NIST Technical Note 2040

Measurement of Semi-Volatile Organic Chemical (SVOC) Emission Parameters for Building Materials Using a Solid-Phase Microextraction (SPME)-Based Method

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Abstract

Semi-volatile organic compounds (SVOCs) are ubiquitous indoors and associated with adverse health effects. Characterizing the emission of SVOCs from source materials is essential to estimating indoor SVOC concentrations in different phases, and thus the assessment of human exposure to SVOCs. It has previously been shown that y_0 (the SVOC concentration in air close to the material surface) is the key parameter to predict SVOC emissions from source materials. However, to develop consensus standard methods (i.e., ASTM) for measuring y_0 , better understanding and validation of current approaches are needed. A solid-phase microextraction (SPME)-based method published in the literature was chosen for this study. Tris(1-chloro-2-propyl) phosphate (TCPP) from spray polyurethane foam (SPF) and di-2-ethylhexyl phthalate (DEHP) from polyvinyl chloride (PVC) flooring were chosen as target chemicals. First, TCPP concentrations in two SPF materials were measured. The values for open-cell and closed-cell SPF were 1.24×10^{6} mg m^{-3} and 2.84×10^{5} mg m^{-3}, respectively. Second, to apply the SPME-based method, an improved method to calibrate chemical mass collected on SPME fibers was evaluated. In this calibration method, liquid standards were directly spiked on the SPME fiber. The results show that, for DEHP and benzo[*a*]pyrene (BaP), the direct SPME loading method was able to calibrate masses collected on SPME fibers, but not for more volatile chemicals (TCPP and 2,2′,5,5′-tetrachlorobiphenyl (PCB 52)). The results also showed that the transfer efficiency of splitless liquid injections were typically much lower than the efficiency of SPME injections. Hence, splitless liquid injection may not be suitable to calibrate SPME for the SVOCs studied here. Unfortunately, the application of the improved direct loading method may be limited due to the need for evaluation of every target chemical, the physical challenge of spiking onto the fiber, and the variability of SPME fibers’ adsorption property. Third, y_0

values for DEHP from PVC flooring at different temperatures were measured using the SPME-based method and a specially designed stainless-steel chamber. Measured y_0 of DEHP from the selected PVC flooring at 25 °C was 1.8 μg/m^3. However, due to the potential problems relating to the variability of SPME fibers' adsorption property, the variability of measured y_0 values may be as large as a factor of two. Overall, given the essential drawbacks of SPME-based method for measuring y_0, it is not recommended until the problems relating to SPME calibration and the variability of SPME fiber adsorption property are overcome.

Keywords

Semi-volatile organic compound (SVOC), Spray polyurethane foam (SPF), Polyvinyl chloride (PVC) flooring, Tris(1-chloro-2-propyl) phosphate (TCPP), Di-2-ethylhexyl phthalate (DEHP), Solid-phase microextraction (SPME)

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1. Introduction

1.1 SVOC emission parameters

Semi-volatile organic compounds (SVOCs) are ubiquitous indoors and commonly used in consumer products as additives to enhance product performance, such as plasticizers and flame retardants. In some products, SVOCs may account for a mass fraction of up to 10 % [1, 2]. In addition, SVOCs can be generated by incomplete combustion, e.g., polycyclic aromatic hydrocarbons (PAHs) [1, 2]. Humans may be exposed to indoor SVOCs after their emission into air and subsequent transport to different indoor media, such as dust, indoor surfaces, and airborne particles[1, 3-6]. Human exposure to certain SVOCs has been associated with adverse health effects, including cancer [7, 8], endocrine disruption [9, 10], respiratory problems [11], reproductive and developmental effects [12], obesity [13], and diabetes [14]. Therefore, there is significant interest in assessment of human exposure to SVOCs [2, 6, 15, 16].

Characterizing the emission of SVOCs from source materials has been shown to be essential to estimate SVOC concentrations in different phases, e.g., gas phase, particle phase, sorbed surface, and settled dust, as well as the resulting human exposure [2, 15]. As illustrated in Figure 1, the SVOC concentration in air close to the material surface, (y_0, µg/m^3) is the key emission parameter [17], and can be expressed as $y_0 = C_0/K$, in which C_0 is the SVOC concentration in the source material, µg/m^3, and K is the partition coefficient between source material and air. Hence, it is important to measure y_0 for different SVOC source materials and its relationship with C_0 to better understand emission characteristics.

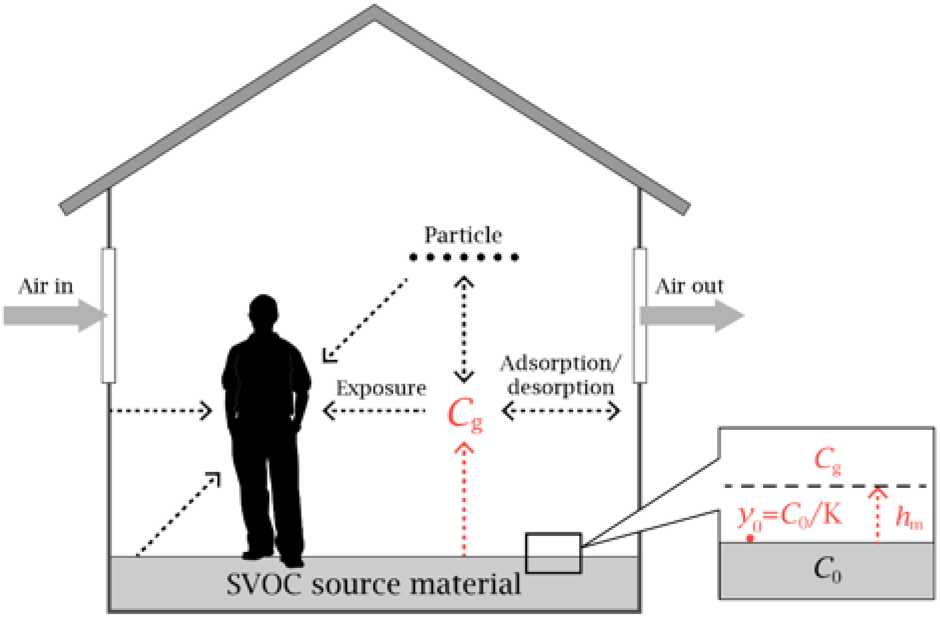


Figure 1. Illustration of SVOC emission process in a room (Adapted from Figure 1 in Little et al. [2]). y_0 is the SVOC concentration in air close to the material surface, µg/m^3; C_0 is the SVOC concentration in the source material, µg/m^3; K is the partition coefficient between source material and air, dimensionless; h_m is the convective mass transfer coefficient at the surface of source material, m/s; C_g is the SVOC concentration in gas phase, µg/m^3.

1.2 Existing methods for measuring y_0

Multiple methods have been developed to measure y_0 [18]. The features, advantages and disadvantages of these methods are summarized in Table 1. These methods either use ventilated chambers with active air sampling, e.g., sampling using Tenax tubes with pumps, or sealed chambers with passive sampling, e.g., solid-phase microextraction (SPME). Typically, the sealed chamber with passive sampling methods require shorter experimental time (days) than ventilated chambers (days to months). Compared with the ventilated chamber method, the sealed chamber method can eliminate the requirement to measure the convective mass transfer coefficient on different surfaces, which may be a significant source of uncertainty in the measured y_0 values. However, to date, methods using sealed chambers have only been applied to one kind of material, i.e., vinyl flooring, and one group of chemicals, i.e., phthalates. Also, there is no direct comparison

Table 1. Summary of existing methods for measuring y_0 (adapted from Table 1 in Cao et al. [19])

Methods	**Summary**	**Experimental time**[1]	**Advantages, Disadvantages, Limitations**
CLIMPAQ[a] **or FLEC**[b] [20]	• Monitoring SVOC concentration at outlet of a ventilated chamber with source material in it until steady state • Calculate $y_0 = (1+Q/h_mA)\cdot y_{ss}$; Q is airflow rate; A is source surface area; h_m is convective mass transfer coefficient; y_{ss} is the SVOC concentration in chamber at steady state	≈ 150 days	• Long experimental time • Complicated experimental system • Uncertainty in h_m reduces the accuracy of y_0
Sandwich-like chamber [21, 22]	• Same as CLIMPAQ but using a specially-designed chamber with maximized source area and minimized sorption area	2 to 20 days	• Relative short experimental time • Complicated experimental system • Uncertainty in h_m reduces the accuracy of y_0
Early stage C-history method [23]	• Monitoring SVOC concentration at outlet of a ventilated chamber • Calculating y_0 and h_m by fitting a simplified model to the experimental data before reaching steady state	10 days	• Relative short experimental time • Complicated experimental system • Uncertainty in chamber wall/air partition coefficient K_s reduces the accuracy of y_0
C_m-history or PFS [24, 25]	• Monitoring sorbed-phase SVOC concentration before steady state in a sealed chamber with both source and sorption material in it • Calculating y_0 by fitting mass transfer model to measured data	5 to 70 days	• Long experimental time • Uncertainty in L (the thickness of the sealed chamber) reduces the accuracy of y_0
Thermal desorption tube [26]	• Monitoring the total mass of SVOC accumulated in the tube sampler placed on the SVOC material surface • Calculating y_0 and K (tube surface/air partition coefficient) by fitting mass transfer model to measured data	7.5 days	• Relative short experimental time • Simple experimental system • Estimating two parameters from a single data set reduces accuracy of y_0
SPME-based [19]	• Monitoring gas phase SVOC concentration at steady state in a sealed chamber with source material using SPME • Calculating y_0 by linear curve fitting with measured data	1 day	• Short experiment time • Simple experimental system and sampling procedure • Only one fitting parameter, but uncertainty in SVOC diffusion coefficient reduces the accuracy of y_0

[a] Chamber for Laboratory Investigations of Materials, Pollution, and Air Quality

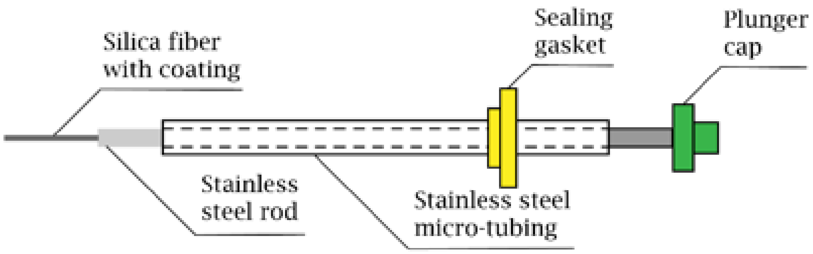
[b] Field and Laboratory Emission Cell

[c] Experimental time were determined based on the measurement of y_0 for Di-2-ethylhexyl phthalate (DEHP) from polyvinyl chloride (PVC) flooring

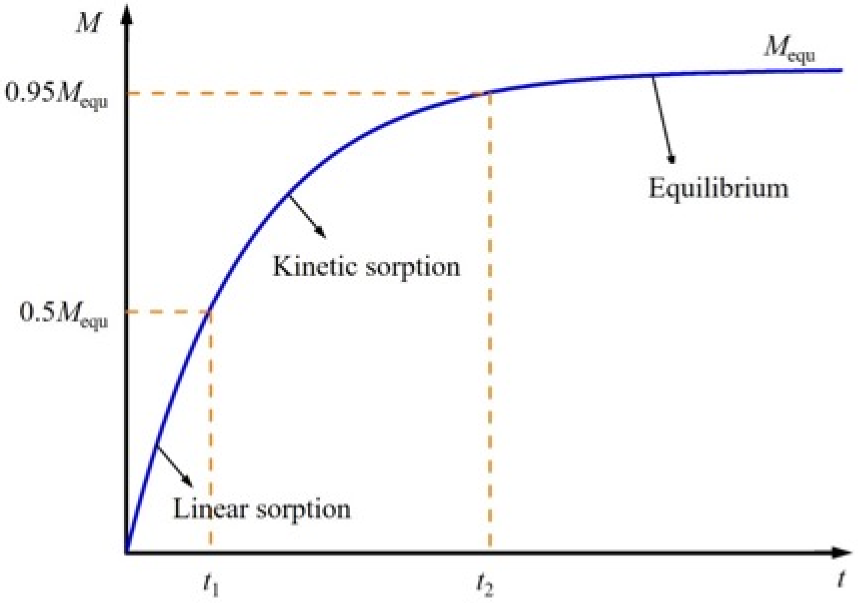
of different methods for measuring the same material. Hence, to support the development of consensus standard methods (i.e., ASTM) for measuring SVOC emission parameters, a better understanding and evaluation of current methods is needed. In this study, the SPME-based method using sealed chambers developed by Cao et al. [19] was chosen for evaluation, due to its short experiment time, ease of sampling procedure, simplicity of experimental system, and potential for use in an ASTM standard test method.

1.3 SPME-based method for measuring y_0

The principle of the SPME-based method was proposed and described in detail by Cao et al. [19]. Briefly, SVOC source materials are first put in a specially designed sealed chamber that maximizes source material surface area and minimizes exposed chamber surface area. When the emission process reaches steady state, the SVOC concentration in the air is equal to y_0. To obtain the gas-phase concentration of the SVOC in the chamber, SPME is used, as illustrated in Figure 2(a). A stainless-steel plunger is used to insert a fused silica fiber with coating material into the chamber, where the fiber is exposed to the chamber air and the target SVOC is sorbed onto the fiber. After removal from the chamber, the SPME fiber then is injected directly into the gas chromatography-mass spectroscopy (GS-MS) for quantification of the sorbed mass of the target SVOC. Repeating the process provides the sorbed mass of target SVOC after different sampling times.



(a)



(b)

Figure 2. (a) Structure of SPME; (b) Sorption process of SVOC to SPME fiber, M is the sorbed mass of SVOCs on SPME fiber, t is the sampling time, M_{equ} is the sorbed mass of SVOCs on SPME fiber at equilibrum. (adapted from Figure 2 in Cao et al. [19])

Figure 2 (b) illustrates a typical plot of the mass of SVOC sorbed onto the fiber (M) versus sampling time (t), from which y_0 can be determined based on the following principle. As shown in Figure 2 (b), if the SPME sampling time is sufficiently short, M is proportional to the product of sampling time (t) and gas-phase SVOC concentration in the chamber air (y_0), $M = ky_0t$, in which k is a constant, m^3/s, that can be estimated based on boundary layer theory, i.e., $k = D_aS$, where D_a is the SVOC diffusion coefficient in air, m^2/s, and S is the estimated shaping factor, m. The value of S is calculated based on equation (4) in Cao et al. [19], while the value of D_a can be obtained either from the literature or by calculation using an empirical correlation [27]. Hence, given the *slope* between sorbed mass and sorption time, the SVOC concentration in chamber air (y_0) can be calculated by $y_0 = slope/(D_a S)$.

1.4 SPME calibration methods

To apply the SPME-based method described above, calibration of the mass adsorbed onto the SPME fiber is required. Traditionally, the SPME sampling process ends after reaching equilibrium between the fiber coating and the target chemical. However, for SVOCs with low volatility, it could take several days to weeks to reach equilibrium [28, 29]. To shorten sampling times, non-equilibrium sampling methods have been developed [19, 28]. However, to use the non-equilibrium adsorption period of SPME to measure the SVOC concentration in air, measurement of the absolute analyte amount on the SPME fiber is required. To quantify the absolute analyte amount on SPME, splitless injection of liquid standard into GC inlet is most often used (used by Cao et al. [19] for their SPME-based method). The feasibility of using splitless liquid injection as a SPME calibration method depends on the assumption that SPME injections have the same transfer efficiency as splitless liquid injections. However, the transfer efficiency for both SPME injection and splitless liquid injection are influenced by factors such as the type of liner, temperature profile of the injector, and the cross-sectional area of the space between column and liner. Hence, the transfer efficiencies could be significantly different for these two injection techniques [30]. Thus, calibrating SPME using liquid splitless injection may cause large uncertainties in the absolute analyte amount and ultimately the calculated y_0 value.

As a result, researchers have sought other means to load known amounts of the solute of interest directly onto a SPME fiber to provide an injection calibration environment that matches the injection environment used for SPME sampling. Fiber loading methods have been developed to measure concentrations based on the inverse adsorption and desorption principle [31]. Among those loading techniques, headspace extraction often has detection limit problems for chemicals with low volatility, such as SVOCs. Another fiber loading technique is direct syringe-fiber loading, that is, a syringe is used to place a small drop of standard solution directly onto the fiber. After the solvent evaporates, the SPME is injected into the GC-MS. Direct syringe-fiber loading has been shown to have transfer efficiencies greater than 95 % for low volatility chemicals, is convenient and does not require specialized equipment [31]. However, the primary limitation of syringe-fiber loading is that it only works for chemicals with low volatility. Gura [32] addressed this limitation by using an inkjet microdrop printing method to load 1 nL of solution onto the fiber. In this method, the SPME can be injected into a GC-MS directly without the requirement of solvent evaporation as is required for normal syringe-fiber injection. However, this method requires additional instrumentation and operator knowledge that is not common in analytical laboratories. Hence, currently the inkjet printing approach is typically not practical to use as a calibration method.

Given the low volatility of the majority of SVOCs and the convenience of direct syringe-fiber loading, this method could be feasible for calibrating SPME for measuring gas phase SVOC concentrations, especially in chamber methods used to determine y_0. However, no study has been conducted to examine the feasibility of this method for SVOCs. In addition, existing direct syringe-fiber loading studies did not use an internal standard, which would reduce the uncertainty associated with this technique.

1.5 Objective

Two types of building materials and one SVOC from each material were chosen as target materials and chemicals. Spray polyurethane foam (SPF) insulation is being increasingly used in the United

States to reduce the heat loss through building envelopes [33]. Two different kinds of SPF, open-cell (low density) and closed-cell (medium density), can be produced on site via an exothermic reaction of two sets of chemicals. One of the main components in SPF is the flame retardant, tris(1-chloro-2-propyl) phosphate (TCPP), which can be present in foam at mass fraction up to 12 %.[34] and has been associated with asthma, reproductive and developmental problems [35]. Hence, TCPP from SPF was chosen as a target chemical. Di-2-ethylhexyl phthalate (DEHP) has been widely used as plasticizer to enhance the flexibility of polyvinyl chloride (PVC) products. DEHP can be present in PVC flooring at tens-of-percent levels and has been associated with adverse health effects, including endocrine disruption, asthma and allergies [36]. In addition, emission of DEHP from PVC flooring has been measured by other researchers [19, 20, 26, 37-41], which allows comparisons to measured y_0 values by different labs and using different methods. Therefore, DEHP from PVC flooring was chosen as another target chemical, with the same PVC flooring tested in published papers used in this study.

The objectives of this study were to: (1) measure TCPP concentration in the SPF, C_0; (2) evaluate the syringe-fiber loading method for calibrating SPME for measuring concentration of gas phase SVOCs; (3) apply the SPME method to measure y_0 for TCPP from SPF and for DEHP from PVC flooring. While not all the goals were fully achieved, the lessons learned while pursuing them are valuable for future studies.

2. Methods

2.1 Measurement of C_0

The PVC flooring tested in this study is the same material tested in published papers [26, 37, 38]. The mass fraction of DEHP in the PVC flooring was reported to be 23.3 % by weight, while C_0 was 3.26×10^{11} μg/m^3 [38]. Hence, only values of C_0 for TCPP in SPF were measured in this study.

2.1.1 Materials

One closed-cell SPF and one open-cell SPF were tested. Both SPFs were produced by the American Chemistry Council's Center for the Polyurethanes Industry (CPI). The foams are research formulations developed in 2011 to be representative of SPF then available in the marketplace. The SPFs were first sprayed in factory settings under controlled conditions, and then were packaged and shipped overnight to NIST in an insulated cooler in accordance with ASTM standard D7859[42]. Detailed information about the tested SPFs is shown in Table 2. Analytical standards for TCPP and triamyl phosphate (TAP) were purchased from Sigma-Aldrich, Inc.

Table 2. SPF samples tested

Foam type	Density[1], kg/m^3	Spray date	Test date
Open-cell	8.3	9/2/2015	4/3/2015
Closed-cell	42	9/2/2015	11/21/2015

[1]Density determined by measured initial mass and volume.

2.1.2 Method

The open-cell SPF was extracted with methanol, while the closed-cell SPF was extracted with dichloromethane. The choice of solvent was determined by previous extraction efficiency testing (data not shown). First, a 100 mg piece of SPF was cut into small pieces (less than roughly 0.5 cm^3) and put into a 40 mL glass vial. Second, each sample was ultrasonicated for 1 h with 25 mL of solvent at 25 °C, and the extraction for each sample was repeated four times with fresh solvent each time. Third, all four extracts were transferred to a 100 mL volumetric flask. The extract was then diluted with the same solvent to a volume of 100 mL. Fourth, 100 µL TAP were added into 50 µL of the extract as an internal standard before analysis. Finally, all the samples were analyzed using gas chromatography - mass spectrometry (GC-MS).

2.1.3 GC-MS analysis

The analyses were performed on an Agilent 7890B GC coupled with a 5977B MS. The chromatographic column was Rtx-5MS (30m × 0.25 mm (i.d.) × 0.25 µm thickness). The carrier gas was high purity helium (> 99.99%). The MS was operated in scan mode from 40 amu to 450 amu. The source and quadrupole temperature were 250 °C and 150 °C, respectively. Extracts (1 µL) were injected into a Gerstel cooled injection system (CIS) through a septumless head at 30 °C. The CIS was then ramped up to 275 °C at a rate of 12 °C/s with a 50:1 split ratio. The column oven temperature was held for 2 min at 40 °C, and then ramped up to 300 °C at a rate of 20 °C/min and held for 2 min. The TCPP concentrations for standard curves ranged from 1 ng/µL to 100 ng/µL. The TAP concentration was 25 ng/µL.

2.1.4 Quality assurance / Quality control

Three replicate samples were measured for each tested foam. Matrix recovery rates were measured by spiking 5 mg of TCPP onto SPF (100 mg) and equilibrating at room temperature for 30 min before extraction. Blank spike recovery rates were measured by adding 5 mg of TCPP to the extraction vial directly. As shown in Table 3, all the recovery rates were within 85 % to 105 %, with relative standard deviations 15 % or less. Note that TCPP 1 and TCPP 2 in Table 3 are two isomers of TCPP, and all the reported TCPP concentrations in this report are the sum of these two isomers. One re-extraction of each sample was measured to check if the SPF was extracted effectively by four repeated extractions. TCPP concentrations in all the re-extracts were below the detection limit, i.e., 0.3 ng/µL. Three laboratory blanks were measured in each set of experiments. No TCPP was detected in any of the laboratory blank samples. The R square values of all the standard curves used were greater than 0.98.

Table 3. Summary of recovery rates for extraction[a]

Sample type	Recovery	TCPP 1	TCPP 2
Open-cell	Blank spike recovery (n =3)	91 % (4 %)	88 % (6 %)
	Matrix spike recovery (n =3)	102 % (12 %)	92 % (15 %)
Closed-cell	Blank spike recovery (n =3)	101 % (3 %)	95 % (2 %)
	Matrix spike recovery (n =3)	92 % (15 %)	96 % (9 %)

[a]Data are shown in means (relative standard deviations in parenthesis).

2.2 Calibration of SPME

2.2.1 Materials

In addition to the main target chemicals in this study, i.e., TCPP and DEHP, we also evaluated the applicability of the improved direct fiber loading calibration method for several other commonly analyzed SVOCs, including benzo[*a*]pyrene (BaP) and 2,2′,5,5′-tetrachlorobiphenyl (PCB 52), to examine if this method can be used for a broader range of SVOCs. These SVOCs represent four typical SVOC groups (i.e., flame retardants, plasticizers, polycyclic aromatic hydrocarbons, and heat-transfer fluids) that have widespread use and are associated with adverse human health effects[1].

Analytical standards for TCPP, DEHP, BaP and PCB 52 were purchased from Sigma-Aldrich, Inc. The corresponding internal standard, i.e., TAP, DEHP-d_4, and BaP-d_{12} were also purchased from Sigma-Aldrich, Inc., while the ^{13}C-labelled standard, i.e. ^{13}C PCB 52 was purchased from Cambridge Isotope Laboratories, Inc. Detailed chemical properties for these chemicals are listed in Table 4.

Table 4. Chemical properties and quantification ions for target chemicals and their corresponding internal standards

Chemical name	Acronym	CAS No.	MW, g/mol	Boiling point, °C[a]	log P_s, atm[a]	Quantification Ion
Tris(1-chloro-2-propyl) phosphate	TCPP	13674-84-5	328	276	-6.33	125, 99
Triamyl phosphate	TAP	2528-38-3	308	325	-7.26	99
Di-2-ethylhexyl phthalate	DEHP	117-81-7	391	457	-11.85	149
Di-2-ethylhexyl phthalate-3,4,5,6-d_4	DEHP-d_4	93951-87-2	395	[b]	[b]	153
Benzo[*a*)pyrene	BaP	50-32-8	252	515	-10.25	252
Benzo[*a*]pyrene-d_{12}	BaP-d_{12}	63466-71-7	264	[b]	[b]	264
2,2′,5,5′-Tetrachlorobiphenyl	PCB 52	35693-99-3	292	361	-7.54	292
2,2′,5,5′-Tetrachlorobiphenyl ($^{13}C_{12}$)	^{13}C PCB 52	208263-80-3	304	[b]	[b]	304

[a] SPARC online calculator: http://archemcalc.com/sparc-web/calc, calculated on Dec. 15, 2017.

[b] Not available.

SPME fibers were also purchased from Sigma-Aldrich, Inc. (Supelco Analytical) with a polydimethylsiloxane (PDMS) coating material, which is recommended for nonpolar SVOC sampling. The thickness and length of the PDMS coating are 7.0 μm and 1.0 cm, respectively, while the diameter of the SPME fiber is 110 μm.

2.2.2 Method

As shown in Figure 3a, for direct syringe-fiber loading, only the standard liquid was spiked directly onto the fiber in a previous study [31]. To reduce the influence of GC-MS variability, the internal standard was also spiked onto the fiber in the current study (Figure 3b). After the solvent evaporated, the target chemical and its corresponding internal standard were retained on the fiber. Then, the SPME was manually placed into the injector. Since the fiber for a standard sample was injected in the same way as the SPME fiber for an unknown sample, it is reasonable to assume the transfer efficiencies of both injections were the same.

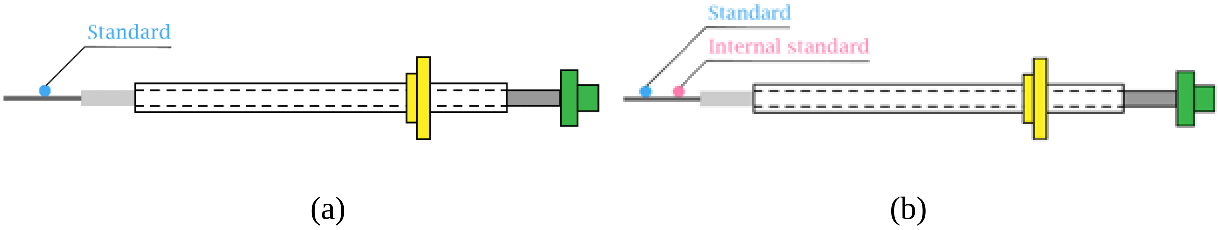
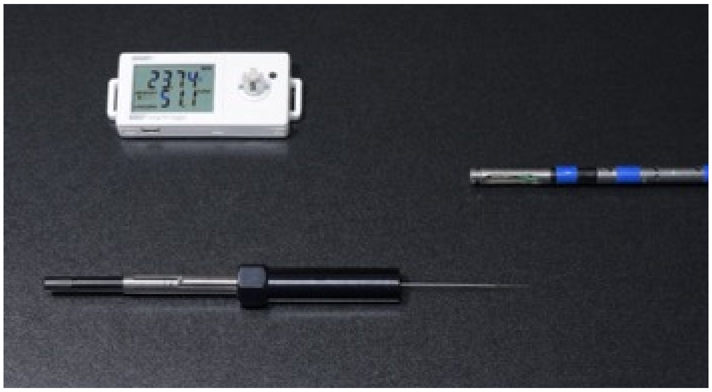


Figure 3. Direct loading (a) spike standard onto fiber [31]; (b) spike both standard and internal standard onto fiber



(a)

(b)

Figure 4. (a) Photo of experimental setup during spiking showing location of temperature and relative humdity data logger andanemometer; (b) Photo of spiking liquid standard onto SPME fiber

Figure 4 shows the experimental setup during spiking and the spiking process. All the spiking operations were conducted in a fume hood. Temperature (*T*) and relative humidity (RH) close to the fiber were monitored using a HOBO® data logger, with manufacture specified accuracy of ± 0.24 °C and ± 2.5 % for *T* and *RH* at a resolution of 15 s. Air velocities (*V*) near the fiber during spiking were monitored using VelociCalc Plus air velocity meter with manufacture specified accuracy of ± 0.015 m/s at a resolution of 5 s. Minimum, maximum and mean values of the velocity during the spiking period were recorded.

In this study, we evaluated the direct-loading method by checking the repeatability of spiking, the solute loss during evaporation, influence of velocity around the fiber, and linearity of the standard curve. Note that when evaluating the direct-loading method, target chemical and internal standard were spiked separately. This is because when an air sample from the chamber was taken by SPME, the target chemical was adsorbed from the gas phase onto the fiber during sampling while the internal standard was spiked onto the fiber in methanol. To maintain consistency of the internal standard spiking, the internal standard was also spiked onto the same location for standard injections (Figure 3) while the target chemical was spiked separately in methanol onto a different location.

First, the repeatability of standard loading was examined by analyzing triplicates of two different concentrations of standard spiking samples. Second, a series of standard spiking samples were exposed to air for different lengths of time to evaluate the influence of solute loss during solvent evaporation. To do this, for each sample, a 1 μL standard liquid was spiked onto the fiber first, and then after different times 1 μL of the corresponding internal standard was spiked onto the fiber. By doing so, the standard spiked onto the fiber were allowed to evaporate for different times for each sample, while the internal standard evaporated for constant times for each sample. Similarly, to check the influence of evaporation for the internal standard, 1 μL internal standard liquid was spiked onto the fiber and evaporated for different times for each sample, while 1 μL of the corresponding standard was spiked onto the fiber and evaporated for constant times for each sample. Third, the influence of air velocity over the fiber on the solute evaporation was also examined by changing the opening of the fume hood. Fourth, the linearity of the standard curve was evaluated by spiking a 1 μL standard at different concentrations and a 1 μL internal standard with the same concentration. After the above four evaluations, liquid standards were also analyzed using splitless liquid injection method for comparison with direct SPME loading and injection In this study, internal standards were analyzed in addition to used to account for the variability of GC-MS, instead of analyzing the liquid standard without an internal standard as done in previous studies [19, 28].

2.2.3 GC-MS analysis

All samples were analyzed by Agilent 7890B GC coupled with 5977B MS. A SPME liner (i.d. 1 mm) was used for SPME injection, while a baffled liquid injection liner (i.d. 2 mm) was used for splitless liquid injection. For SPME injection, the split/splitless injector was set to 290 °C for SPME conditioning and 285 °C for SPME sample analysis. The injector was operated in splitless mode for 5 min. For liquid standard analysis, the injector temperature was 285 °C and operated in splitless mode for 5 min. The chromatographic column was Rtx-5MS (30 m × 0.25 mm (i.d.) × 0.25 μm thickness). The carrier gas was high purity helium (> 99.99%). The GC oven temperature was initially 40 °C, held for 2 min, ramped to 300 °C at 20 °C/min, and then held for 5 min. The MS was operated in scan mode from 40 amu to 450 amu. The source and quad temperature were 250 °C and 150 °C. The quantification ions for each target compound are listed in Table 4.

Table 4. Chemical properties and quantification ions for target chemicals and their corresponding internal standards

. Three standard SPME spikes for each target chemical were injected twice continuously to make sure that any carryover from the first injection was below the detection limit, i.e., 0.05 ng.

2.3 Measurement of y_0

2.3.1 Principle

In Cao et al. [19], a cylindrical chamber was designed and the PVC flooring was used to seal the chamber. In this study, a similar chamber, shown in Figure 5, with a diameter of 10 cm and an inner height of 3 cm was designed. A convex ring with a thickness of 2 mm and height of 1 cm in the middle of the chamber was used to hold the material. O-rings and threads at the top and bottom of the chamber were used to seal the chamber. This chamber design avoids the requirement of using the material to seal the chamber and allows analysis of soft materials, such as spray polyurethane foam. The temperature of the chamber was controlled using a peltier cooled incubator by Government Scientific Source, Inc, with manufacture specified accuracy of ± 0.5 °C.

2.3.2 TCPP from spray polyurethane foam

Based on the results described later in section 3.2.1, the direct loading SPME calibration method could not be used for TCPP. Therefore, y_0 for TCPP emission from spray polyurethane foam was not measured using the SPME-based method.

2.3.3 DEHP from PVC flooring

After PVC flooring was put into the chamber for 24 hours, the DEHP concentration in the chamber was considered to reach equilibrium and be uniform based upon preliminary studies (not described here). A SPME was first conditioned in the injector at 290 °C for five minutes to make sure the remaining masses of DEHP and DEHP-d_4 in the SPME coating were below the detection limits.

Then, the SPME fiber was inserted into the chamber, as shown in Figure 5. SPME fibers were exposed to the chamber air for six different times, i.e., 0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, and 3 h. For each time, at least three samples were taken. Once the SPME was removed from the chamber, the external surface of the stainless-steel rod of the SPME plunger was wiped at least 4 times using Kim Wipes soaked with methanol. Then, 1 µL of DEHP-d_4 was spiked onto the stainless-steel rod or fiber close to the connection point of fiber and rod after pushing the fiber out, followed by injection of the fiber into the GC-MS system. Standard curves were produced to calculate the sorbed mass onto the SPME using the direct loading method described in section 2.2.2. Finally, the DEHP concentration in the chamber was calculated using the method described in section 1.3. The experiments were conducted at four different temperatures, i.e., 15 °C, 20 °C, 25 °C, and 30 °C. Additional experiments examined the DEHP loss from the SPME fiber after chamber sampling during the process of spiking DEHP-d_4. The experiments were conducted by first pushing the fiber out and then after different times, spiking 1 µL of the corresponding internal standard onto the fiber. Thus, the target chemical adsorbed onto the fiber was allowed to evaporate for different times for each sample, while the spiked internal standard and evaporated for constant times for each sample.

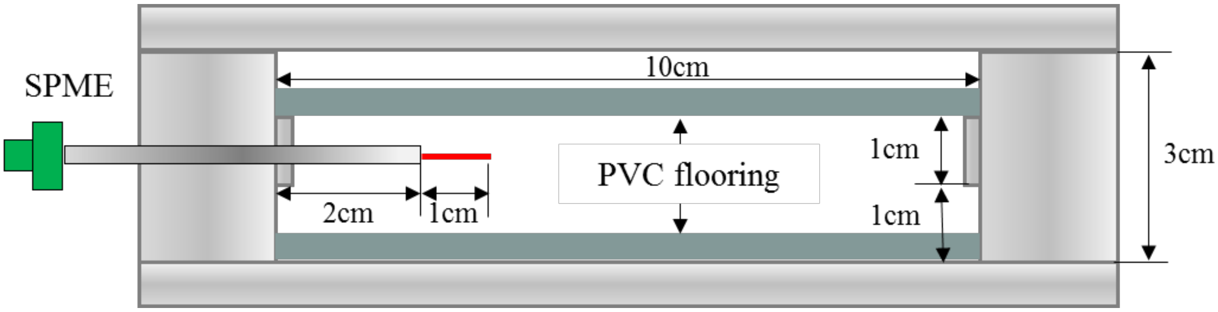
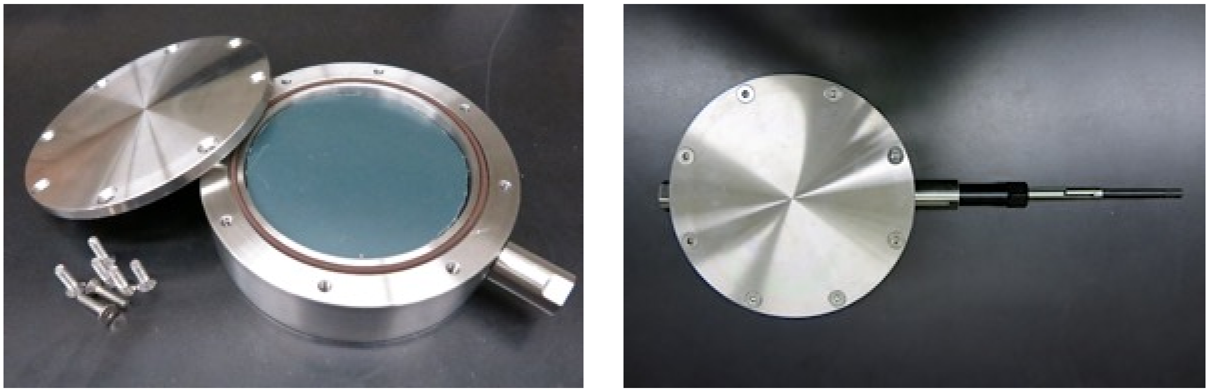


Figure 5. Illustration of the cylindrical chamber and SPME sampling with PVC flooring in it



(a) (b)

Figure 6. SPME sampling from a sealed chamber. (a) chamber; (b) sampling.

3. Results and discussion

3.1 Measurement of C_0

The results show that open-cell foam contained a TCPP mass fraction of 12.5 %, while closed-cell foam contained a TCPP mass fraction of 6.8 % (Table 5). The values of C_0 are also shown in Table 5, which were determined based on the measured mass fraction and the density of foam. The total measured mass fractions are similar to the manufacture's reported TCPP mass fraction for these SPF (open-cell 12.6 %, closed-cell 7.9 %) [34].

Table 5. Measured TCPP mass fraction and C_0 in both open-cell and closed-cell foam[a]

Foam type	**Chemical**	**Mass fraction, %**	**C_0, mg/m^3**
Open-cell, n = 3	TCPP 1	10.0 (1%)	8.3×10^5 (1%)
	TCPP 2	2.5 (3%)	2.1×10^5 (3%)
	Total TCPP	12.5	
Closed-cell, n = 3	TCPP 1	5.5 (6.5%)	2.3×10^6 (6.5%)
	TCPP 2	1.3 (10%)	5.4×10^5 (10%)
	Total TCPP	6.8	

[a]Data are shown in mean values (relative standard deviation in parenthesis).

3.2 Evaluation of SPME calibration method

3.2.1 TCPP

The response ratios (ratios of peak areas in chromatogram by GC-MS) of TCPP to TAP for three samples spiked with TCPP solution at 1 ng/µL and TAP solution at 0.9 ng/µL were consistent (relative standard deviation (RSD) < 10 %, n =3), when TCPP evaporated for 180 s and TAP evaporated for 140 s. However, as shown in Figure 7, when TAP was evaporated for 140 s, while TCPP evaporated for different times, the response ratio of TCPP to TAP decreased with the increase of TCPP evaporation time. The fastest that both the TAP and TCPP can be spiked onto the fiber and have the solvent evaporate is 160 s. The hypothesis of this effort was that the spiked TCPP did not evaporate from the fiber during the first 160 s. Since we cannot measure what is happening during the solvent evaporation period of the first 160 s, we looked to see if the TCPP was stable after the 160 s time frame. Since the TAP mass is assumed to be constant given the constant TAP evaporation time (140 s), there was an increasing loss of TCPP with increasing solvent evaporation time (160 s to 330 s). Since more TCPP appears to be evaporating with increased solvent evaporation time, the mass of TCPP on the SPME fiber when it goes into the GCMS injector (after 160 s) would be less than the spiked mass. Hence, direct SPME loading should not be used for SPME calibration for TCPP.

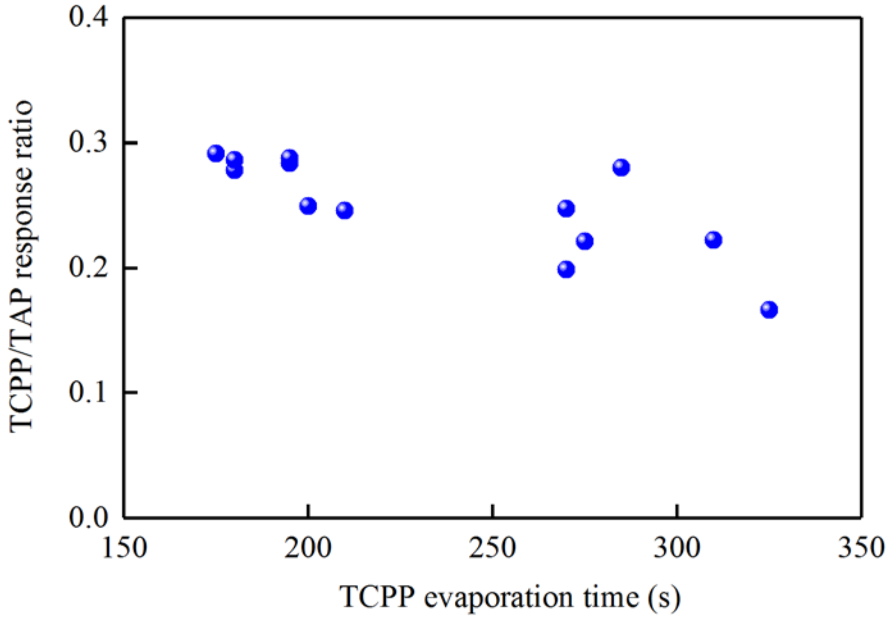


Figure 7. Evaluation of evaporation loss of TCPP. 1 µL TCPP solution at 1 ng/µL and 1 µL TAP solution at 0.9 ng/µL were spiked onto fiber for each sample.

3.2.2 DEHP

The RSD of response ratios of DEHP and DEHP-d_4 for three samples spiked with DEHP solution at 1 ng/µL and DEHP-d_4 solution at 0.9 ng/µL was 6 % (n=3), when DEHP evaporated for 420 s and DEHP-d_4 evaporated for 390 s. In addition, Figure 8 shows that both the evaporation time of DEHP and the evaporation time of DEHP-d_4 did not influence the response ratio of DEHP and DEHP-d_4. Hence, if the evaporation time of DEHP is within the examined time range (less than 1080 s or 18 min), the evaporation loss should not impact the response for DEHP. In addition, the air velocity close to SPME also did not influence the ratio with RSD < 10 % (n=6) for the three velocities tested (Figure 9). The linearity of the standard curve for direct loading is high with R-square (R^2) greater than 0.99 (Figure 10). Overall, the direct loading method could be used to calibrate the amount of DEHP sorbed to SPME.

The same mass of DEHP was injected into the GC-MS using both the splitless liquid injection and the direct-syringe loading method within 24 hours. As shown in Figure 11, the DEHP absolute response area by liquid injection was 10 to 20 times lower than the response area by direct loading for the same mass injected. Similar differences between splitless liquid injection and SPME injection were also reported for 2,4-dinitrotoluene (MW = 182 g mol^{-1}, boiling point = 300 °C), diphenylamine (MW = 169 g mol^{-1}, boiling point = 302 °C) and ethyl centralite (MW = 268 g mol^{-1}, boiling point = 330 °C) by Gura et al. [32]. The lower response of DEHP by splitless liquid injection indicates that the sorbed amount of DEHP on SPME will be overestimated if splitless injection is used for SPME calibration. Therefore, if SPME chamber sampling with splitless liquid calibration is used to determine y_0, the y_0 value will be overestimated. The difference in response between the two methods is related to the transfer efficiencies of the methods in the injector. There are many factors that affect transfer efficiency for both methods, e.g., the diameter of the injection liner. The fact that the response was lower for liquid injection may be due to flash vaporization of the solvent, which may result in inconsistent and inefficient transfer of the analyte to the column.

After adjustment by the response of the internal standard, the difference of DEHP and DEHP-d_4 response ratio between two methods is much smaller. The ratio ranges from 1.0 to 1.3 (Figure 10 and Figure 12), which means the difference of calibrated DEHP amount on SPME using two methods will be less than 30 %. The possible reason for the similarity is that DEHP and DEHP-d_4 have very similar chemical properties and eluted from the capillary column at the same time, which may result in similar transfer efficiency during any potential back-flash. Therefore, splitless liquid injection with DEHP-d_4 as an internal standard could be an alternative way to calibrate SPME for DEHP if 30 % response difference is acceptable. Liquid samples can be injected automatically and will save substantial amount of time, while a SPME sample spiked with standard/internal standard by direct syringe loading can only be injected manually.

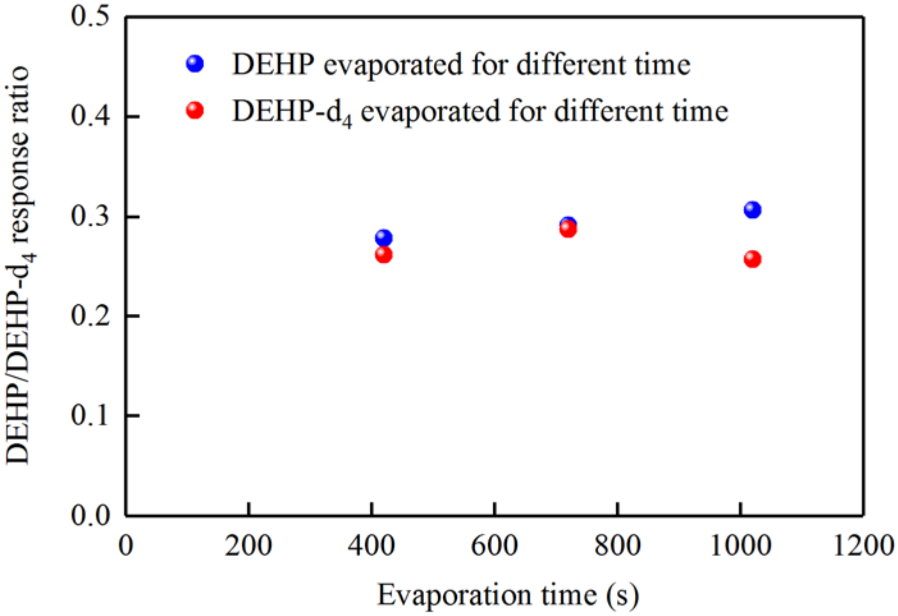


Figure 8. Evaluation of evaporation loss of DEHP and DEHP-d_4. 1 µL DEHP solution at 1 ng/µL and 1 µL DEHP-d_4 solution at 0.9 ng/µL were spiked onto the fiber for each sample. Temperature (T) was at (23.2 ± 0.2) °C. Relative humidity (RH) was at (43.9 ± 0.3) %. Velocity (V) was at (0.47 ± 0.02) m/s. The values for T, RH and V in this figure and the following figures are presented in the format of mean ± stantdard deviation.

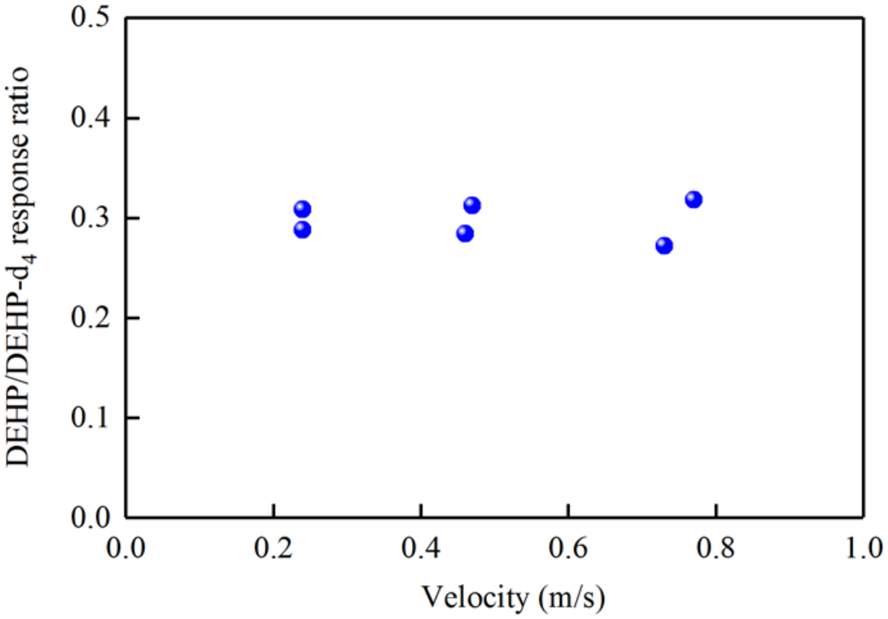


Figure 9. Evaluation of air velocity influence. 1 µL DEHP solution at 1 ng/µL and 1 µL DEHP-d_4 solution at 0.9 ng/µL were spiked onto the fiber for each sample. T was at (23.3 ± 0.2) °C. RH was at (48.4 ± 3.9) %.

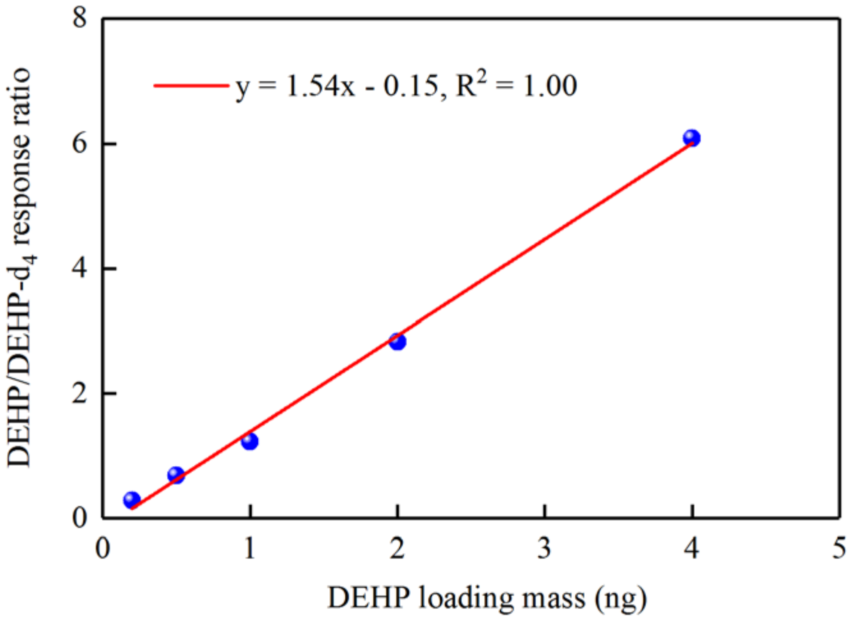


Figure 10. Standard curve for DEHP by SPME injection. 1 µL DEHP solution at (0.2 or 0.5 or 1 or 2 or 4) ng/µL and 1 µL DEHP-d4 solution at 0.9 ng/µL were spiked onto the fiber for each sample. T was at (23.3 ± 0.2) °C. RH was at (52.7 ± 0.3) %. V was at (0.46 ± 0.02) m/s.

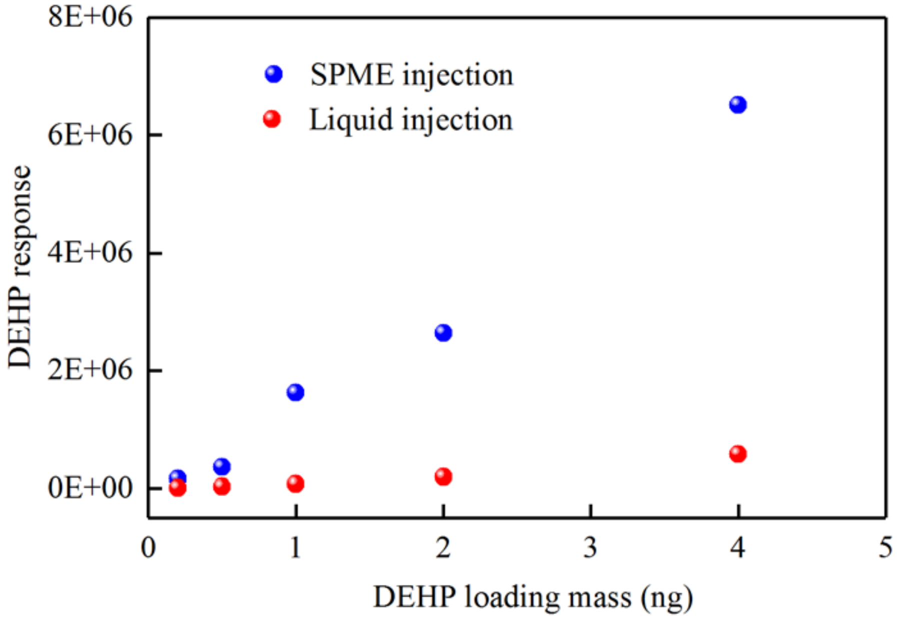


Figure 11. Comparison of DEHP response by SPME injection and splitless liquid injection. 1 μL DEHP solution at (0.2 or 0.5 or 1 or 2 or 4) ng/μL and 1 μL DEHP-d_4 solution at 0.9 ng/μL were spiked onto the fiber for each SPME sample. T was at (23.3 ± 0.2) °C. RH was at (52.7 ± 0.3) %. V was at (0.46 ± 0.02) m/s.

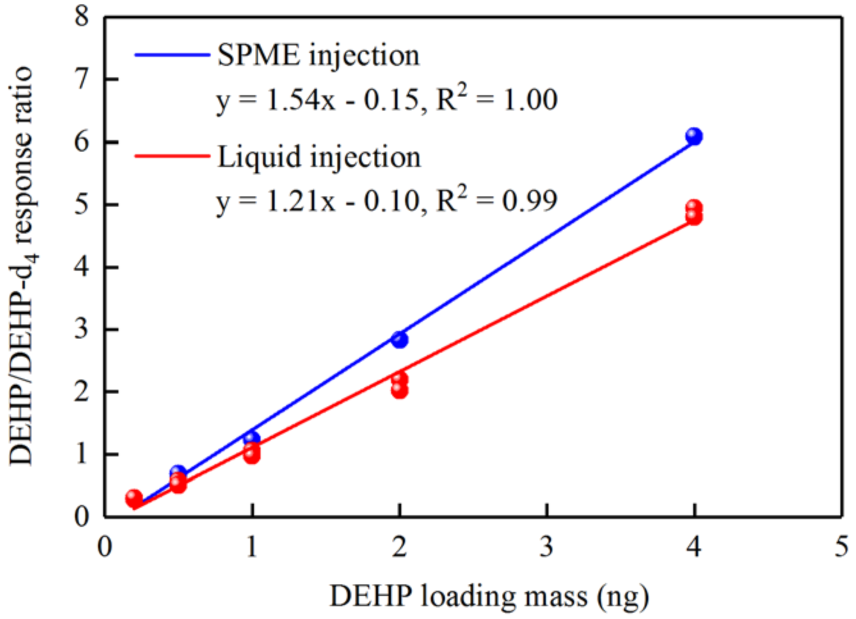


Figure 12. Comparison of DEHP and DEHP-d_4 response ratio by SPME injection and splitless liquid injection.

3.2.3 BaP

The RSD of response ratios of BaP and BaP-d_{12} samples spiked with BaP solution at 0.6 ng/μL and BaP-d_{12} solution at 5 ng/μL was 7 % (n=3), when BaP evaporated for 480 s and BaP-d_{12} evaporated for 440 s. Figure 13 shows that both the evaporation time of BaP and the evaporation time of BaP-d_{12} did not influence the response ratio of BaP and BaP-d_{12}. Hence, if the evaporation time of BaP is within the examined time range (< 1080 s), the evaporation loss will not impact quantification. In addition, the air velocity close to SPME also did not influence the ratio with RSD < 10 % (n = 3) for three velocities tested (Figure 14). The R^2 of three standard curves for direct loading were larger than 0.98 (Figure 15). Overall, the direct loading method can be used to calibrate BaP mass sorbed to SPME.

Comparison of SPME injection and splitless liquid injection was conducted three times for BaP (Figure 16). Similar to DEHP, the BaP absolute response area for direct loading was much higher (2 to 6 times) than the BaP absolute response area for liquid injection for the same mass injected. The lower response of BaP by splitless liquid injection indicates that the sorbed amount of BaP on SPME will be overestimated if splitless injection is used for SPME calibration. After adjustment by the response of the internal standard, the difference between the two methods was smaller. However, the difference in the ratios for the two methods still ranged from 1 to 2 (Figure 15 and Figure 17), which means the difference of calibrated BaP amount on SPME using the two methods could be as large as 200 %. Therefore, splitless liquid injection either with internal standard or without internal standard should not be used to calibrate SPME for BaP.

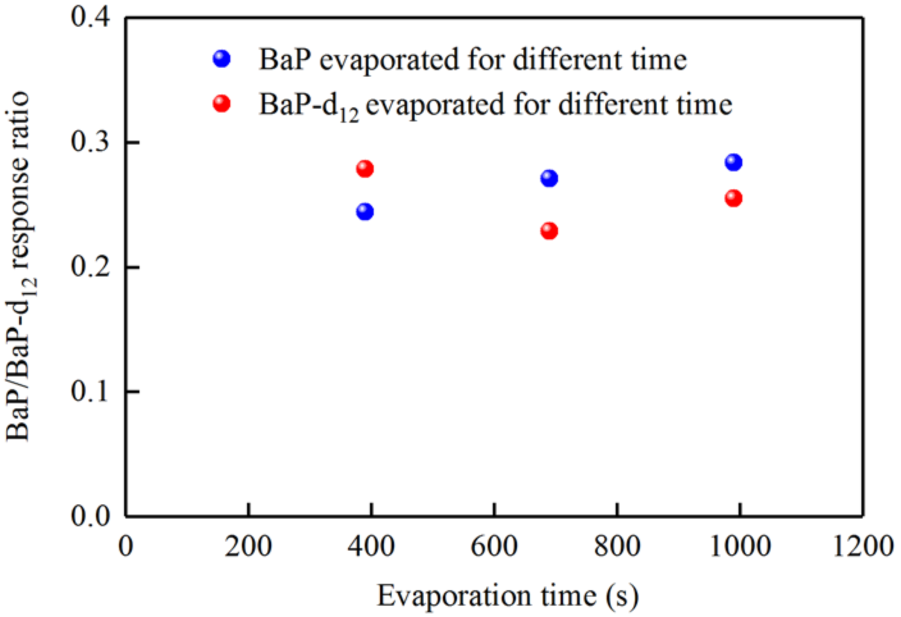


Figure 13. Evaluation of evaporation loss of BaP and BaP-d_{12}. 1 µL BaP solution at 0.6 ng/µL and 1 µL BaP-d_{12} solution at 5 ng/µL were spiked onto the fiber for each sample. T was at (23.3 ± 0.1) °C. RH was at (41.5 ± 2.2) %. V was at (0.41 ± 0.02) m/s.

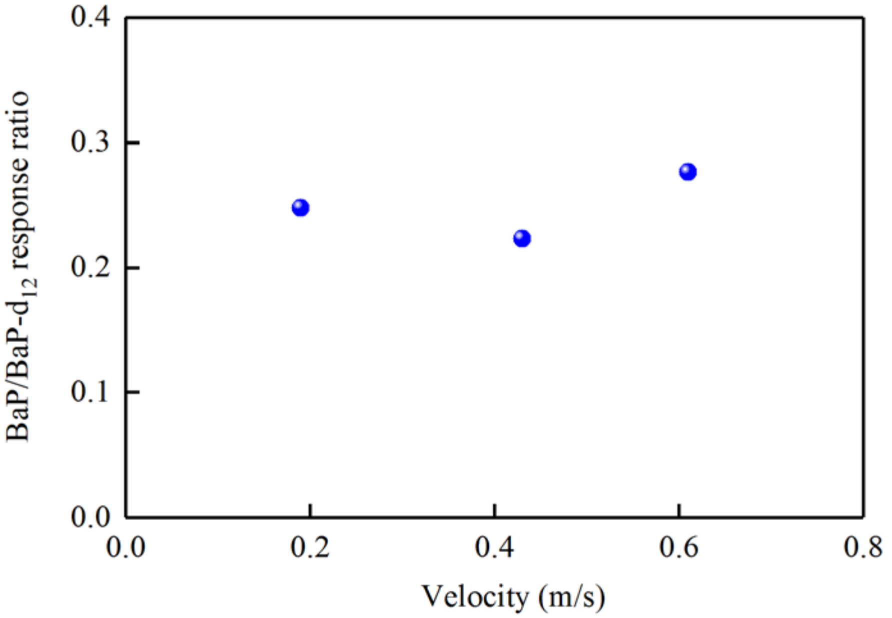


Figure 14. Evaluation of air velocity influence. 1 µL BaP solution at 0.6 ng/µL and 1 µL BaP-d_{12} solution at 5 ng/µL were spiked onto the fiber for each sample. T was at (23.4 ± 0.1) °C. RH was at (50.2 ± 0.4) %.

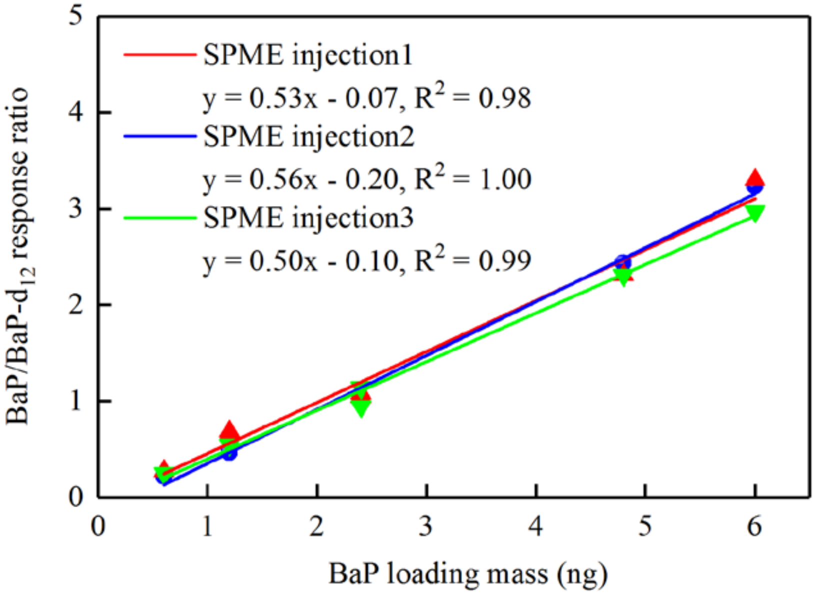


Figure 15 . Standard curves for BaP by SPME injection. 1 µL BaP solution at (0.6 or 1.2 or 2.4 or 4.8 or 6) ng/µL and 1 µL BaP-d12 solution at 5 ng/µL were spiked onto the fiber for each sample. T was at (24.0 ± 1.1) °C. RH was at (52.9 ± 4.3) %. V was at (0.41 ± 0.04) m/s.

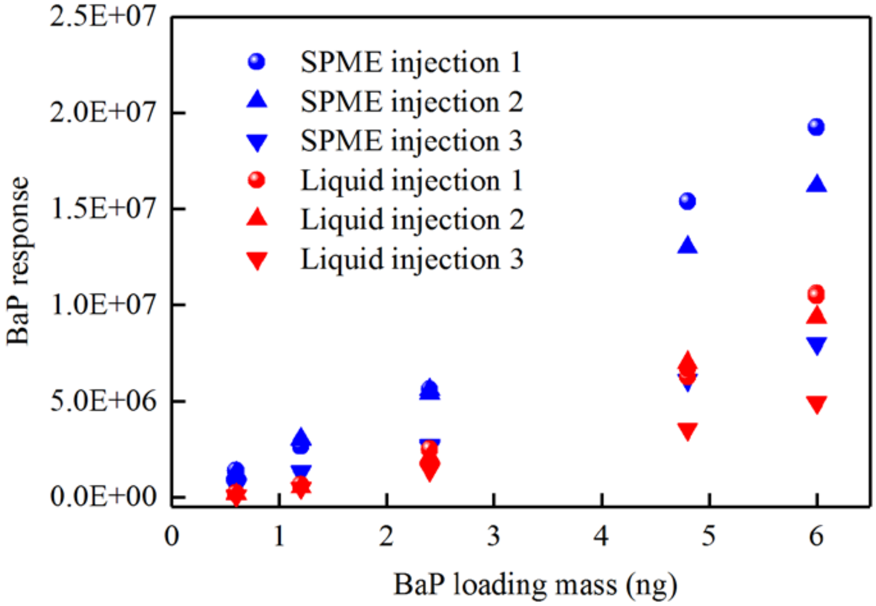


Figure 16. Comparison of BaP absolute response by SPME injection and splitless liquid injection. Three pairs of comparison, i.e. SPME injection 1 and liquid injection 1, SPME injection 2 and liquid injection 2, SPME injection 3 and liquid injection 3, were conducted within 24 hours, separately. GC-MS was not tuned between each pair of SPME injection and liquid injection. 1 µL BaP solution at (0.6 or 1.2 or 2.4 or 4.8 or 6) ng/µL and 1 µL BaP-d12 solution at 5 ng/µL were spiked onto the fiber for each SPME sample. T was at (24.0 ± 1.1) °C. RH was at (52.9 ± 4.3) %. V was at (0.41 ± 0.04) m/s.

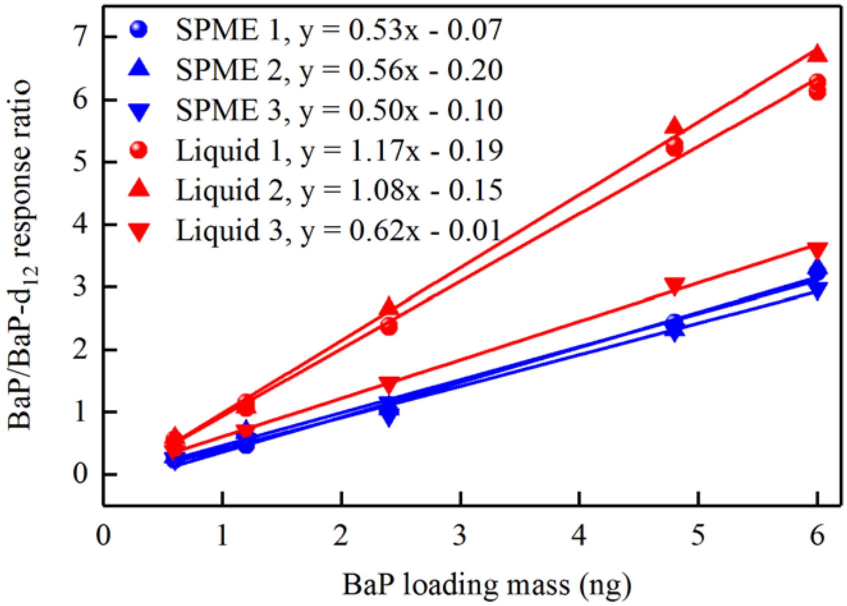


Figure 17. Comparison of BaP and BaP-d_{12} response ratio by SPME injection and splitless liquid injection. R squares for all the curves in this figure are larger than 0.98.

3.2.4 PCB 52

The RSD for response ratios of PCB 52 and ^{13}C PCB 52 for three samples spiked with PCB 52 solution at 0.5 ng/µL and ^{13}C PCB 52 solution at 1 ng/µL were consistent (RSD < 10%, n=3), when PCB 52 evaporated for 480 s and ^{13}C PCB 52 evaporated for 440 s. However, when ^{13}C PCB 52 evaporated for 440 s for each sample while PCB 52 was allowed to evaporate for different times, the response ratio PCB 52 and ^{13}C PCB 52 decreased with the increasing PCB 52 evaporation time. This is similar to what was observed for TCPP as mentioned above. Hence, there was a significant loss of PCB 52 during solvent evaporation, and direct SPME loading should not be used for SPME calibration for PCB 52.

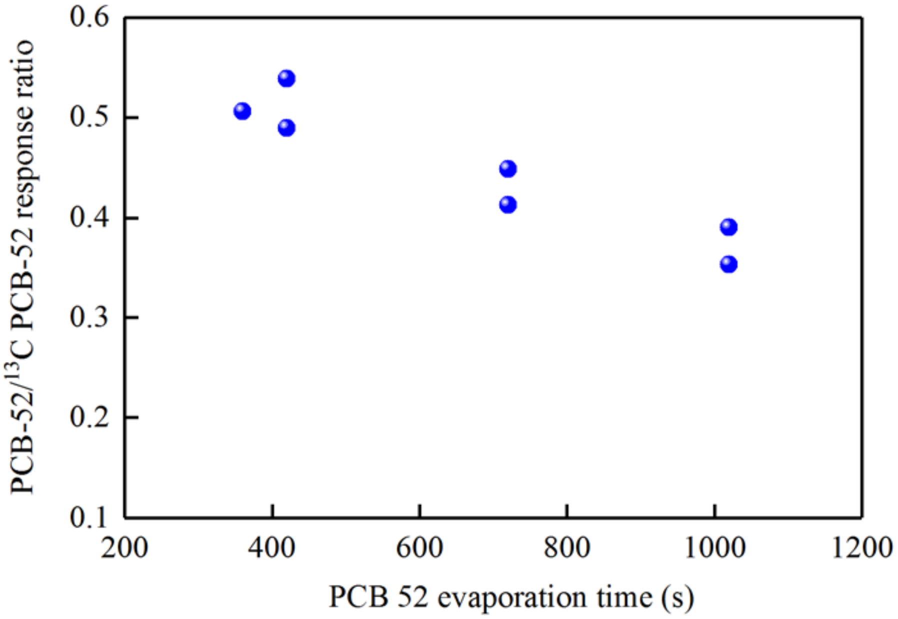


Figure 18. Evaluation of evaporation loss of PCB 52. 1 µL PCB 52solution at 0.5 ng/µL and 1 µL ^{13}C PCB 52 solution at 1 ng/µL were spiked onto the fiber for each sample. T was at (23.6 ± 0.1) °C. RH was at (45.5 ± 0.8) %. V was at (0.46 ± 0.02) m/s.

3.2.5 Summary

A summary of the experiments is shown in Table 6. For the two less volatile chemicals, i.e. BaP and DEHP, the experiments show that direct loading method is appropriate for calibrating SPME. In contrast, for the two more volatile chemicals, TCPP and PCB 52, the evaporation loss experimental results do not support the use of the direct loading method for calibrating SPME.

Table 6. Summary of the direct loading evaluation experiments.

Target chemical	Repeatability[a]	Evaporation loss[b]	Influence of velocity$_{c}$	Linearity of standard curve[d]
TCPP	✓	×	NA[e]	NA
PCB-52	✓	×	NA	NA
DEHP	✓	✓	✓	✓
BaP	✓	✓	✓	✓

[a] ✓ in this column means the relative standard deviation (RSD) of triplicated samples was less than 10%; [b] ✓ in this column means the RSD of samples with different evaporation times was less than 10%; [b] × in this column means the response ratio standard and internal standard showed a decay trend with evaporation time; [c] ✓ in this column means the RSD of samples spiked at different air velocities was less than 10%; [d] ✓ in this column means the R-square of the standard curve was larger than 0.98; [e] NA means “not applicable since previous tests were not sufficient”

3.3 Measurement of y_0

3.3.1 DEHP from PVC flooring

As mentioned in section 2.3.3, the DEHP evaporation loss from the SPME fiber after chamber sampling during the process of spiking DEHP-d_4 was examined. Figure 19 shows that the DEHP evaporation loss is insignificant, with less than 10 % RSD of the DEHP and DEHP-d_4 response ratio for 0.5 h samples (n=3). This low variation indicates that the direct loading method works for SPME sampling from air. The calculated SPME sorption amounts using the standard curves by direct loading for different sampling times and different temperatures are shown in Figure 20a. The sorbed amount of DEHP onto the fiber was linearly correlated with the sampling time ($R^2 > 0.95$). The slope was obtained by linear curve fitting using Origin Pro 2017. With the slope of the curves, the DEHP concentration in chamber air at equilibrium, which equals to y_0, was calculated. The temperature dependence of y_0 can be described by the van't Hoff equation (Figure 17b), which also has been reported by previous studies [19, 22]. The y_0 at 25 °C, 1.8 µg/m^3, measured in this study is somewhat lower than both of the values reported by Wu et al. [26], 2.9 µg/m^3, and Liang et al. [22], 2.4 µg/m^3. The variation of adsorbability for the SPME fiber, as discussed in section 3.4.2 below, may be part of the reason.

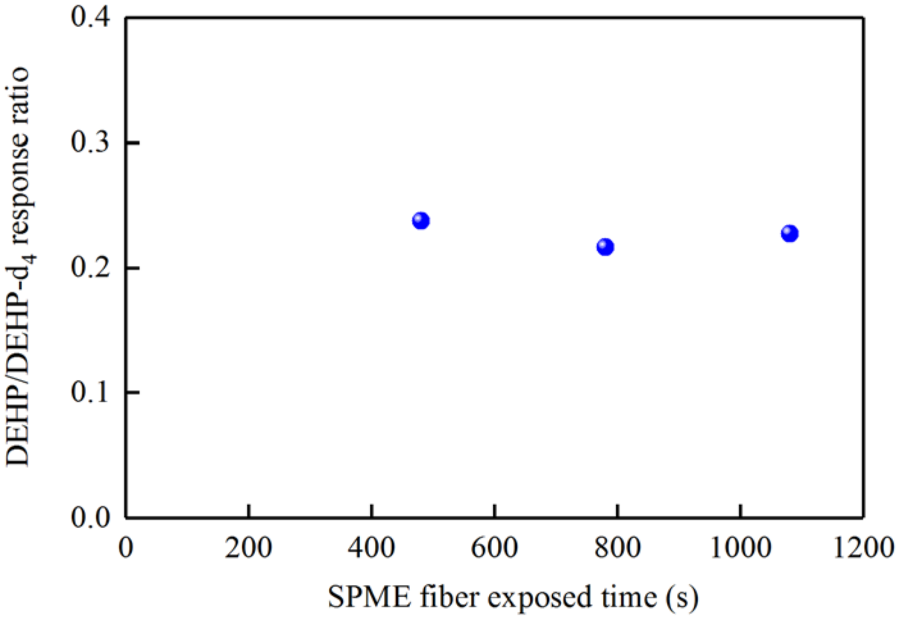
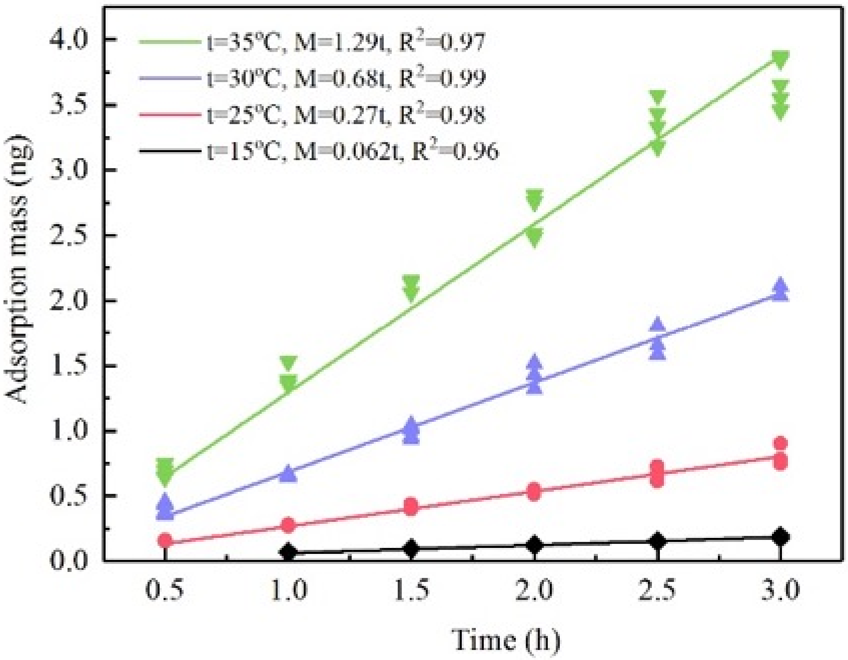
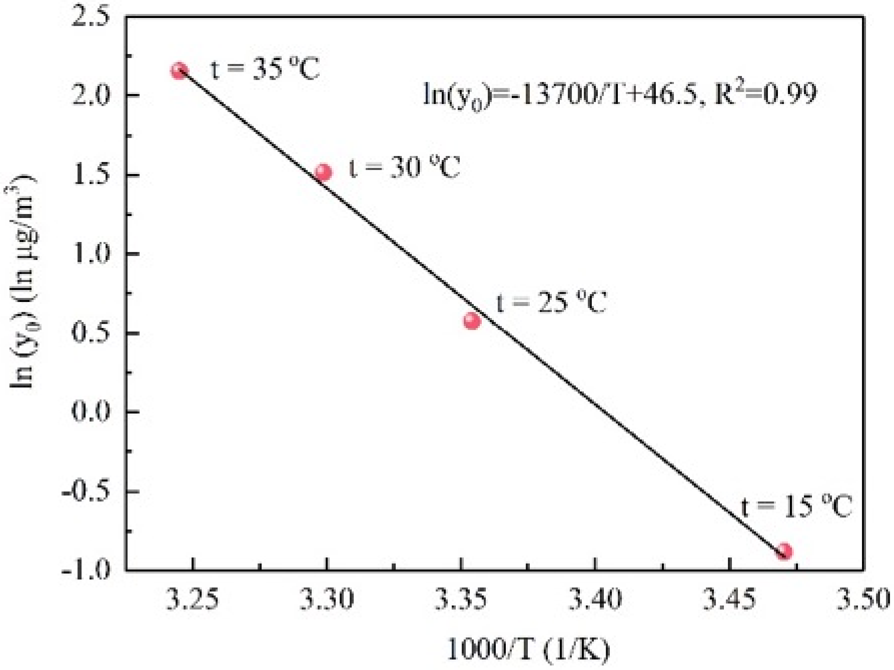


Figure 19. Evaluation of DEHP loss from SPME fiber after chamber sampling during the process of spiking DEHP-d_4. 1 µL DEHP-d_4 solution at 0.9 ng/µL were spiked onto the fiber for each sample. During spiking, T was at (23.6 ± 0.1) °C, RH was at (45.5 ± 0.8) %, and V was at (0.46 ± 0.02) m/s.



(a)



(b)

Figure 20. (a) SPME adsorption amount of DEHP; (b) Relationship between y_0 and temperature

3.4 Potential problems with SPME-based method for determining y_0

A key part of the SPME-based method for measuring y_0 is to calibrate the SPME accurately and consistently. A second key part of the method is that the adsorbability of SPME fiber needs to be stable with time and among different fibers. However, from the experiments we have conducted, we found that it is challenging to spike onto the SPME fiber reliably and the adsorbability of SPME fibers may vary among new fibers or change with time for a single fiber.

3.4.1 Difficulties with SPME calibration

As demonstrated in section 3.2, splitless liquid injection should not be used to calibrate SPME as its injection transfer efficiency typically is much lower than SPME injection. Even when normalizing by the internal standard, the transfer efficiencies are significantly different. Direct syringe loading for calibration of SPME sampling has several advantages over liquid injection methods. The primary advantage is that the SPME standard injector environment more closely mimics the SPME sample injector environment. However, there are some limitations that may limit its application.

Direct syringe loading can only be applied to chemicals with low volatility. For some chemicals, the chemical will evaporate to a significant degree during the solvent evaporation, e.g., TCPP and PCB 52. In addition, it is challenging to define a clear criterion prior to experiments to judge whether the direct loading method will work for a specific chemical or not. Therefore, there is a need for time consuming evaluation of direct loading for every target chemical before applying this method.

Due to the small diameter of SPME fiber, i.e., 110 μm, it was difficult to consistently spike 1 μL of liquid onto the fiber. Whether the 1 μL of liquid can be fully transferred to SPME fiber depends on the skill of the operator and spiking angle, which is difficult to control. A skillful operator can still fail to fully spike the liquid onto the fiber even after hundreds of spikes. Another limitation of the direct SPME loading method is that in the calibration experiments, SPME can only be injected in a time-consuming manual operation.

3.4.2 Difficulties with SPME fiber

To examine the difference of adsorption capability between different fibers, three fibers were used to take samples from the chamber described in section 2.3.3 at 25 °C. Among the three tested fibers, two "old" fibers were conditioned or desorbed in the GC-inlet for more than 100 hours, while one "new" fiber was conditioned or desorbed for only about 3 hours. The results in Figure 21 show that the response of samples taken by the same fiber was consistent (RSD < 10 %), while the response of samples taken by the new fiber was about 1.7 times of the samples taken by the old fibers. This difference may be a potential reason for the lower y_0 measured in this study (one of the "old" fibers was used) compared to the reported values, as discussed in section 3.3.1. The difference of adsorption properties between fibers may result from the difference between fibers when they are produced or aging of fibers as they are being desorbed or conditioned. Regardless of the reason for the difference between the fibers, the significant variability of adsorbability prevents the application of the SPME-based method for y_0 measurements when high accuracy is required for y_0.

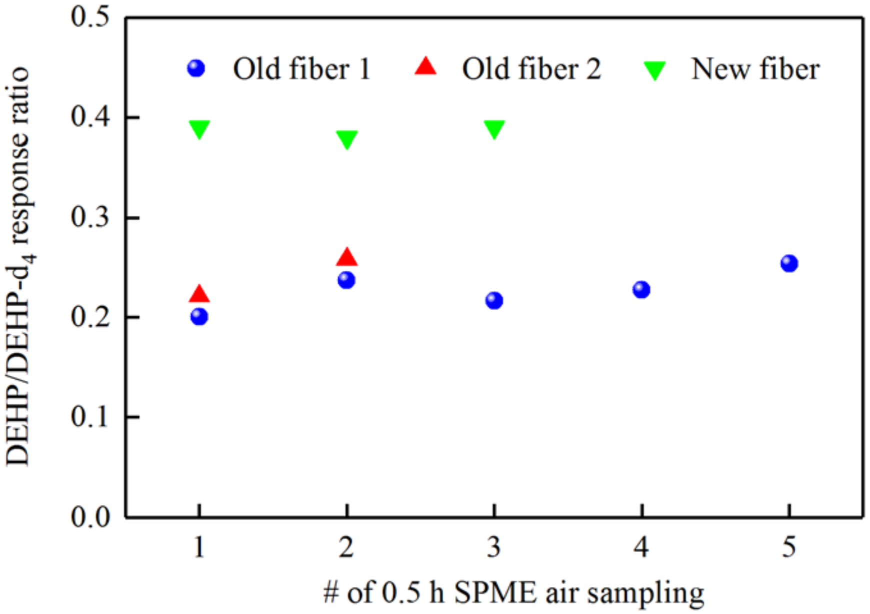


Figure 21. Comparison of adsorption property for different SPME fibers. Each point in this figure represents a 0.5 h sample from the chamber described in section 2.3.3.

4. Conclusions

The objective of these studies was to measure y_0 for TCPP from polyurethane foam and for DEHP from PVC flooring, and the following work was completed:

(1) TCPP concentrations in both open-cell SPF and closed-cell SPF have been measured. C_0 for TCPP in open-cell SPF was 1.24 x 10^6 mg m^{-3}, while C_0 for TCPP in closed-cell SPF was 2.84 x 10^5 mg m^{-3}.

(2) An improved method to calibrate chemicals collected on SPME fibers was evaluated in detail. It was shown, for DEHP and BaP, the direct SPME loading method is appropriate for calibrating masses collected on SPME fibers. However, this was not true for more volatile chemicals (TCPP and PCB 52). Unfortunately, the application of the direct loading method may be limited due to the following reasons: the need of evaluation for every target chemical, the physical challenge of spiking onto the fiber and the variability of SPME fiber's adsorbability. In addition, the transfer efficiency of splitless liquid injection were typically much lower than the transfer efficiency of SPME injection. Hence, splitless liquid injection should not be used to calibrate SPME for the SVOCs studied.

(3) Experiments have been conducted to measure y_0 of DEHP from PVC flooring at different temperatures using the SPME-based method and a specially-designed stainless-steel chamber. Specifically, the measured value y_0 of DEHP from PVC flooring at 25 °C was 1.8 μg/m^3. However, due to the potential problems relating to the variability of SPME fiber's adsorbability, the variability of measured y_0 may be as large as a factor of two.

Overall, given the potential significant drawbacks of SPME-based method, it is not recommended for measuring y_0 of SVOCs from building materials until the problems relating to SPME calibration and the variability of SPME fiber's adsorbability are overcome.

5. Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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