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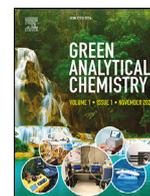
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New SPME-based method for on-site measurement of gas-phase concentration of phthalates and alternatives at the surface of PVC floorings

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ABSTRACT

Phthalates are part of the semi-volatile organic compounds. They are widely used as plasticizers in polyvinyl chloride (PVC) floorings and are ubiquitous indoor pollutants. Some of them are even classified as carcinogenic, mutagenic, reprotoxic (CMR), and as we spend more time indoors, it is necessary to develop methods to assess emission strength of indoor materials. One of the key parameters to measure this potential is the concentration at the source material surface (y_0). To measure directly this parameter, an in-situ sampling method using solid-phase microextraction (SPME) into an emission cell was developed. The main challenge with this method is calibration. Firstly, based on the headspace analysis of seven floorings, four samples were identified as sources of diisobutyl phthalate (DiBP), dibutyl terephthalate (DBTP) and benzoate esters. Secondly, an atmosphere generation system using a flooring sample as source of compounds and coupled with an active sampling with Tenax tubes was developed to perform an external calibration of the SPME based-MOSEC cell method suitable for y_0 measurement. Calibration curves were set up on a wide range of exposure doses extending up to $96 \mu\text{g min/m}^3$ for DiBP and $184 \mu\text{g min/m}^3$ for DBTP. Low detection limits, $0.46 \mu\text{g/m}^3$ for DiBP and $1.50 \mu\text{g/m}^3$ for DBTP were determined considering an extraction time of 15 min. The principal limitation in the sampling conditions was identified as the 288 h required to reach steady state in the emission cell before the extraction step. Finally, y_0 measured at the surface of PVC floorings ranged from 2.2 to $5.5 \mu\text{g/m}^3$ for DiBP and from 6.1 to $13.5 \mu\text{g/m}^3$ for DBTP.

1. Introduction

Several pollutants contribute to degrade indoor air quality. Among them are SVOCs, defined by the World Health Organization (WHO) as « all organic compounds with a boiling point between 240 and $400 \text{ }^\circ\text{C}$ » [1]. The scientific community is paying more and more attention to them because of their toxicity. Indeed, some SVOCs are associated with asthma, allergies, endocrine disruption, reproductive troubles or even cancers [2–5]. Among SVOCs, we can find polychlorobiphenyl, organochloride, organophosphate, alkylphenol, aromatic polycyclic hydrocarbons, pyrethroid, synthetic musks, bisphenol, oxadiazolones, parabens, organotins, perfluorinated, dioxins, flame retardants or phthalates [3,6]. A recent epidemiological study with regard to 2500 adults and 1100 kids living in France showed that the entire population has been exposed to at least one phthalate at a quantifiable urine concentration level [7]. Same result has been found in Japan: among the 461 kids and adults tested, 80% showed a detectable level of urinary metabolites of DiBP, di(2-ethylhexyl) phthalate (DEHP) and mono-(2-ethyl-5-carboxypentyl) phthalate [8]. Phthalates are commonly used

as plasticizers: in Europe, more than 90% of the production is used to make soft and flexible PVC, the rest being used in non-PVC applications [9–12]. Because of their CMR classification, two phthalates (DEHP and dibutyl phthalate (DBP)) are now banned from material construction [13]. Due to their low volatility, they can be found in gaseous phase but also in airborne and settled particles and on the surfaces. According to studies carried out in seven different countries, DiBP, diethyl phthalate (DEP) and DBP are reported as the main phthalates with concentrations between 61 and 377 ng/m^3 , 61 – 1300 ng/m^3 and 75 – 1080 ng/m^3 respectively [14]. Among airborne and settled particles, DEHP is the major compound with concentration between 104 and $3214 \mu\text{g/g}$ [15]. So, exposition pathways are multiple: inhalation, skin contact and ingestion [16–19].

It is then necessary to determine the exposure level to phthalates and to identify their emission sources. The gaseous concentration at the surface of the material (y_0) is one of the key parameters in the characterization of material emission [20]. Measurements made at the surface of PVC materials identified DBP at concentrations between 35 and $50 \mu\text{g/m}^3$, DiBP at concentrations between 100 and $140 \mu\text{g/m}^3$ and

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Table 1
Characteristics of the studied compounds.

Compound	Boiling Point (°C)	Pv (Pa at 25°C)	Molecular mass (g/mol)	Molecular formula	CAS n°
Diisobutyl phthalate	320	6.34×10^{-3}	278.35	C ₁₆ H ₂₂ O ₄	84–69–5
Dibutyl phthalate	340	2.68×10^{-3}	278.35	C ₁₆ H ₂₂ O ₄	84–74–2
Di(2-ethylhexyl) phthalate	386	1.30×10^{-2}	390.36	CH ₂₂ O ₄	117–81–7
Dibutyl terephthalate	381	Not available	278.34	C ₁₆ H ₂₂ O ₄	1962–75–0

DEHP at concentrations between 0.10–3.0 µg/m³ [21]; but also di-n-octyl phthalate at a concentration level of 0.004 µg/m³ and diisononyl phthalate at a concentration level of 0.40 µg/m³ [22]. Several methods to determine y_0 has been developed. Measurements in laboratory use emission chambers. However, with these devices, compounds adsorption onto inner walls occurs and leads to inaccurate determination of y_0 [23]. The use of micro-chamber, recommended by the ISO 16,000–25 standard for SVOCs [24] is an alternative to reduce adsorption thanks to the small device's size and the possibility to perform emission test at high temperatures. Using a micro-chamber type thermal extractor (μ -CTE), Braish [21] has developed a method for indirect determination of y_0 at ambient temperature by extrapolation from higher temperatures according to the Clausius-Clapeyron equation, assuming that phthalates emission from vinyl flooring is only governed by vaporization. Another method developed by Cao et al. was based on samplings in an air layer trapped between two samples of studied material, allowing to neglect losses by adsorption. Phthalates emitted by the material are sampled by SPME technique [25]. This type of chamber, called “sandwich-like”, allows direct determination of y_0 at ambient conditions but is still not applicable for on-site measurement [26]. Two methods, developed respectively by Wu et al. [27] and by Shinohara et al. [28] can be used for on-site measurements. The first one consists in a Tenax tube placed directly onto the surface of the material. However, due to adsorption on the tube wall, y_0 is not directly determined and required modeling. The method proposed by Shinohara et al. also uses an emission cell whose bottom is coated with an adsorbent. This method measures an emission rate (in ng/h). The concentration y_0 can be calculated from an estimated value of convective transfer coefficient. Another method, allowing on-site measurement of y_0 was developed by Ghislain et al. [29]. It consists in a 60 mL glass emission cell equipped with a septum for SPME fiber introduction. The measurement principle consists in placing the cell, called MOSEC (Midget On-Site Emission Cell), on the material surface. When the concentration of the emitted SVOCs in the air enclosed in the cell is stable, they are then sampled by SPME. When the gaseous concentration is stable in the cell, the mass transfers from the source material to air and from air to the cell walls become zero. The steady state gaseous concentration can be assimilated to y_0 [29]. This method was successfully applied to on-site measurement of organophosphate flame retardants (OPFRs) emitted by upholstered furniture [29]. Moreover, SPME is particularly well suited to on-site measurements due to its ease of use. However, its calibration is challenging for air sample analysis because generation of atmosphere containing compounds of interest at known and controlled concentrations is required. For VOCs, several generation methods are suitable such as permeation tube, syringe pump or compressed gas cylinder. Unfortunately, they can't be used for SVOC because of their low volatility [30]. Moreover, previous methods for generating SVOC require very long times (days or even months) to reach stable concentration [31]. Recently, an original external calibration of the SPME-based method was developed in our laboratory for accurate y_0 measurements of OPFRs [30]. It consists in dynamic standard gas generation using emitting material as source of OPFRs coupled with Tenax tube active sampling. This generating system is able to deliver stable concentrations after about 200 h of operation with variation not exceeding $\pm 5\%$.

The goal of this study was therefore to develop an environmental-friendly method consisting of on-site sampling by the SPME based-MOSEC cell and an associated solventless calibration procedure for ph-

thalates emitted by plastic floorings. Firstly, a screening of several floor samples was carried out by headspace-SPME- GC-MS/FID to select a set of the most emitting ones. The calibration method using emitting materials was developed. Then, the operating parameters of the MOSEC method were optimized for y_0 measurements of phthalates: the time to reach steady state in the cell, SPME extraction time and the performance of the method were determined.

2. Material and method

2.1. Selected samples and compounds

During this study, different floorings made of PVC have been tested (n°1–7). Floorings n°5 was given as decontaminant and n°6 was made at 50% with recycled material. Moreover, PVC 1–4 were from the same brand. All the floorings have been designed to be used in Receiving Public Establishment (RPE).

Three phthalates and one terephthalate were studied. DEHP, DiBP and DBP (purity > 99%) has been furnished by Sigma-Aldrich (Saint-Louis, USA). Dibutyl terephthalate (DBTP) (purity = 95%) has been furnished by Ambiter (Orleans, France). Physico-chemical properties of the compounds have been summarized in Table 1. Standard solutions were done in methanol (purity > 99%) furnished by Honeywell (Charlotte, USA).

2.2. Measurement of emitted SVOC

2.2.1. SPME-GC-MS/FID

The SPME fiber consists in a silica bar covered with stationary phase and is directly exposed to the sample (in this case, the gaseous phase of the vial or the MOSEC cell). The analytes were sorbed by the stationary phase and then desorbed into the injection port of a GC. A 100 µm PDMS SPME fiber was selected for this study (Supelco, Bellefonte, PA, USA). Before each series of measurements, the fiber was conditioned during 20/30 min into the injection port of GC at 250 °C in split mode (split ratio 30).

Fiber analysis was done with an Agilent 7890B gas chromatograph (Agilent Technologies, Les Ulis, France) equipped with dual MS/FID detection. Acquisition was done in scan mode (50–400 amu). The injection port was equipped with a 0.75 mm i.d. liner and operated at 250 °C in splitless mode. Carrier gas was helium with a flow rate of 2 mL/min. A 5% phenyl Elite-5 capillary column (PerkinElmer, Waltham, USA) of 60 m, 0.25 mm i.d. and 0.25 µm film thickness was used. The temperature of the oven was maintained at 85 °C for 2 min, then ramped to 300 °C at 15 °C/min and maintained for 18 min. Transfer line to MS was maintained at 300 °C and ion source at 230 °C. Quantitative analysis was performed by FID based on an external calibration. To do so, standard mixtures of the four studied compounds in methanol were injected and analyzed under the same chromatographic conditions than those for SPME desorption and analysis. Due to volume expansion of standard solutions during vaporization in the injection port, a small volume (0.1 µL) compatible with the 0.75 mm i.d. liner was injected [32].

2.2.2. Headspace-SPME

Headspace-SPME (HS-SPME) analysis were performed on flooring samples for a screening of emitted compounds. 2 g of material were

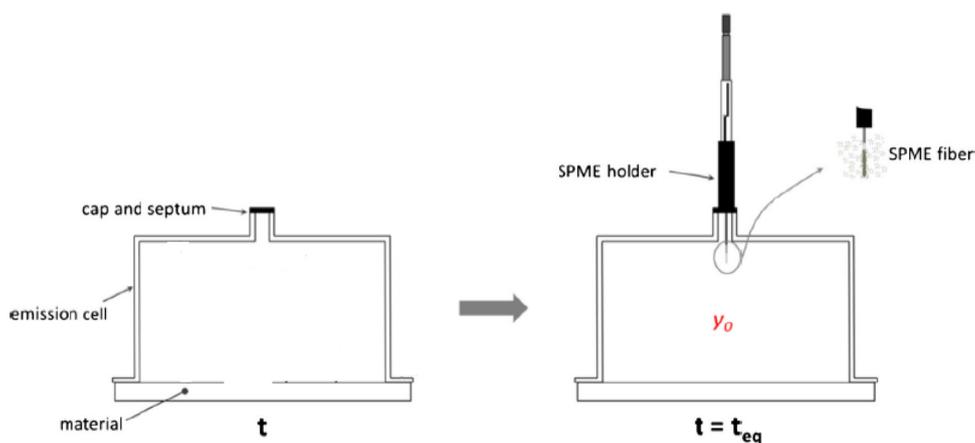


Fig. 1. illustration of the MOSEC cell [26].

precisely weighed and cut into small pieces (1 mm x 1 mm). Those pieces were introduced into a 10 mL glass headspace vial which was hermetically closed and then heated at 60 °C during 4 h to reach a stable composition in the gaseous phase. Compounds emitted by the floorings are then extracted by SPME during 10 min. Headspace-SPME was made thanks to a CombiPal autosampler (CTC Analytics, Zwingen, Switzerland) associated with the GC-MS/FID described above.

2.2.3. Emission cell (MOSEC)

Determination of SVOC concentration at the surface of the source material (y_0) has been performed thanks to the SPME based-MOSEC cell method. The device consists in a 60 mL cylindrical glass cell with a sampling surface of 17 cm². The top of the cell was equipped with a cap and a septum which allows the introduction of the SPME fiber. The cell was placed directly at the surface of the tested material. During the test, the temperature was maintained at 23 °C. When the steady state was reached into the cell, a SPME fiber was introduced through the septum to sample SVOCs emitted into the gaseous phase (Fig. 1b). Extraction time can be adjusted and optimized according to the expected concentration or for calibration purpose. Based on previous studies, 15 min is commonly applied [30]. This technique is representative of the flooring surface emission and can easily be use on-site.

2.3. Calibration

2.3.1. Implemented experimental device for calibration

The protocol followed for generating atmosphere containing phthalates and terephthalates is based on the one from Plaisance et al. [30]. PVC flooring n°1 was selected as source of phthalates and introduced into 5 inox tubes (internal diameter of 5 mm, length of 9 cm). Each tube contains 0.7 g of material to reach a sufficient concentration of the two emitted compounds. Tubes were connected in series and flowed by humidified clean air at stable conditions of relative humidity and temperature (HR=50 ± 3% at T=23 ± 2 °C) produced by a dry zero air generator (AZ 2020, Claind, Lenno, Italy) and a humidifier made of a water bubbler and regulated by mass flow controllers. Airflow rate was maintained at 50 mL min⁻¹ during all the tests. The air flow was transferred from the tubes to MOSEC cell via a needle introduced in two septa (the one placed in the nut of the last tube and the other one at the cap of MOSEC cell). First, emission cell was continuously flushed by air coming from the tubes containing the source material until the gas-phase SVOC concentrations became stable (Fig. 2a). The SPME-based method described in Section 2.2 was used to monitor the gaseous SVOC concentration in the cell and its stabilization. To do so, the MOSEC cell was temporally isolated and hermetically sealed thank to a Micro QT valve (Entech, Quimper, France) for samplings as shown in Fig. 2c. When the gaseous concentrations were stabilized, an active sampling with Tenax tubes was performed at 40 mL/min for 16 h (Fig. 2b). This allowed to

measure the gaseous SVOC concentrations under the stable conditions of the generation system. Then, a series of SPME samplings with variable extraction time from 5 to 25 min was carried out (in isolated cell) in order to plot the calibration curve between the amount of compound adsorbed on the fiber and the product of its gaseous concentration (assessed by active sampling method with Tenax tube) and the extraction time [33]. This method of calibration was used to convert the compound amount sampled by SPME into a gaseous concentration.

2.3.2. Tenax tube analysis by ATD-GC-MS/FID

Analysis of Tenax tubes were done with a TurboMatrix 650 ATD thermal desorption system (PerkinElmer, Waltham, USA). Tenax tubes were heated at 320 °C for 15 min, using a 100 mL/min helium flow rate without inlet split to desorb the analytes and focus them into a cold trap kept at 1 °C. Desorption trap was ramped at 99 °C/min to 350 °C, held for 10 min, with an outlet split of 5 mL/min. The transfer line to the GC and the valve were maintained at 250 °C. Separation and detection were performed with a PerkinElmer Clarus 680 gas chromatograph. The carrier gas was helium with a flow rate of 1.3 mL/min. A 5% phenyl Elite-5 capillary column (PerkinElmer, Waltham, MA, USA) of 60 m, 0.25 mm i.d. and 0.25 mm film thickness was used. The oven temperature was maintained 2 min at 50 °C, then ramped at 15 °C/min to 200 °C, held for 2 min, then ramped at 15 °C/min to 300 °C, held for 14 min. The gas chromatograph was equipped with dual MS/FID detection. MS is a PerkinElmer Clarus SQ 8T. Acquisition was operated in full scan (50–470 amu) using electron impact mode (70 eV). Transfer line and ion source were maintained at 180 °C. MS data were used to identify target SVOCs and check there was no co-elution with other compounds. Quantitative analysis was performed by FID and based on an external calibration. To this end, Tenax tubes were loaded with 2 mL of standard mixtures of the analytes in methanol using a GC syringe and then purged for 5 min with a helium flow of 50 mL/min to remove the solvent [29]. Calibration range are from 37 to 331 ng for DiBP, 37 to 333 ng for DBP, 45 to 407 ng for DBTP and 27 to 242 ng for DEHP.

2.4. Analytical blanks

To check eventual contamination and memory effect due to SPME fiber and MOSEC cell, blanks were analyzed. No contamination due to cell, fiber, Tenax tubes or analytical system was observed in the chosen analytical conditions.

3. Results and discussion

3.1. Screening of emitting materials using headspace (HS) analysis

Results of the qualitative screening by HS-SPME-GC-MS/FID are shown in the following histograms (Figs. 3a-b).

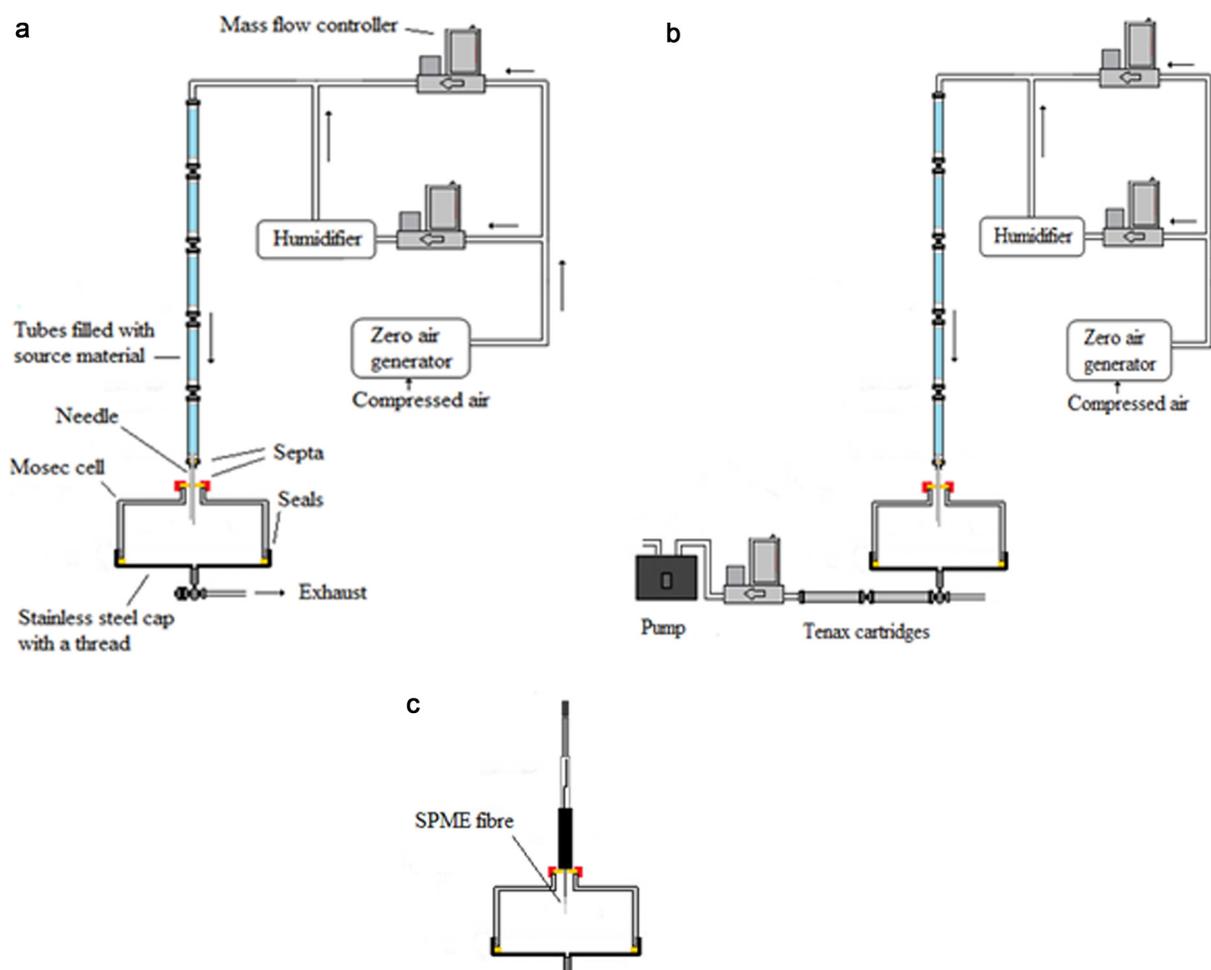


Fig. 2. Fig. 2-a-A calibration atmosphere generation system (without device for Tenax sampling) [26]; Fig. 2-b-Calibration atmosphere generation system (with device for Tenax sampling) [26]; Fig. 2-c -SPME sampling in isolated emission cell [26].

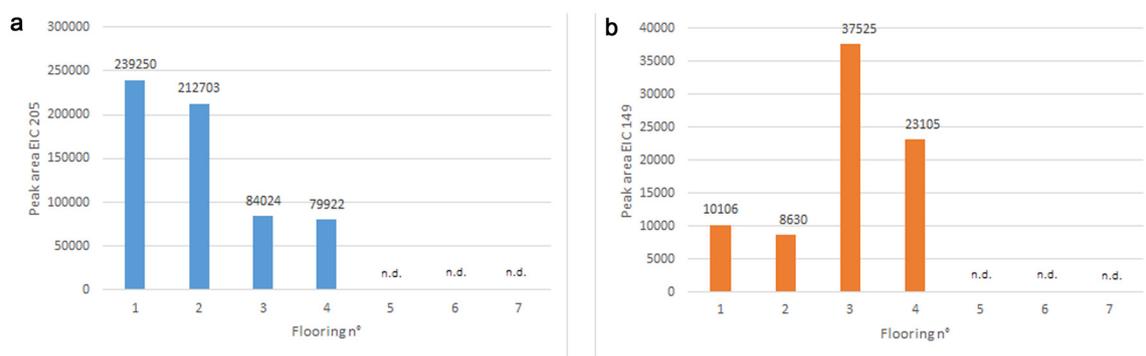


Fig. 3. Fig. 3-a-A peak areas obtained by HS-SPME-GC-MS/FID for DBTP; Fig. 3-b-Peak areas obtained by HS-SPME-GC-MS/FID for DiBP.

Floorings 5–7 did not release the target compounds. This may be due to the fact that flooring 5–7 are from a different manufacturer than 1–4. PVC floorings 1–4 emitted the same phthalate: DiBP. No DEHP or DBP were identified, in agreement with the banning of these compounds in Europe. However, the emission of a terephthalate (DBTP) and benzoates were observed. Terephthalates and benzoates are plasticizing agents recently introduced as alternatives for phthalates [34–36]. Based on the mass spectra and chemical formula, the benzoates detected are more likely to be octyl benzoate or heptyl benzoate. Further investigations would be needed to confirm their identification.

3.2. Calibration – Development of the calibration system

According to the screening study, the chosen source material for standard gas generation was PVC flooring n°1. Fig. 4 shows the generated concentrations of DiBP and DBTP obtained with the experimental device described in Section 2.3.2. Results are expressed in gaseous concentrations thanks to the calibration curves below.

For DiBP, stability was quickly reached (24 h) and the mean concentration obtained was $6.1 \mu\text{g}/\text{m}^3$. After those 24 h, the concentrations did not exceed the mean value by more than $\pm 7\%$. For DBTP, the con-

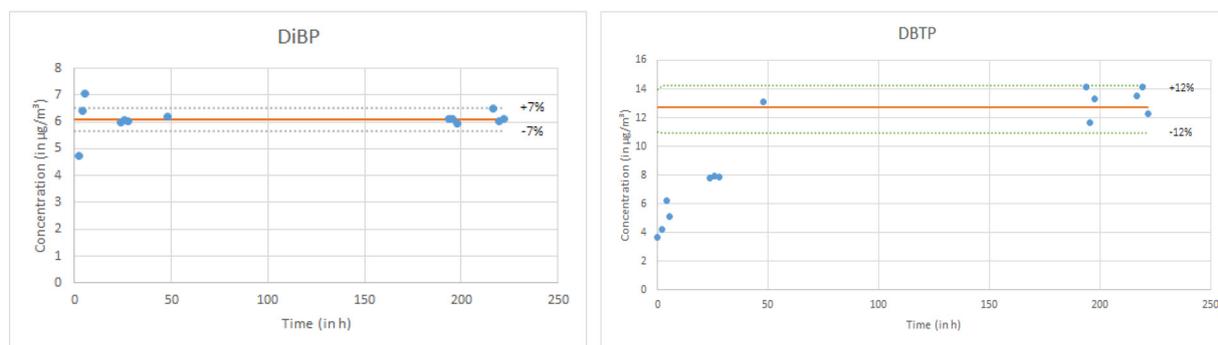


Fig. 4. Time variation of and TCPP concentrations produced by the generation system. Solid line corresponds to the mean concentration during stable generating state. The dotted lines represent the intervals of $\pm 7\%$ and $\pm 12\%$ around this mean concentration.

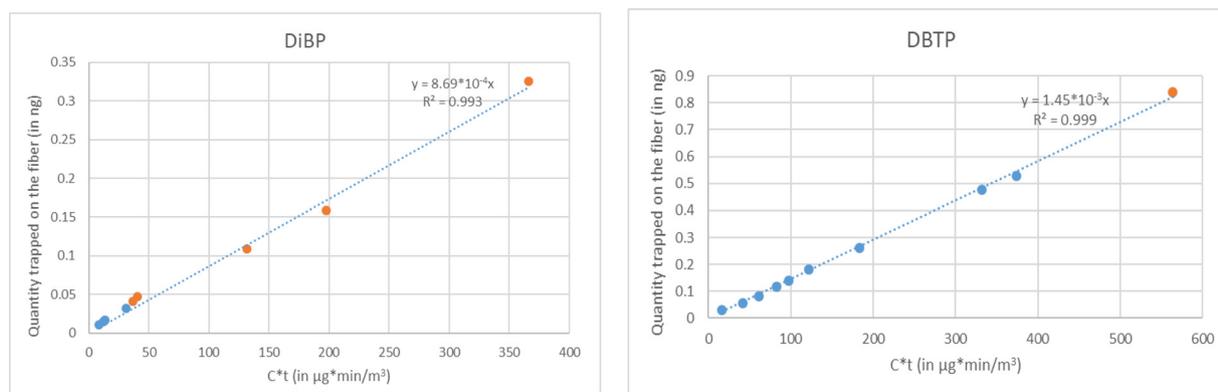


Fig. 5. Calibration curves for DiBP and DBTP. Extracted mass by SPME versus the product of sampling time (t) and gas-phase concentration (C) by combining the data of two calibration series (blue points are associated with test $n^{\circ}1$ and orange with $n^{\circ}2$).

centration increased during the first 50 h and then reached stability. The mean concentration obtained is $13.2 \mu\text{g}/\text{m}^3$ and after the 50 h, the concentrations did not exceed the mean value by more than $\pm 12\%$. Coefficients of variation calculated from the last six measures were 3.8% for TBP and 10.3% for TCPP. So, this experimental device provides a technical solution for calibration of phthalate and terephthalate measurement method.

Fig. 5 shows the calibration curves obtained on a wide range of exposure dose extending up to $96 \mu\text{g min}/\text{m}^3$ for DiBP and $184 \mu\text{g min}/\text{m}^3$ and DBTP. Concentration determined by active sampling method with Tenax tubes was considered here as reference value. To check linearity and robustness in calibration, several SPME samplings were done by changing sampling time (from 5 to 25 min) and three series with different samples of flooring $n^{\circ}1$. These results confirmed good linearity between the amount sampled by SPME fiber and the product of gaseous concentration by the exposure time with a squared correlation coefficient greater than 0.99. No significant deviation was observed between points belonging to different calibration series. These results demonstrate that the linear sorption domains extend up to $96 \mu\text{g min}/\text{m}^3$ for DiBP and $184 \mu\text{g min}/\text{m}^3$ and DBTP. When the sampling time is increased, this SPME method is sensitive enough to measure concentrations in the $\mu\text{g}/\text{m}^3$ range. However, the SPME fiber extracts a SVOC amount at each sampling and it may not exceed the SVOC amount in the gas phase of the cell. Based on the slopes of calibration curves given in Fig. 4, the uptake rates of DiBP and DBTP on the SPME fiber are 1.09 and 1.42 mL/min respectively. Considering the volume of the cell (60 mL) and these uptake rates, the sampling time required to extract the total amount in gas phase is 55 min for DiBP and 43 min for DBTP. Then, the extraction time should be less than 40 min.

3.3. Development of MOSEC method for phthalates

To determine y_0 for DiBP and DBTP, the first step was to determine the time to reach the steady state for gaseous concentration in the MOSEC cell. For each flooring, MOSEC cells were placed directly at the surface of the sample and 15 min SPME samplings were done each 24 h during 360 h. Concentrations of DiBP and DBTP vs time are shown in Fig. 6-a and 6-b. Error bars represent the standard deviation, calculated over the five last points of each curve. Concerning DBTP concentration, PVC floorings $n^{\circ}1$, $n^{\circ}3$ and $n^{\circ}4$ present similar stabilization time (264, 288 and 300 h). As they come from the same product line, this similarity is not surprising. However, the stabilization time for flooring $n^{\circ}4$ is a bit shorter: 150 h. Concerning DiBP, concentration, stability is reached really fast (24 h) for all the floorings. Then, stabilization time is governed by DBTP for all the flooring and is situated between 150 h ($n^{\circ}2$) and 300 h ($n^{\circ}4$). As the two compounds are positional isomers, their vapor pressures should be close and would not explain the difference in reaching stability (the vapor pressure of DBTP was not found in the literature). Another hypothesis was that DiBP could be found in the upper layer of the soil while DBTP could be found in the lower layer, leading to a difference in the diffusion of the two compounds. Some tests have been realized to determine a potential difference in the emissions from the different layers of the floorings. No significant difference could be observed.

Considering the beginning of increase in concentration in Fig. 6-a and 6-b, the initial emission rates in the cell can be calculated (see Table 2). Based on the calibration curve and the steady state concentrations, uptake rates on the SPME fiber can also be determined (see Table 2). For DiBP, uptake rate is 26 times higher than

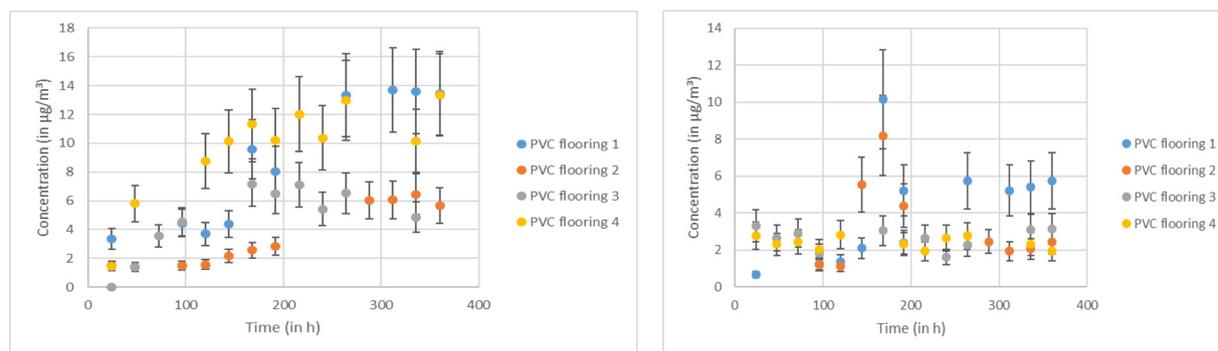


Fig. 6. A Gas-phase concentration of DBTP versus time after that the MOSEC cell is placed on the PVC floorings; Fig. 6-b–Gas-phase concentration of DiBP versus time after that the MOSEC cell is placed on the PVC floorings.

Table 2

Uptake rates on the fiber and emission rates for each flooring.

	Uptake rate for DiBP (ng/min)	Uptake rate for DBTP (ng/min)	Emission rate for DBTP (ng/min)	Emission rate for DiBP (ng/min)
Flooring n°1	6.1×10^{-3}	1.9×10^{-3}	2.3×10^{-4}	1.4×10^{-4}
Flooring n°2	2.4×10^{-3}	8.5×10^{-3}	9.3×10^{-5}	6.2×10^{-5}
Flooring n°3	2.8×10^{-3}	8.7×10^{-3}	1.1×10^{-4}	6.5×10^{-5}
Flooring n°4	2.5×10^{-3}	1.6×10^{-2}	9.7×10^{-5}	6.1×10^{-5}

Table 3

LOD and LOQ obtained from six replicates on flooring n°1 with the emission cell coupled to SPME-based method.

	FID	TIC	EIC 149	EIC 205
DiBP:				
LOD ($\mu\text{g}/\text{m}^3$)	0.5	1.0	1.0	X
LOQ ($\mu\text{g}/\text{m}^3$)	2.0	4.0	4.0	X
DBTP:				
LOD ($\mu\text{g}/\text{m}^3$)	2.0	0.4	X	0.4
LOQ ($\mu\text{g}/\text{m}^3$)	5.0	2.0	X	1.0

mission rate. For DBTP, the ratio between uptake rate and emission rate is higher than 100. So, the extracted amount by SPME during sampling mainly comes from the gas-phase. The emission rate is too slow for that a significant part emitted by the material during the extraction phase contributes to the amount sampled by the fiber.

3.4. Method performance

For the SPME-GC-MS/FID analysis, the limits of detection and limits of quantification has been determined for y_0 together with the repeatability over six replicates on flooring n°1 ($n = 6$). Extraction time was 2 min to get close from the limit of detection of mass detector and FID. LOD, LOQ and RSD have been calculated for FID, TIC (Total Ion Chromatogram) and EIC (Extracted Ion Chromatogram) signals. Concerning the EIC signal, ions with $m/z = 149$ and $m/z = 205$ has been selected. The first one is the major ion in DiBP-MS spectra and the second one is the major ion in DBTP MS spectra. Results are available in Table 3 and 4. LOD and LOQ are respectively three times and ten times the standard

Table 5

y_0 measured by SPME-GC-MS/FID for DiBP and DBTP.

Flooring n°	y_0 for DiBP (in $\mu\text{g}/\text{m}^3$)	y_0 for DBTP (in $\mu\text{g}/\text{m}^3$)
1	6.0 ± 0.3	14.0 ± 0.1
2	2.0 ± 0.3	6.1 ± 0.3
3	3.0 ± 0.6	6.0 ± 1.0
4	2.0 ± 0.4	12.0 ± 2.0

deviation divided by the slope of the calibration curve $n = f(C^*t)$. They are calculated for an extraction time of 15 min.

For DiBP, limit of detection is between 0.5 (for FID) and $1.0 \mu\text{g}/\text{m}^3$ (for EIC 149); and limit of quantification is between 2.0 (for FID) and $4.0 \mu\text{g}/\text{m}^3$ (EIC 149). For DBTP, limit of detection is between 0.4 (for EIC 205) and $2.0 \mu\text{g}/\text{m}^3$ (for FID); and limit of quantification is between 1.0 (for EIC 205) and $5.0 \mu\text{g}/\text{m}^3$. To compare, LOD and LOQ obtained in MS (TIC mode) by Ghislain et al. [29] during their experiments on flame retardants are between $1.10 \mu\text{g}/\text{m}^3$ and $7.6 \mu\text{g}/\text{m}^3$ (for a 15 min extraction time). So, our method is more sensitive. However, RSD obtained by Ghislain et al. [29] are ranged from 2.8 to 9.5% depending on the compound. This difference can be explained by low concentrations in DiBP and DBTP in our case. y_0 for floorings 1–4 have also been determined and reported in Table 5 (with extraction time of 15 min). Mean and standard deviation have been determined over the five last points of each curve in Fig. 4.

To compare, y_0 of DiBP measured on PVC at 25°C by Cao et al. is $68 \mu\text{g}/\text{m}^3$ [37] and the one measured by Liang and Xu is $49.8 \mu\text{g}/\text{m}^3$ [38]. More recent studies also realized on PVC by Yang et al. show a y_0 equals to $13.5 \mu\text{g}/\text{m}^3$ for DiBP [39]. These concentrations are higher but the floorings have been purchased outside of Europe, so the legislation concerning phthalates is not the same.

Table 4

RSD obtained from six replicates on flooring n°1 with the emission cell coupled to SPME-based method.

	Number of replicate measurements	y_0 ($\mu\text{g}/\text{m}^3$) mean \pm standard deviation	RSD (%)			
DiBP	6	0.8 ± 0.2	FID	TIC	EIC 149	EIC 205
DBTP	6	3.0 ± 0.5	28%	8.8%	10.7%	X
			19.1%	3.7%	X	3.2%

4. Conclusion

As we spend more time into indoor environments, indoor air quality is becoming a huge concern and in-situ methods are highly needed to determine the exposure level to pollutants and identify their emission sources. The goal of this study was to adapt and develop an in-situ method from Ghislain et al. (2017) to characterize phthalates emitted by PVC floorings. First, HS-SPME-GC-MS/FID analysis were done to identify which flooring are phthalate emitters and which phthalates are emitted. Several compounds have been detected: DiBP, DBTP and benzoate esters (mentioned in the literature as alternatives for phthalates). Then, an experimental device for generating atmospheres with phthalates was developed to calibrate the SPME based-MOSEC cell method. The device used a PVC flooring as source of DiBP and DBTP. When the steady state was reached (300 h), concentrations are determined thanks to active sampling with Tenax tubes. Generated concentrations for DiBP and DBTP were ranged from 2.0 to 5.0 $\mu\text{g}/\text{m}^3$ and from 4.0 to 7.0 $\mu\text{g}/\text{m}^3$ respectively. Calibration of the SPME based-MOSEC cell method has been successfully realized for both compounds and calibration curves (extracted mass by SPME versus the product of sampling time and gas-phase concentration) showed a satisfying linearity ($R^2 > 0.99$). For DiBP, limit of detection is between 0.5 (for FID) and 1.0 $\mu\text{g}/\text{m}^3$ (for EIC 149); and limit of quantification is between 2.0 (for FID) and 4.0 $\mu\text{g}/\text{m}^3$ (EIC 149). For DBTP, limit of detection is between 0.4 (for EIC 205) and 2.0 $\mu\text{g}/\text{m}^3$ (for FID); and limit of quantification is between 1.0 (for EIC 205) and 5.0 $\mu\text{g}/\text{m}^3$. Finally, the SPME based-MOSEC cell method was used to determine the concentration at the interface air/material (y_0) of the four emitting floorings. The y_0 values were ranged from 2.0 to 6.0 $\mu\text{g}/\text{m}^3$ for DiBP and from 6.0 to 14.0 $\mu\text{g}/\text{m}^3$ for DBTP. The time required to reach steady state concentration in the emission cell is much longer for DBTP (around 24 h) than for DiBP (>200 h).

This method has the advantage to be environmental-friendly: the consumption of solvents is limited by the use of GC instead of HPLC for SVOCs analysis and sampling is done by SPME, a solventless and reusable technique. Moreover, the calibration method is based on emitting material, avoiding the use of pure or concentrated toxic standards. The phthalate concentrations in the generated gas are therefore very low (few $\mu\text{g}/\text{m}^3$) thus reducing the risks of air pollution and of health impact for operators.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] ANSES, Connaissances relatives à la réglementation, à l'identification, aux propriétés chimiques, à la production et aux usages des composés de la famille des phtalates (Tome 1), (2017). <https://www.anses.fr/fr/system/files/SUBSTANCES2009SA0331Ra-Tome1.pdf> (accessed December 11, 2021).

[2] C.-G. Bornehag, J. Sundell, C.J. Weschler, T. Sigsgaard, B. Lundgren, M. Hasselgren, L. Hägerhed-Engman, The association between asthma and allergic symptoms in children and phthalates in house dust—A nested case-control study, *Environ. Health Perspect.* 112 (2004) 1393–1397, doi:10.1289/ehp.7187.

[3] R.A. Rudel, L.J. Perovich, Endocrine disrupting chemicals in indoor and outdoor air, *Atmos. Environ.* 43 (2009) 170–181, doi:10.1016/j.atmosenv.2008.09.025.

[4] B.B. Mughal, B.A. Demeneix, Flame retardants and increased risk of thyroid cancer, *Nat. Rev. Endocrinol.* 13 (2017) 627–628, doi:10.1038/nrendo.2017.123.

[5] C.C. Carignan, Inguez-A.L. M., C.M. Butt, P.L. Williams, J.D. Meeker, H.M. Stapleton, T.L. Toth, J.B. Ford, R. Hauser, Urinary concentrations of organophosphate flame retardant metabolites and pregnancy outcomes among women undergoing in vitro fertilization, *Environ. Health Perspect.* 125 (2017) 087018, doi:10.1289/EHP1021.

[6] F. Mercier, E. Gilles, G. Saramito, P. Glorennec, B. Le Bot, A multi-residue method for the simultaneous analysis in indoor dust of several classes of semi-volatile organic compounds by pressurized liquid extraction and gas chromatography/tandem mass spectrometry, *J. Chromatogr. A* 1336 (2014) 101–111, doi:10.1016/j.chroma.2014.02.004.

[7] SPF, Imprégnation de la population française par les phtalates – Programme national de biosurveillance, Esteban, (2016). <https://www.santepubliquefrance.fr/import/impregnation-de-la-population-francaise-par-les-phtalates-programme-national-de-biosurveillance-esteban-2014-2016> (accessed January 3, 2022).

[8] Y. Ait Bamai, A. Araki, T. Kawai, T. Tsuboi, E. Yoshioka, A. Kanazawa, S. Cong, R. Kishi, Comparisons of urinary phthalate metabolites and daily phthalate intakes among Japanese families, *Int. J. Hyg. Environ. Health* 218 (2015) 461–470, doi:10.1016/j.ijheh.2015.03.013.

[9] European Chemicals Bureau, Risk Assessment Report: 1,2-benzenedicarboxylic acid, di-C8–10-branched alkyl esters, C9-rich and di-“isononyl” phthalate (DINP), (2003). <https://echa.europa.eu/documents/10162/83a55967-64a9-43cd-a0fa-d3f2d3c4938d> (accessed January 25, 2022).

[10] European Chemicals Bureau, Risk Assessment Report: benzyl butyl phthalate (BBP), (2007). <https://echa.europa.eu/documents/10162/bad5c928-93a5-4592-a4f6-e02c5e89c299> (accessed January 25, 2022).

[11] European Chemicals Bureau, Risk Assessment Report: bis(2-ethylhexyl)phthalates (DEHP), (2008). <https://echa.europa.eu/documents/10162/060d4981-4dfb-4e40-8c69-6320c9debb01> (accessed January 25, 2022).

[12] European Chemicals Bureau, Risk Assessment Report: dibutyl phthalate, (2007). <https://echa.europa.eu/documents/10162/fcd6797a-395c-4f40-83b5-38653200f6cb> (accessed January 25, 2022).

[13] Journal of the French Republic, Decree of 30 April 2009 relating to the conditions for selling construction and decoration products containing carcinogenic, mutagenic or reprotoxic substances of category 1 or 2, (2009). <https://www.legifrance.gouv.fr/jorf/id/JORFTEXT000020671607> (accessed January 25, 2022).

[14] O. Blanchard, P. Glorennec, F. Mercier, N. Bonvallot, C. Chevrier, O. Ramalho, C. Mandin, B.L. Bot, Semivolatile organic compounds in indoor air and settled dust in 30 French dwellings, *Environ. Sci. Technol.* 48 (2014) 3959–3969, doi:10.1021/es405269q.

[15] L. Wang, M. Gong, Y. Xu, Y. Zhang, Phthalates in dust collected from various indoor environments in Beijing, China and resulting non-dietary human exposure, *Build. Environ.* 124 (2017) 315–322, doi:10.1016/j.buildenv.2017.08.006.

[16] J.M. Weiss, Å. Gustafsson, P. Gerde, Å. Bergman, C.H. Lindh, A.M. Kraus, Daily intake of phthalates, MEHP, and DINCH by ingestion and inhalation, *Chemosphere* 208 (2018) 40–49, doi:10.1016/j.chemosphere.2018.05.094.

[17] M. Pelletier, N. Bonvallot, P. Glorennec, Aggregating exposures & cumulating risk for semivolatile organic compounds—A review, *Environ. Res.* 158 (2017) 649–659, doi:10.1016/j.envres.2017.06.022.

[18] E.D. Schreder, N. Uding, M.J. La Guardia, Inhalation a significant exposure route for chlorinated organophosphate flame retardants, *Chemosphere* 150 (2016) 499–504, doi:10.1016/j.chemosphere.2015.11.084.

[19] C.J. Weschler, W.W. Nazaroff, SVOC exposure indoors—Fresh look at dermal pathways, *Indoor Air* 22 (2012) 356–377, doi:10.1111/j.1600-0668.2012.00772.x.

[20] J.C. Little, C.J. Weschler, W.W. Nazaroff, Z. Liu, E.A. Cohen Hubal, Rapid methods to estimate potential exposure to semivolatile organic compounds in the indoor environment, *Environ. Sci. Technol.* 46 (2012) 11171–11178, doi:10.1021/es301088a.

[21] J. Pei, Y. Yin, J. Cao, Y. Sun, J. Liu, Y. Zhang, Time dependence of characteristic parameter for semi-volatile organic compounds (SVOCs) emitted from indoor materials, *Build. Environ.* 125 (2017) 339–347, doi:10.1016/j.buildenv.2017.08.052.

[22] T. Braish, Development of Sensitive Analytical and Measurement Methods for Characterizing the Emissions of SVOCs from Building and Consumer Materials into Indoor Air, Phdthesis, Université de Pau et des Pays de l'Adour, 2019 <https://tel.archives-ouvertes.fr/tel-02927151> accessed December 17, 2021.

[23] C.J. Weschler, W.W. Nazaroff, Semivolatile organic compounds in indoor environments, *Atmos. Environ.* 42 (2008) 9018–9040, doi:10.1016/j.atmosenv.2008.09.052.

[24] ISO 16000-25, Determination of the emission of semi-volatile organic compounds by building products – micro-chamber method, (2011). <https://www.iso.org/obp/ui/#iso:std:iso:16000:-25:ed-1:v1:en> (accessed January 25, 2022).

[25] G. Ouyang, J. Pawliszyn, SPME in environmental analysis, *Anal. Bioanal. Chem.* 386 (2006) 1059–1073, doi:10.1007/s00216-006-0460-z.

[26] J. Cao, X. Zhang, J.C. Little, Y. Zhang, A SPME-based method for rapidly and accurately measuring the characteristic parameter for DEHP emitted from PVC floorings, *Indoor Air* 27 (2017) 417–426, doi:10.1111/ina.12312.

[27] Y. Wu, M. Xie, S.S. Cox, L.C. Marr, J.C. Little, A simple method to measure the gas-phase SVOC concentration adjacent to a material surface, *Indoor Air* 26 (2016) 903–912, doi:10.1111/ina.12270.

[28] N. Shinohara, A. Mizukoshi, M. Uchiyama, H. Tanaka, Emission characteristics of diethylhexyl phthalate (DEHP) from building materials determined using a passive flux sampler and micro-chamber, *PLoS One* 14 (2019) e0222557, doi:10.1371/journal.pone.0222557.

[29] M. Ghislain, J. Beigbeder, H. Plaisance, V. Desauziers, New sampling device for on-site measurement of SVOC gas-phase concentration at the emitting material surface, *Anal. Bioanal. Chem.* 409 (2017) 3199–3210, doi:10.1007/s00216-017-0259-0.

[30] H. Plaisance, M. Ghislain, V. Desauziers, Assessment of gas-phase concentrations of organophosphate flame retardants at the material surface using a midgett emission cell coupled to solid-phase microextraction, *Anal. Chim. Acta* 1186 (2021) 339100, doi:10.1016/j.aca.2021.339100.

- [31] Z. Chen, A. Afshari, J. Mo, A method using porous media to deliver gas-phase phthalates rapidly and at a constant concentration—Effects of temperature and media, *Environ. Pollut.* 262 (2020) 113823, doi:10.1016/j.envpol.2019.113823.
- [32] L. Tuduri, V. Desauziers, J.L. Fanlo, Determination of absolute amount extracted by solid-phase microextraction—Different approaches under examination, *J. Microcolumn Sep.* 12 (2000) 550–557 [10.1002/1520-667X\(2000\)12:10<550::AID-MCS4>3.0.CO;2-P](https://doi.org/10.1002/1520-667X(2000)12:10<550::AID-MCS4>3.0.CO;2-P).
- [33] L. Tuduri, V. Desauziers, J.L. Fanlo, A simple calibration procedure for volatile organic compounds sampling in air with adsorptive solid-phase microextraction fibres, *Analyst* 128 (2003) 1028–1032, doi:10.1039/B300968H.
- [34] T. Bohnert, R. Izadi, S. Pitman, B. Stanhope, Recent developments—Benzoate esters in polyvinyl resilient flooring, *J. Vinyl Addit. Technol.* 5 (1999) 143–147, doi:10.1002/vnl.10324.
- [35] W.D. Arendt, E.L. McBride, R.D. Hanes, New dibenzoate plasticizer blends for PVC applications, *J. Vinyl Addit. Technol.* 20 (2014) 137–142, doi:10.1002/vnl.21343.
- [36] M.J. Stimpson, M.S. Holt, Terephthalates as plasticizers in vinyl acetate polymer composition, (2012). <https://patentimages.storage.googleapis.com/a1/50/0a/90cda7367045dc/US8088854.pdf> (accessed January 25, 2022).
- [37] J. Cao, C.J. Weschler, J. Luo, Y. Zhang, C-History Method, a novel approach to simultaneously measure source and sink parameters important for estimating indoor exposures to phthalates, *Environ. Sci. Technol.* 50 (2016) 825–834, doi:10.1021/acs.est.5b04404.
- [38] Y. Liang, Y. Xu, Emission of phthalates and phthalate alternatives from vinyl flooring and crib mattress covers—The influence of temperature, *Environ. Sci. Technol.* 48 (2014) 14228–14237, doi:10.1021/es504801x.
- [39] T. Yang, H. Wang, X. Zhang, J. Xiong, S. Huang, P. Koutrakis, Characterization of phthalates in sink and source materials—Measurement methods and the impact on exposure assessment, *J. Hazard. Mater.* 396 (2020) 122689, doi:10.1016/j.jhazmat.2020.122689.