	3.04	49.4	7.4	9.99	1.89
Min value [μg/m ²]	1.09	2.1	29.3	8.5	3.23	1.77	45.1	3.6	8.00	1.37
Max value [μg/m ²]	1.39	8.0	40.9	20.7	4.02	4.02	57.9	9.3	11.01	3.08

MDL value – 0.032 μg/m²; μ-CTE – results obtained using Micro-Chamber/Thermal Extractor™; PFS – results obtained using home-made emission flux sampler.

The total value of the BTEX compounds and styrene released from the samples with the polyurethane foam underlay is the following: $\Sigma\text{BTEX}_{\mu\text{CTE}} = 109.4 \pm 13.6 \mu\text{g}/\text{m}^2$, $\Sigma\text{BTEX}_{\text{PFS}} = 107.0 \pm 7.9 \mu\text{g}/\text{m}^2$. While interpreting the results concerning the quantity of emissions released from the polyurethane foam underlay, one should remember that there is no clear necessity of using it in a residential area as a floor covering additional underlay. Moreover, the underlay

material is placed on an untreated flat surface and floor covering is placed upon it. For this reason, the transport of pollutants from the underlay material to the indoor environment is much more difficult (an additional diffusion barrier in the form of floor covering with a defined thickness - synthetic fibres together with a underlay to which they were glued), as chemical compounds must be released from the surface of the underlay material and next be transported

Table 5
The result of the emissions of selected monoaromatic hydrocarbons from the surface of studied floor covering samples with polyamide fibers with a felt underlay and samples of single commercially-available underlay (installed under floor coverings) made of polyurethane foam.

Floor covering with polyamide fibers (fleece/pile weight - 300 g/m ²); underlay type – felt; number of samples - 10										
Parameter	Benzene (μ-CTE)	Benzene (PFS)	Toluene (μ-CTE)	Toluene (PFS)	Etylbenzene (μ-CTE)	Etylbenzene (PFS)	p,m-Xylene (μ-CTE)	p,m-Xylene (PFS)	Styrene (μ-CTE)	Styrene (PFS)
Mean [μg/m ²]	2.9	3.4	9.5	13.0	1.57	2.7	6.0	4.52	3.6	1.29
Stan. dev. [μg/m ²]	1.2	1.0	1.8	3.3	0.30	1.4	1.3	0.69	1.8	0.35
Median [μg/m ²]	3.3	3.6	9.5	12.3	1.61	2.4	6.3	4.68	3.4	1.25
Min value [μg/m ²]	1.1	1.4	5.8	10.1	1.01	1.3	2.6	3.29	1.5	0.80
Max value [μg/m ²]	4.5	4.6	12.9	21.5	2.21	5.2	7.0	5.53	6.9	1.81
Floor covering with polyamide fibers (fleece/pile weight - 560 g/m ²); underlay type – felt; number of samples - 10										
Parameter	Benzene (μ-CTE)	Benzene (PFS)	Toluene (μ-CTE)	Toluene (PFS)	Etylbenzene (μ-CTE)	Etylbenzene (PFS)	p,m-Xylene (μ-CTE)	p,m-Xylene (PFS)	Styrene (μ-CTE)	Styrene (PFS)
Mean [μg/m ²]	4.8	6.1	13.0	27.9	5.0	3.8	11.0	7.5	4.2	1.77
Stan. dev. [μg/m ²]	1.6	3.3	3.4	11.2	2.2	2.1	4.0	3.0	2.1	0.85
Median [μg/m ²]	4.8	6.2	12.9	30.8	4.2	3.3	10.3	7.3	3.5	1.76
Min value [μg/m ²]	2.7	2.5	8.3	7.7	2.5	1.2	5.6	2.9	2.4	0.61
Max value [μg/m ²]	8.4	12.1	20.1	40.7	9.4	7.7	16.8	12.2	8.8	3.30
Underlay (installed indoors under floor coverings) made of polyurethane foam; number of samples - 10										
Parameter	Benzene (μ-CTE)	Benzene (PFS)	Toluene (μ-CTE)	Toluene (PFS)	Etylbenzene (μ-CTE)	Etylbenzene (PFS)	p,m-Xylene (μ-CTE)	p,m-Xylene (PFS)	Styrene (μ-CTE)	Styrene (PFS)
Mean [μg/m ²]	1.46	16.0	37.2	40.4	4.12	8.73	55.4	33.6	11.2	8.18
Stan. dev. [μg/m ²]	0.13	3.8	6.6	1.5	0.74	0.18	4.9	1.9	1.2	0.47
Median [μg/m ²]	1.48	16.7	34.2	40.0	3.91	8.74	54.6	33.6	11.3	8.15
Min value [μg/m ²]	1.29	11.0	29.5	38.7	3.68	8.38	50.2	31.0	9.7	7.47
Max value [μg/m ²]	1.67	21.0	50.8	42.3	6.18	8.94	65.3	36.6	13.4	8.78

MDL value – 0.032 μg/m²; μ-CTE – results obtained using Micro-Chamber/Thermal Extractor™; PFS – results obtained using home-made emission flux sampler.

through the thickness of the floor covering layer. Additionally, attention should be paid to the fact that, according to the information provided by manufacturers and suppliers of underlay for floor covering made of polyurethane foams, the installation of such building/finishing materials is advised against if an under-floor heating system is used in the apartment. As a result of increased temperatures, the process of thermal degradation of the underlay material (polyurethane foam) might occur, which, as a result, can lead to the formation of additional pollutants that can be emitted to the gaseous phase of indoor environment.

3.2. Emission rate of selected monoaromatic hydrocarbons from flexible floor coverings made of poly(vinyl chloride)

Another type of floor coverings that are made wholly of a plastic that is commonly used in blocks of flats and public utility buildings are flexible floor coverings made of poly(vinyl chloride) (PVC). Table 6 presents the results of emissions of selected monoaromatic hydrocarbons emitted from selected samples of flexible poly(vinyl chloride) floor coverings differing in the thickness of the abrasive layer. The use of an abrasive layer in such floor covering promotes the comfort of use, dampens sounds resulting from walking around the flat and increases the durability of the flexible floor coverings. While referring to the data presented in Table 6, it can be noticed that, while comparing the numerical values of the calculated standard deviations (SD), the samples of PVC flexible floor coverings were characterised by adequate uniformity (very low as compared to the determined average values, the standard deviation values) of the structure of randomly-selected samples. The occurrence of possible differences between individual measurements for the same type of samples may result from the presence of various colourants used at the manufacturing stage to obtain a defined colour, shade or colour effect on the flexible floor coverings surfaces. The differences in the obtained results of measurements can be also caused by characteristics of the structure/area density (patterns) of the surface of the flexible floor coverings - the presence of various hollows aimed at obtaining the desired visual effect. It was noticed, however, that a significant influence on emissions of pollutants into the indoor environment released from the surface of flexible floor covering samples has the thickness of the used abrasive layer. The release of organic compounds from the surface of the flexible floor coverings made of PVC, which does not have an abrasive layer, can mostly result from the solvents used at the production stage of the main material from which the floor covering is made and from colourants used to improve the aesthetic quality. If the flexible PVC floor covering is additionally equipped with an abrasive layer with a defined thickness (the thickness of the abrasive layer determines the potential place/area in which the floor covering is to be installed), an additional source of emissions of organic compounds from monoaromatic hydrocarbons into the indoor environment occur. The intensity of emissions and, as a result, the quantity of organic compounds released into the indoor environment increases. If flexible floor covering does not have an abrasive layer, the total quantity of the determined monoaromatic hydrocarbons emitted from the surface of the studied samples amounted to: $\Sigma\text{BTEX}_{\mu\text{CTE}} = 19.5 \pm 2.9 \mu\text{g}/\text{m}^2$, $\Sigma\text{BTEX}_{\text{PFS}} = 5.1 \pm 1.8 \mu\text{g}/\text{m}^2$. While the use of an abrasive layer in flexible floor covering with the average thickness of 0.15 mm (the total thickness of the floor covering was 1.3 mm) caused a significant increase in the total quantity of determined organic compounds emitted into the indoor air. These values were equal to: $\Sigma\text{BTEX}_{\mu\text{CTE}} = 86.9 \pm 5.8 \mu\text{g}/\text{m}^2$, $\Sigma\text{BTEX}_{\text{PFS}} = 21.8 \pm 5.3 \mu\text{g}/\text{m}^2$. As regards the use of the abrasive layer with the average thickness of 0.50 mm in the studied samples of flexible floor covering caused an increase in emissions of the total quantity of determined organic

compounds by over 16 times (for the $\Sigma\text{BTEX}_{\mu\text{CTE}}$ value) and by over 10 times (in the case of the $\Sigma\text{BTEX}_{\text{PFS}}$ value) as compared to the flexible floor covering without an abrasive layer. The occurrence of such a phenomenon shows unambiguously that the thickness of the abrasive layer influences the quantity of organic compounds released into the indoor environment from the surface of flexible PVC floor coverings.

3.3. Discussion of the differences between obtained results of emission rate using two different types of analytical devices

While making an attempt at explaining differences between the factors influencing the differences between the obtained results using two different analytical devices - a stationary miniature emission chambers system - $\mu\text{-CTE}^{\text{TM}}$ 250 and the home-made PFSs, one should take into account the general structure of the studied floor covering surface. The potential processes and phenomena in which chemical compounds present in floor covering with synthetic fibres can take part are presented schematically in Fig. 3.

Assuming that the floor covering structure in which fibres are made of synthetic material (PP or PA) one can put forward the thesis that emissions of chemical compounds from floor covering into the indoor environment can take place as a result of 4 basic processes: (i) direct release into the indoor environment of chemical compounds from the underlay used (synthetic jute or felt) to which numerous synthetic fibres are attached (glued); (ii) direct emissions of chemical compounds present in the adhesive or resins used for combining (glued) synthetic fibres with an appropriate base - very often the layer of the substance that combines the fibres to the base does not have a uniform thickness, which might cause fluctuations of emissions of organic compounds; (iii) direct transport of chemical compounds used at the manufacturing stage (synthesis of the defined polymer) and aesthetic processing (the addition of colourants and refining substances) of synthetic fibres present in the structure of synthetic fibres in the floor covering - direct emissions of pollutants from fibres into the indoor environment; (iv) secondary emissions of chemical compounds adsorbed on the surface of synthetic fibres or the underlay - as a result of long-term storage of floor covering in the commercial and service company (up to 6 months), the phenomenon of sorption/retention of chemical compounds present in the environment of the indoor area on the surface of synthetic fibres or the underlay. As a result of mechanical intervention into the floor covering structure (regular use of a residential area) and environmental factors (temperature, humidity and exposure to solar radiation), chemical compounds adsorbed on the surface of synthetic fibres or the underlay can be released into the indoor environment in which they are installed.

The aforementioned processes can be regarded as the first important factor that can significantly influence the differences between the obtained results carry out using the $\mu\text{-CTE}^{\text{TM}}$ 250 system and the home-made PFSs. Another basic factor includes the principle of operation together with the measuring process/the stage of the collection of analyte samples from the gaseous phase, including the sorption medium. In the case of the use of the miniature emission chambers system - $\mu\text{-CTE}^{\text{TM}}$ 250, the process of collecting analyte samples from the gaseous stage takes place in a dynamic manner at an increased temperature (increased in relation to the average temperature of indoor air). A sample of indoor materials is placed inside the chamber; the temperature conditions and the inert gas flow rate are stabilized and the process of collecting analyte samples from the gaseous phase occurs: in this case, the type and the amount of chemical compounds released from the whole surface of the floor covering sample (top, edges and the bottom surface of studied material) placed inside the chamber. The influence of external factors is eliminated almost completely (the



Table 6

The results of the emissions of selected monoaromatic hydrocarbons emitted from the surface of studied flexible floor covering samples made of PVC.

The flexible floor covering made of PVC; no abrasive layer; number of samples - 10										
Parameter	Benzene (μ -CTE)	Benzene (PFS)	Toluene (μ -CTE)	Toluene (PFS)	Etylbenzene (μ -CTE)	Etylbenzene (PFS)	p,m-Xylene (μ -CTE)	p,m-Xylene (PFS)	Styrene (μ -CTE)	Styrene (PFS)
Mean [$\mu\text{g}/\text{m}^2$]	<MDL	0.43	6.6	1.75	1.69	0.86	6.87	1.49	4.30	0.52
Stan. dev. [$\mu\text{g}/\text{m}^2$]	<MDL	0.08	1.2	0.39	0.22	0.44	0.79	0.59	0.72	0.26
Median [$\mu\text{g}/\text{m}^2$]	<MDL	0.43	7.3	1.76	1.79	0.81	7.18	1.51	4.47	0.44
Min value [$\mu\text{g}/\text{m}^2$]	<MDL	0.32	5.0	1.10	1.39	0.30	5.74	0.55	3.24	0.26
Max value [$\mu\text{g}/\text{m}^2$]	<MDL	0.57	8.0	2.40	1.93	1.46	7.79	2.26	5.23	0.99
The flexible floor covering made of PVC; abrasive layer – 0.15 mm; number of samples - 10										
Parameter	Benzene (μ -CTE)	Benzene (PFS)	Toluene (μ -CTE)	Toluene (PFS)	Etylbenzene (μ -CTE)	Etylbenzene (PFS)	p,m-Xylene (μ -CTE)	p,m-Xylene (PFS)	Styrene (μ -CTE)	Styrene (PFS)
Mean [$\mu\text{g}/\text{m}^2$]	3.32	2.3	42.2	9.3	8.42	2.12	28.1	6.10	4.91	2.0
Stan. dev. [$\mu\text{g}/\text{m}^2$]	0.84	1.2	2.8	2.0	0.46	0.26	1.2	0.64	0.54	1.2
Median [$\mu\text{g}/\text{m}^2$]	3.43	1.8	43.1	9.2	8.55	2.12	28.4	6.20	4.96	1.9
Min value [$\mu\text{g}/\text{m}^2$]	2.11	1.1	35.8	6.5	7.23	1.72	25.4	4.96	3.74	0.85
Max value [$\mu\text{g}/\text{m}^2$]	4.92	3.8	45.0	11.9	8.80	2.63	29.2	6.93	5.58	5.0
The flexible floor covering made of PVC; abrasive layer – 0.25 mm; number of samples - 10										
Parameter	Benzene (μ -CTE)	Benzene (PFS)	Toluene (μ -CTE)	Toluene (PFS)	Etylbenzene (μ -CTE)	Etylbenzene (PFS)	p,m-Xylene (μ -CTE)	p,m-Xylene (PFS)	Styrene (μ -CTE)	Styrene (PFS)
Mean [$\mu\text{g}/\text{m}^2$]	3.53	2.2	36.1	18.6	10.1	1.62	34.6	4.27	5.50	1.24
Stan. dev. [$\mu\text{g}/\text{m}^2$]	0.53	1.3	2.5	5.6	1.6	0.46	5.1	0.59	0.81	0.38
Median [$\mu\text{g}/\text{m}^2$]	3.52	1.7	35.4	17.4	10.5	1.51	36.2	4.30	5.79	1.21
Min value [$\mu\text{g}/\text{m}^2$]	2.82	1.2	33.4	12.5	7.3	1.19	25.2	3.32	4.11	0.50
Max value [$\mu\text{g}/\text{m}^2$]	4.26	4.9	39.9	28.1	12.3	2.82	41.3	5.34	6.83	1.90
The flexible floor covering made of PVC; abrasive layer – 0.50 mm; number of samples - 10										
Parameter	Benzene (μ -CTE)	Benzene (PFS)	Toluene (μ -CTE)	Toluene (PFS)	Etylbenzene (μ -CTE)	Etylbenzene (PFS)	p,m-Xylene (μ -CTE)	p,m-Xylene (PFS)	Styrene (μ -CTE)	Styrene (PFS)
Mean [$\mu\text{g}/\text{m}^2$]	8.5	3.1	232	34	16.9	3.7	56.2	10.2	7.27	2.9
Stan. dev. [$\mu\text{g}/\text{m}^2$]	1.5	2.1	52	15	2.3	1.5	8.8	2.8	0.88	1.0
Median [$\mu\text{g}/\text{m}^2$]	8.2	2.0	207	30	16.2	3.4	53.7	10.5	7.24	2.9
Min value [$\mu\text{g}/\text{m}^2$]	6.7	1.4	183	17	14.8	2.2	48.0	6.6	6.12	1.7
Max value [$\mu\text{g}/\text{m}^2$]	11.1	7.1	344	63	21.4	6.9	75.1	15.9	8.44	5.1

MDL value – 0.032 $\mu\text{g}/\text{m}^2$; μ -CTE – results obtained using Micro-Chamber/Thermal Extractor™; PFS – results obtained using home-made emission flux sampler.

potential influence on the final result of the determination of chemical compounds present in the indoor environment) and, due to the use of high-quality polished stainless steel, the wall memory effect was eliminated nearly completely. As a result, all of these aspects make this analytical information about the emission rate reliable, and it reflects the characteristics of the studied sample with high probability. Additionally, due to the forced flow, the process of analyte collection from the gaseous phase takes a relatively short time with the use of a relatively small piece (the dimensions of the indoor material sample are defined by the internal volume of the chamber) of the studied material.

Also, attention should be paid to the fact that, in the case of research performed using stationary environmental test chambers (ETCs), no equilibrium process occurs. Chemical samples released from the sample surface of the indoor material are removed from the interior of the chamber directly onto the sorption bed keeping the continuity of emissions until those compounds are almost completely removed from a given sample of indoor material. The process of releasing analytes from the studied material is forced all the time by the concentration gradient. In the case of studies conducted using the home-made PFSs, the process of analyte collection from the gaseous phase takes place in a passive manner, which is described by Fick's diffusion laws without a forced flow, which means that the mass transport process is slower. For this reason, the influence of external factors in the indoor environment (air exchange with the area, relative temperature and humidity) and appropriate preparation of the passive sampler for work can have a significant influence on the final results.

If fibres are glued to the floor covering base (underlay), the phenomenon of the lack of tightness might occur between the floor covering surface and the home-made PFSs cover (resilient fibres might lift the sampler without pressing the device to the underlay), and analytes from the indoor environment can be transported inside the sampler. For this reason, those factors can have a considerable influence on the final results. Moreover, the operation time of the passive sample under real conditions is much longer than the time of operation of the previous described stationary device (μ -CTE™ 250). However, one should be aware of the fact that analytical information obtained as a result of using the portable home-made PFS has a screening character and is related to the quantity of emissions of chemical compounds released mostly from the surface of the studied indoor material (from the sample surface) and not, as in the case of stationary emission chambers from the whole sample of the studied material. It seems important from the construction point of view of both analytical devices that various sorption mediums are used as tools for collecting analyte samples from the gaseous phase. In the μ -CTE™ 250 system, a commercially-available polymer sorption material of the Tenax TA type is used. While in the home-made PFS, the sorption medium is a commercially-available cylindrical container made of stainless steel net filled with the graphitized charcoal Carboxograph 4.

The third important factor that may significantly influence the differences between the obtained results is directly related to floor covering samples, including their composition, the surface structure of the material and the storage/seasoning time in the indoor area of the service and commercial company. The colours of the

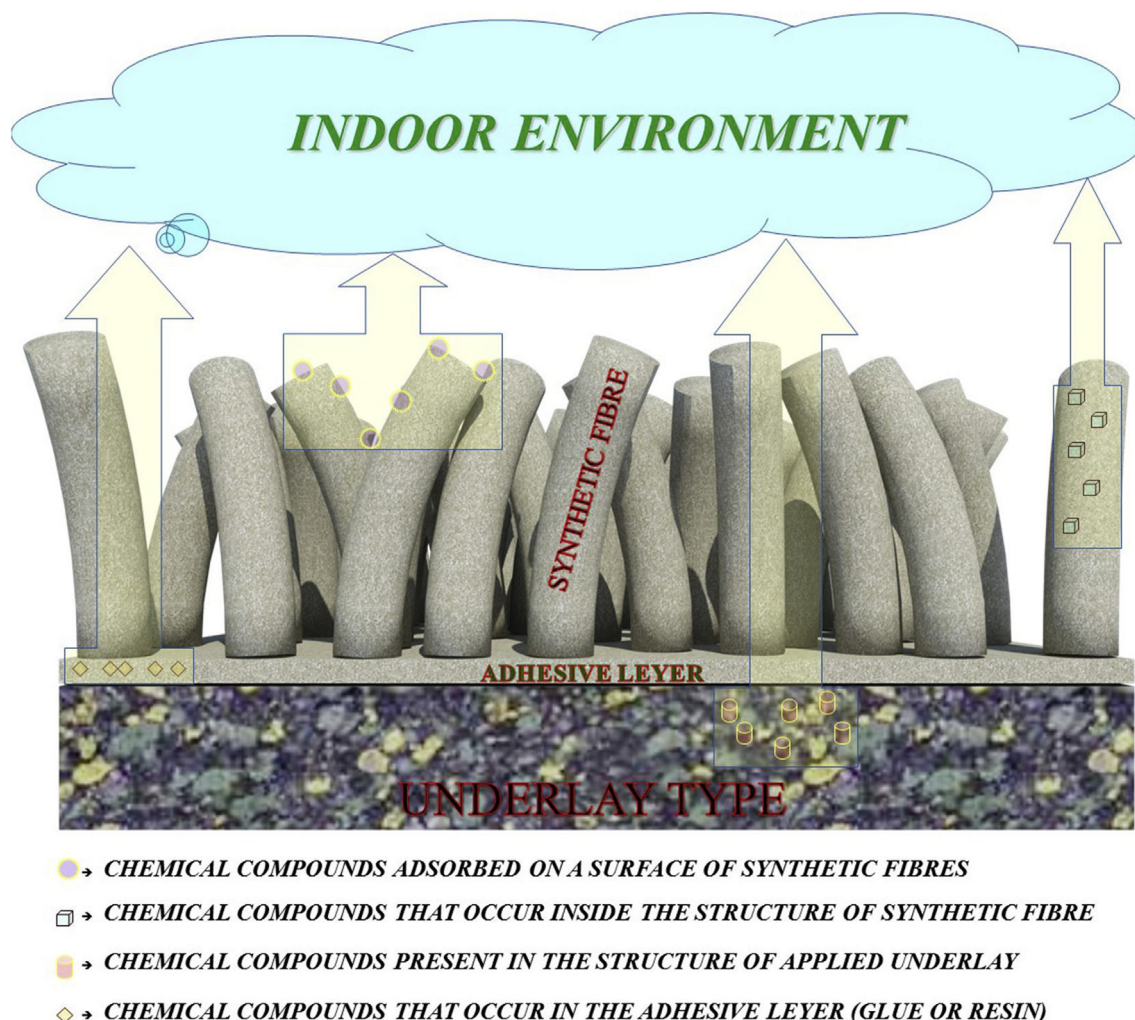


Fig. 3. Schematic presentation of potential sources of pollutant emissions into the indoor environment as released from various components of floor coverings made of synthetic fibres.

studied floor covering samples were not uniform. In each case, the floor covering was characterised by various colours, designed to encourage the potential consumer to purchase them. Moreover, as a result of a long storage/seasoning time of bales/batches of floor covering at the service and commercial company, chemical compounds present in the indoor environment can be adsorbed directly into the fibres of the studied floor covering. Next, as a result of measurements, they can be released into the gaseous phase, thus affecting the final result of determinations. Additionally, the surface of the studied floor covering samples itself with synthetic fibres and ones made of PVC was not characterised by high homogeneity, which could also influence the final results. This is confirmed by the fact that the obtained results of emissions of monoaromatic hydrocarbons both for the μ -CTE™ 250 system and for the home-made PFSS, where a polyurethane foam as an underlay was the subject of the studies, were similar. This results from the fact that the structure underlay made of polyurethane foam was characterised by the greatest homogeneity.

As an additional information showing the differences between obtained results using two types of analytical devices, the Pearson correlation coefficients (PCCs) were calculated taking as an input data the obtained results for different floor coverings (Supplementary Table 1). Also to present the linkage between the

determined chemical compounds variables the hierarchical dendrogram was created (Supplementary Fig. 1). It can be noticed that in the calculated values of PPCs there are still fluctuations and differences between calculated values. Mostly, it is caused by the fact that described analytical devices works in a different operating/working conditions (passive and dynamic/active analytes sampling from the gaseous phase) and in a different indoor conditions (laboratory conditions and indoor environment conditions – real in-situ conditions). According to created hierarchical dendrogram it is readily seen that benzene differs significantly (by its concentration levels for different floor coverings and described analytical devices studies) from the other four chemicals. They form two groups of similarity: (i) toluene and ethylbenzene; (ii) p, m xylene and styrene. The occurrence of such relationships can lead to the conclusion that those compounds can be used at the stage of formation of given synthetic material as solvents and next, at the regular-use stage, can be released into the indoor environment.

4. Conclusions

The results described in this paper can be the basis for concluding that various types of floor coverings in which fibres are made of synthetic material can be a significant source of emissions

of organic compounds from the monoaromatic hydrocarbons group into the indoor environment. It was shown that the type and quantity of organic compounds emitted to the gaseous phase are influenced by factors such as: the fleece/pile weight, the type of the underlay used to which synthetic fibres are attached/combined and the type of polymer from which synthetic fibres are made. It was also shown that an additional source of emissions to indoor air of residential and office areas can be the underlay made of polyurethane foam which might be installed under the floor coverings. As regards the research results presented in the paper, it was also found that the thickness of the abrasive layer used has a significant influence on the type and quantity of organic compounds emitted from the surface of flexible floor coverings. While interpreting the obtained results, one can conclude that, due to the considerable surface occupied by floor covering in residential and public utility areas, they are one of main factors influencing and shaping the air quality in a given indoor environment.

The data obtained from measurements were the basis for determining those factors, which significantly influence the final result of determinations and which are related to both the applied analytical devices and the characteristics of the studied samples. The interpretation of the data collected made it possible to conclude that the final result of determinations (defined as the quantity of emissions) performed with the use of various analytical devices dedicated to the estimation of the emission of chemical compounds mostly depends on factors such as: (i) the operation mode of the analytical device (the method of sample collection from the gaseous phase – dynamic or passive); (ii) the working time of the device used and the surface from which analyte samples emitted to the gaseous phase are collected; (iii) the nature of the research conducted – the in-situ or ex-situ mode; (iv) the tightness of the system, mostly during in-situ research using portable passive analytical devices; (v) the sorption medium that was applied; (vi) morphological characteristics and the metrological structure of studied samples (in the described case - the characteristics of synthetic fibres, floor covering colour, thickness of the adhesive or resin layer used for attaching/combining the fibres to the underlay etc.).

Another conclusion that can be drawn after the interpretation of the obtained results is the use of reference materials or materials that can be regarded as reference materials in future studies - such analytical solutions in which a given product releases a closely-defined amount of analytes (or a single analyte) in a specified unit of time. So far, only a few such solutions are known in which the author's own (in laboratory conditions) reference materials are used (mostly based on the defined quantity of toluene released into the gaseous phase) to estimate the emissions of organic compounds [26–29].

Therefore, while starting the research related to the estimation of emissions of organic compounds released from indoor materials, an analytical chemist must be aware what factors might affect the final result of measurements. The selection of suitable analytical device to obtain reliable analytical information on the type and quantity of organic compounds released into the gaseous phase from indoor materials is really conditioned by two basic factors: (i) the economic-logistic factor depending on the device operation costs, costs of transporting material to the laboratory and the influence of the measurement on the structure of the studied indoor material (in some cases, it is necessary to cut the material – destructive action on its structure); (ii) the type and character of the obtained analytical information on the type and the estimated quantity of organic compounds released into the indoor environment from a given source of emissions. It is also very important to take into account the comfort and opinions of the persons using a given area. If it is necessary to perform measurements quickly and

cheaply (in a non-destructive manner for a given indoor material and without interfering with the normal functioning of the users), which is aimed at identifying an intensive source of emitting organic compounds into the environment, it seems the most justified to use portable emission-passive samplers. They allow for performing screening studies and obtaining data on the main sources of emissions and the information about the most important chemical compounds released into the indoor environment. If very precise measurements are required and the user has sufficient funds and agrees to the fragmentation of a given indoor material, the optimal solution seems to be the use of stationary environmental test chambers (ETCs), including ones such as a miniature emission chambers system - μ -CTE™ 250.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.buildenv.2017.06.035>.

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