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Development of new analytical and measurement methods for characterizing the emission of phthalates from building and consumer materials into indoor air

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Abstract. Phthalates are ubiquitous indoor organic pollutants that are found in different building and consumer materials and are known to cause severe human health problems. In this paper, the emission of these compounds from vinyl floorings (VF) into indoor air has been studied using Automated Thermal Desorption-Gas Chromatography-Mass Spectroscopy (ATD-GC-MS) and a special device known as micro-chamber or thermal extractor (μ -CTETM). So a robust analytical ATD-GC-MS method has been developed and validated to analyse eight selected phthalates. Calibration curves were linear ($R^2 > 0.99$), limit of detection (LOD) was down to 0.004 $\mu\text{g}/\text{m}^3$, and the values of relative standard deviation (RSD) were less than 15% for all chosen phthalates. Then, a new micro-chamber measurement method based on diffusion has been developed for studying the emission of Diisononyl phthalate (DiNP) and Di-n-octyl phthalate (DnOP) from VF at different temperatures and estimating y_0 (gas-phase concentration of phthalates on the surface of the material). This method was quite repeatable with 11% RSD for DiNP and 8% for DnOP.

Keywords. Phthalates, ATD-GC-MS, micro-chamber, vinyl floorings, y_0 , temperature

1. Introduction

Semi-Volatile Organic Compounds (SVOCs) are organic molecules of vapor pressure ranging between 10^{-9} and 10 Pa [1] and boiling temperature between 240 to 400 °C [2]. Phthalates, a family of SVOCs, are a group of synthetic chemical compounds that are commonly and widely used in daily used consumer products [3], [4], [5]. They are added as plasticizers and solvents to polyvinyl chloride (PVC) floorings, wall coverings, electrical cables, and personal care products to enhance their properties [6]. These compounds are physically bound to the polymers to which they are added and thus are susceptible to leach from their hosting materials and be slowly emitted into indoor environments [4], [5], [7]. Therefore, they are considered ubiquitous indoor pollutants [8]. Phthalates are of great research interest due to their potential effect on human health. Research studies have showed that phthalates cause development and reproductive problems, asthma, and allergies in children [9].

Due to their complex physico-chemical properties, SVOCs are greatly partitioned between gaseous and particulate phases. Therefore, phthalates can be found in both gaseous phase and adsorbed on airborne particles, dust, other indoor surfaces, and even residents' bodies [10], [11], [12]. Adsorption on indoor surfaces is known as sink effect. Therefore, humans, especially children, are greatly exposed to phthalates in indoor environments through ingestion, inhalation, and dermal contact [13].

However, few studies are available on SVOCs present in indoor air compared to the ones that study their presence in settled dust [14] or in soil or water [15]. The gas-phase concentration of phthalates in equilibrium with the material surface (y_0) is the key parameter controlling phthalates



emissions into indoor air [13]. Therefore, knowing y_0 is important to estimate the gas-phase concentration of phthalates in indoor environments, and thus predict the risk of human exposure to these compounds.

Several measurements, sampling, and analytical methods have been developed for characterizing the emission of phthalates from indoor materials into indoor air. Measurement methods are categorized as either laboratory or on-site methods. Laboratory measurement methods includes the 1 m³ test chamber, desiccator [16], chamber of laboratory investigations of materials, pollution, and air quality (CLIMPAQ) [5], and sandwich method [13] while on-site ones include field and laboratory emission cell (FLEC) [17], adsorbent tube [18], passive flux sampler (PFS) [19], [20], and an emission cell coupled to (solid-phase micro-extraction) (SPME) [21]. Samples are collected differently using polyurethane foam (PUF), adsorbent tubes (e.g. Tenax TA tubes), solid-phase micro-extraction (SPME), glass fiber filter, or active carbon disk. The collected samples are then either subjected to direct injection or thermal desorption and gas chromatography connected to mass spectroscopy (GC-MS). Automated thermal desorption (ATD) is of higher sensitivity compared to the liquid one. However, background interferences and poor desorption efficiency make it necessary to develop a new analytical method that allows sensitive and accurate analysis of SVOCs [15]. Contamination, in addition to sink effect, is the bottleneck in the analysis of phthalates emitted from indoor materials and thus in determining y_0 . Therefore, every developed measurement method has its limitation including long time for emission to reach steady state, the need of a lot of equipment, or the small sampling surface.

So the objectives of this study are to divided into two parts: 1) Develop and validate a robust and sensitive ATD-GC-MS method for the characterization of eight phthalates selected based on their abundance in indoor environments and the health effects they cause. However, only the validation of this developed method by its performance will be mentioned in this paper. 2) Develop a rapid laboratory measurement method for determining y_0 of emitted phthalates from vinyl floorings using the micro-chamber device.

2. Materials and methods

2.1. Chemicals

To develop the ATD-GC-MS method, eight pure standard phthalates (purity > 98%) (table 1) were purchased from different suppliers: Sigma Aldrich, Acros, and Alfa Aesor. Tetradeuterium ring labeled DEHP (DEHP-d₄, purity > 99%) was used as internal standard and bought from Sigma Aldrich. Stock solutions of the chosen chemicals were prepared in our laboratory using methanol (purity ≥ 99.9%) provided by Honeywell as a solvent. Calibration solutions, in the range of 7 to 1200 ng for DiNP and DiDP and 2 to 400 ng for all other phthalates, were prepared by serial dilutions of the stock solution using also methanol. Tenax TA tubes (60/80 mesh) with glass wool inside, provided by Antelia, were spiked by a 1 μL of DEHP-d₄ solution and 1 μL of the prepared diluted solutions of phthalates (7 levels).

Table 1. The different used phthalates to develop the ATD-GC-MS method.

<i>Phthalate</i>	<i>Abbreviation</i>	<i>Molecular Formula</i>	<i>CAS No.</i>	<i>Ion for SIM acquisition (m/z)</i>
Dimethyl phthalate	DMP	C ₁₀ H ₁₀ O ₄	131-11-3	163
Diisobutyl phthalate	DiBP	C ₁₆ H ₂₂ O ₄	84-69-5	149
Dibutyl phthalate	DBP	C ₁₆ H ₂₂ O ₄	84-74-2	149
Butyl benzyl phthalate	BBP	C ₁₉ H ₂₀ O ₄	85-68-7	149
Bis(2-ethylhexyl) phthalate	DEHP	C ₂₄ H ₃₈ O ₄	117-81-7	149
Di-n-octyl phthalate	DnOP	C ₂₄ H ₃₈ O ₄	117-84-0	149
Diisononyl phthalate	DiNP	C ₂₆ H ₄₂ O ₄	28553-12-0	293
Diisodecyl phthalate	DiDP	C ₂₈ H ₄₆ O ₄	26761-40-0	307
Bis(2-ethylhexyl) phthalate-d ₄	DEHP-d ₄	C ₂₄ D ₄ H ₃₄ O ₄	93951-87-2	153

2.2. Instrumentation

2.2.1. ATD-GC-MS method. The development of a robust analytical ATD-GC-MS method was done using an ATD (TurboMatrix) coupled to a GC (XL) - MS (TurboMass) Perkin-Elmer system. This occurred in terms of temperature, time, outlet split, type of column, and type of adsorbent tubes. A DB-5MS (5% diphenyl 95% dimethyl polysiloxane) GC column of 60 m length, 0.25 mm internal diameter, and 0.25 μm film thickness was used. Tenax TA tubes are exhibited to a two-stage thermal desorption and the MS was operated in SIM mode (table 1). To validate this method, limits of detection (LOD) and quantification (LOQ) and repeatability or relative standard deviation (RSD) were determined. LOD and LOQ are defined as 3 and 10 times the standard deviation at the lowest dilution level, respectively: 7 g for DiNP and DiDP and 2 ng for all other 6 phthalates.

2.2.2. Micro-chamber. The micro-chamber or thermal extractor is a dynamic sampling device fabricated by Marked International [22]. It is made of four stainless steel cells (114 ml capacity) that are airtight, with a constant flow of clean dry or humid air traversing through. This type of test chambers was recommended by ISO 16000 -25 for studying the emissions of SVOCs from building and consumer materials [2].

2.3. Preparation of the micro-chamber and test pieces

Before each experiment, the micro-chamber was thoroughly cleaned. Blank tests using Tenax TA tubes were done to verify the absence of contamination.

Two vinyl floorings (VF_1 and VF_2) were chosen as sources of emission of phthalates. Rapid qualitative scanning using the micro-chamber was done to check the phthalates emission of these two VFs. VF_1 contains DiNP and VF_2 contains DnOP.

When starting the experiment, tiles of the same diameter of the cells of the micro-chamber were cut, their back was covered with aluminum foil to limit emission to the surface [2], and then put in the bottom of the micro-chamber. Temperature and flow rate were adjusted to the desired values and sampling occurred after an equilibration period of 20-30 min [22]. Every test piece was used once to ensure a continuous emission source of phthalates.

2.4. Emission experiments

Emissions of DiNP and DnOP from VF were characterized at different temperatures using the micro-chamber. The sampling time was regulated depending on the temperature so that sampling tubes are not saturated and enough amount of phthalates was collected. Sampling occurred continuously using Tenax TA tubes spiked with DEHP-d4 until steady state in the micro-chamber is reached. Backup tubes were connected to each primary sample tube to check for breakthrough. No breakthrough was observed in any of the tests. The collected samples were then analyzed using the developed ATD-GC-MS method. y_0 was determined according to the model developed by Xu and Little [23] that was later simplified by Xu et al. [24]:

$$y_0 = \frac{Q \cdot y_{SS}}{A \cdot h_m} + y_{SS} \quad (1)$$

Where Q is the air flow rate into the micro-chamber (m^3/s), y_{SS} is the steady-state gas-phase concentration of phthalates ($\mu\text{g}/\text{m}^3$), A is the area of emission surface (m^2), and h_m is the convective mass transfer (m/s).

3. Results

3.1. Validation of the developed ATD-GC-MS method

A robust ATD-GC-MS method has been developed and validated for characterizing the eight selected phthalates. The GC-MS chromatograms obtained are shown in figure 1 and the obtained calibration curves (with 5-6 points) are shown in figure 2.

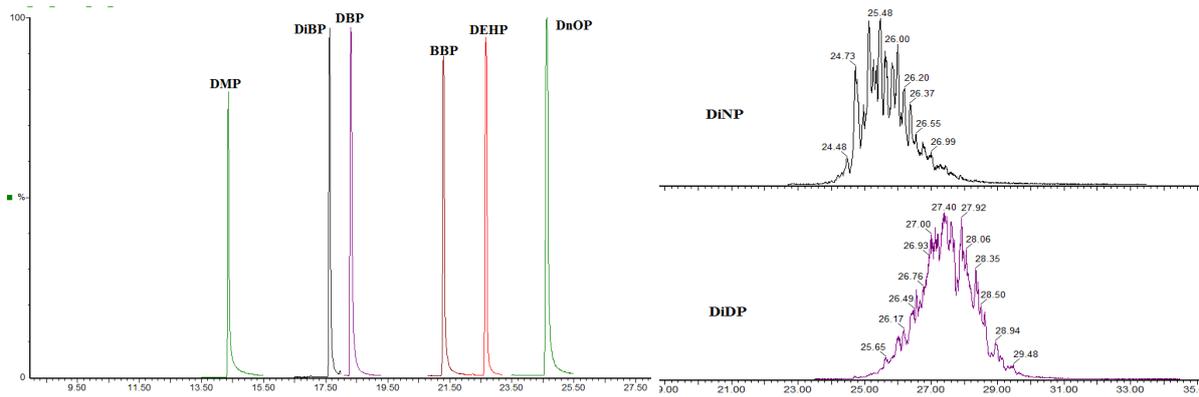


Figure 1. Chromatograms of eight selected phthalates using the developed ATD-GC-MS method.

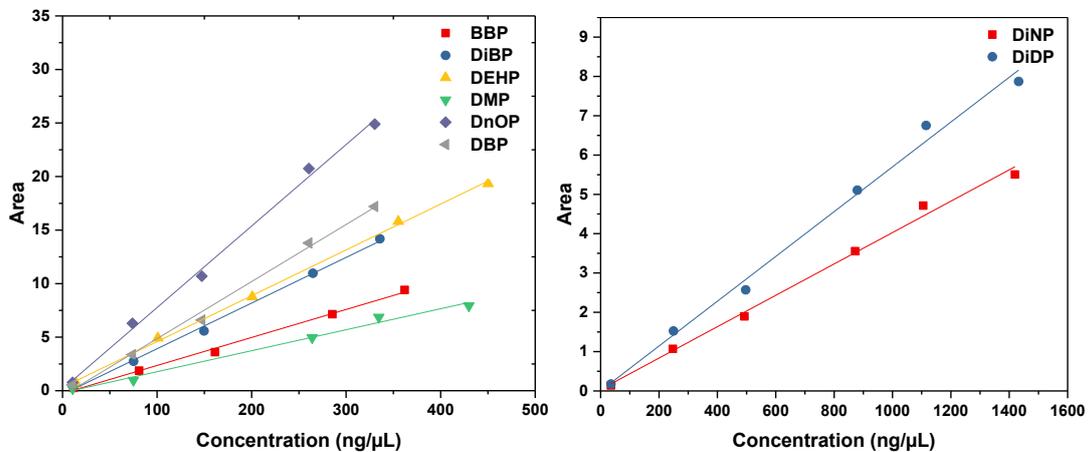


Figure 2. Linearity profile of the calibration curves of eight selected phthalates using the developed ATD-GC-MS method.

3.2. Development of the micro-chamber method

When studying the emission of phthalates from VF using the micro-chamber, y_0 of DiNP increased from $3.4 \mu\text{g}/\text{m}^3$ at 25°C to $291.3 \mu\text{g}/\text{m}^3$ at 80°C , and that of DnOP from $0.5 \mu\text{g}/\text{m}^3$ at 40°C to $24.7 \mu\text{g}/\text{m}^3$ at 80°C . Moreover, the time to reach steady state decreased from 13 days at 25°C to few hours at 80°C for DiNP and from 7 days at 40°C to few hours at 80°C for DnOP (figure 3).

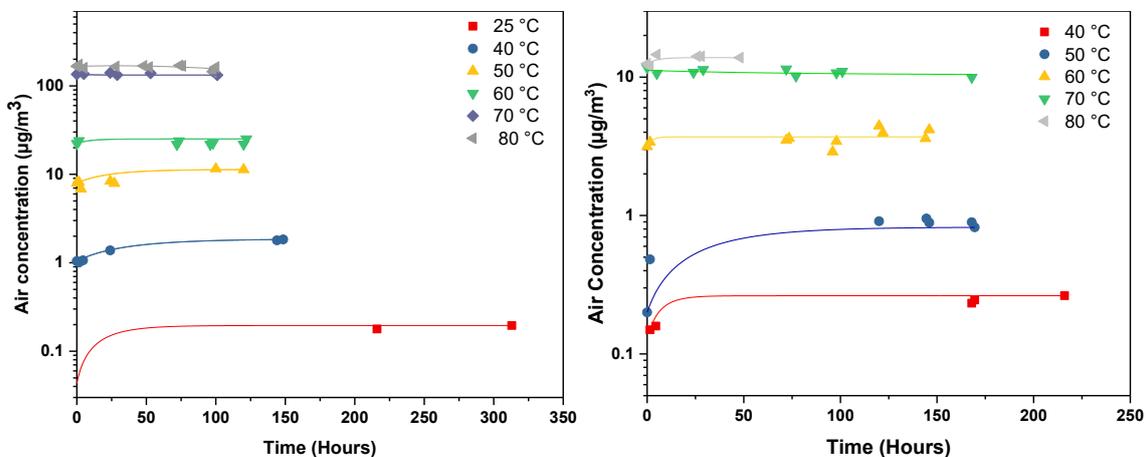


Figure 3. The emission of DiNP (left) from VF₁ and DnOP (right) from VF₂ at different temperatures in the micro-chamber.

4. Discussion

4.1. Validation of the developed ATD-GC-MS method

As shown in the chromatograms of figure 1, all peaks of the 6 chosen phthalates were well separated while DiNP and DiDP signals appear as several peaks since they are composed of a mixture of isomers. The calibration curves were linear and repeatable (3 times) with a correlation coefficient (R^2) of > 0.99 and RSD value between 10 and 15% for all eight chosen phthalates. LOD and LOQ range from 0.004 to 0.02 $\mu\text{g}/\text{m}^3$ and from 0.01 to 0.06 $\mu\text{g}/\text{m}^3$, respectively for an air sampling volume of 72 L at 25 °C.

4.2. Development of the micro-chamber method

Since phthalates are inter-molecularly bound to the resin chains of the materials, the increase in temperature increases the thermal motion of molecular chains and thus liberates phthalates from the material [25], and this is why the y_0 values of emitted DiNP and DnOP increased with increasing temperature. Moreover, adsorption of phthalates on the surfaces of the device is more important at lower temperatures than at higher ones [26] and is greatly affected by its volume [16]. Therefore, the small volume of the cells of the micro-chamber and the ability to heat it up to a high temperature [2] decreased the time to reach steady state as temperature increased. The obtained results were quite repeatable at 40 °C with an RSD value of 11% for DiNP and 8% for DnOP.

However, the main difficulty in studying phthalates remains the contamination of the different used equipment due to their complex physico-chemical properties (high molecular weight and low vapour pressure). This therefore demands intense cleaning of the micro-chamber and the different systems used to make sure that no traces of phthalates are left and eliminate any uncertainties.

5. Conclusion

A robust and sensitive analytical ATD-GC-MS method has been developed and validated for the quantification of eight selected phthalates. This method was applied in developing the micro-chamber measurement method. This latter is a promising method for the characterization of the emission of phthalates from building and consumer materials and determining their y_0 , which is a key parameter in determining the risk of human exposure to these compounds in indoor environments. The small volume of the cells of the micro-chamber and the ability to heat it up to a high temperature reduce sink effect. This method, once fully developed, can be used for:

1. Rapid identification and quantification of the different phthalates emission from different building and consumer materials
2. Predicting the risk of human exposure to these compounds by determining y_0
3. Legislating the material of interest based on its content of phthalates before putting in market.

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