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THÈSE

UNIVERSITE DE PAU ET DES PAYS DE L'ADOUR
Ecole Doctorale Sciences Exactes et leurs Applications

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par **Tamara BRAISH**

pour obtenir le grade de docteur
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Spécialité : **Chimie Analytique et Environnement**

DEVELOPMENT OF SENSITIVE ANALYTICAL AND MEASUREMENT METHODS FOR CHARACTERIZING THE EMISSIONS OF SVOCs FROM BUILDING AND CONSUMER MATERIALS INTO INDOOR AIR

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To my parents

To me, myself, and I

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“No one who achieves success does so without the help of others.” - Alfred North Whitehead

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Abstract

Semi-volatile organic compounds (SVOCs), including phthalates and organophosphorus flame retardants (OPFRs), are used in many building and consumer materials. They are added to different indoor materials in order to enhance their properties as plasticizers or flame retardants. Because of their specific physico-chemical properties, these compounds emitted by the materials can be present both, in the gaseous phase and adsorbed on internal surfaces and dust. As a result, human exposure pathways to SVOCs in indoor environments are multiple leading to complex health risk assessment. In this context, the emission of materials or products, sources of these pollutants in indoor environments, must be characterized.

Many measurement methods have been developed to study the emissions of SVOCs from indoor products and materials. However, these methods still have drawbacks and limitations, in particular due to adsorption of these compounds on the walls of the emission test chambers. In addition, few studies deal with OPFRs and there is no existing method for simultaneously evaluating phthalates and OPFRs emissions. The objective of this work is therefore to develop a new method to characterize the gaseous emissions of phthalates and OPFRs from the materials.

This work is divided into two parts:

- The development of a robust protocol and an innovative method for the characterization of phthalates and OPFRs emitted from vinyl flooring and polyurethane foams (PUF), respectively. For this, a micro-emission test chamber (μ -CTE) recommended by the ISO 16000-25 standard was used. This device allows to carry out tests at temperatures up to 250 °C, which makes it possible to limit the phenomenon of adsorption of the compounds on the walls of the system and to reduce the time of experimentation. Phthalates and OPFRs emitted in the gaseous phase were collected using adsorbent tubes analyzed after by thermal desorption - gas chromatography - mass spectrometry (TD-GC-MS).
- The development of the TD-GC-MS analytical method, including the optimization of the adsorbent tubes desorption parameters and chromatographic parameters in order to be able to simultaneously analyze phthalates and OPFRs at low air concentration levels (at the level of $\mu\text{g}/\text{m}^3$).

The methodology developed enables determining the gas-phase concentration of phthalates and OPFRs in equilibrium with material surface (y_0). Two approaches have been implemented: direct

measurement of y_0 at room temperature by optimizing the volume of the test chamber and extrapolation from y_0 values determined at higher temperatures based on an obtained linear relationship between $\ln(y_0)$ and the reciprocal of temperature adapted from the Clausius-Clapeyron equation. The methodology was validated on vinyl flooring samples and PUF padding. It can be generalized to other materials or products and thus lead to a better understanding of the impact of phthalates and RFOP on indoor air quality and health. It can also be tested for other families of SVOCs.

Keywords:

Semi-volatile organic compounds (SVOCs), analytical and measurement methods, materials emission, indoor air, micro-chamber, y_0

Résumé

Les Composés Organiques Semi-Volatils (COSV), notamment les phtalates et retardateurs de flamme organophosphorés (RFOP), entrent dans la composition de nombreux matériaux de construction et produits de consommation. En effet, ils confèrent à ces produits des caractéristiques techniques spécifiques en tant que plastifiants ou retardateurs de flamme. Du fait de leurs propriétés physico-chimiques spécifiques, ces composés émis par les matériaux peuvent être présents à la fois en phase gazeuse mais également en phase adsorbée sur les surfaces et les poussières intérieures. Par conséquent, les voies d'exposition aux COSV dans les environnements intérieurs sont multiples, et l'évaluation des risques sanitaires complexe. Dans ce contexte, l'émission des matériaux ou produits, sources de ces polluants dans les environnements intérieurs, doit être caractérisée.

De nombreuses méthodes de mesure ont été mises au point pour étudier les émissions de COSV à partir de produits et de matériaux d'intérieur. Mais, celles-ci présentent encore des inconvénients et des limites, notamment dus aux effets d'adsorption sur les parois des chambres d'essai d'émission. De plus, peu d'études traitent des RFOP et aucune méthode ne permet d'évaluer simultanément les émissions de phtalates et de RFOP. L'objectif de ce travail est donc de développer une nouvelle méthode pour caractériser les émissions gazeuses de phtalates et RFOP émis par les matériaux.

La thèse comporte deux parties principales :

- Le développement d'un protocole robuste et d'une méthode innovante de caractérisation de phtalates et de RFOP émis respectivement par des revêtements de sol en vinyle et des mousses de polyuréthane. Pour cela, une micro-chambre d'essai d'émission (μ -CTE), recommandée par la norme ISO 16000-25 a été utilisée. Ce dispositif permet de réaliser des essais à des températures allant jusqu'à 250 °C, ce qui permet de limiter le phénomène d'adsorption des composés sur les parois du système et de réduire les temps d'expérimentation. Les phtalates et RFOPs émis en phase gazeuse ont été prélevés au moyen de cartouches d'adsorbant analysées par ThermoDésorption-Chromatographie Gazeuse - Spectrométrie de Masse (TD-GC-MS).
- Le développement de la méthode d'analyse par TD-GC-MS, incluant l'optimisation des paramètres de désorption des cartouches et les paramètres chromatographiques dans le but de pouvoir analyser simultanément les phtalates et les RFOPs à des niveaux de concentrations faibles dans l'air (inférieurs au $\mu\text{g}/\text{m}^3$).

La méthodologie développée permet de déterminer la concentration de phtalates et de RFOP en phase gazeuse en équilibre avec la surface de matériaux (γ_0). Deux approches ont été mise en œuvre : mesure directe de γ_0 à température ambiante en optimisant le volume de la chambre d'essai et extrapolation à partir de valeurs de γ_0 obtenues à des températures plus élevées selon une relation linéaire entre $\ln(\gamma_0)$ et l'inverse de la température adaptée de l'équation de Clausius-Clapeyron. La méthodologie a été validée sur des échantillons de revêtements de sol en vinyle et des mousses de rembourrage en polyuréthane. Elle peut donc être généralisée à d'autres matériaux ou produits et ainsi conduire à une meilleure connaissance de l'impact des phtalates et RFOP sur la qualité de l'air intérieur et la santé. Elle peut également être testé pour d'autres familles de COSV.

Mots Clés :

Composés organiques semi-volatils (COSV), méthodes d'analyse et de mesure, émission de matériaux, air intérieur, micro-chambre, γ_0

List of Abbreviations

ACH: Air Change Rate

ADEME: Environment and Energy Management Agency

AFRs: Alternative Flame Retardants

AgBB: German Committee for Health-related Evaluation of Building Products

amu: Atomic Mass Unit

ANSES: French Agency for Food, Environmental and Occupational Health & Safety

BBP: Benzyl Butyl Phthalate

BFRs: Brominated Flame Retardants

\overline{CF} : Mean Calibration Factor

CFD: Computational Fluid Dynamics

CI: Chemical Ionization

CLIMPAQ: Chamber of Laboratory Investigations of Materials, Pollution, and Air Quality

CLP: Classification, Labelling, and Packaging

CMR: Carcinogenic, Mutagenic, or Reproduction toxic

CSTB: Centre Scientifique et Technique du Bâtiment

C18: Carbon 18

DBP: Dibutyl Phthalate

DEHP: Di(2-ethylhexyl) Phthalate

DEHP-d4 : Deuterated DEHP

DEP: Diethyl Phthalate

DI: Direct Injection

DiBP: Diisobutyl Phthalate

DiDP: Diisodecyl Phthalate

DiNP: Diisononyl Phthalate

DMEP: Di(methoxyethyl) Phthalate

DMP: Dimethyl Phthalate

DnHP: Di-n-hexyl Phthalate

DnOP: Di-n-octyl Phthalate

EI: Electron Impact

EPA: Environmental Protection Agency

ER: Emission Rate

FLEC: Field and Laboratory Emission Cell
FRs: Flame Retardants
FID: Flame Ionization Detector
FPD: Flame Photometric Detector
He: Helium Gas
HPLC: High Performance Liquid Chromatography
ICL: Indoor Climate Label
IAQ: Indoor Air Quality (QAI in French)
LOD: Limit of Detection (LD in French)
LOQ: Limit of Quantification (LQ in French)
MDL: Method Detection Limit
MIMS: Membrane Introduction Mass Spectrometry
NA and ND: Not Determined
NBFRs: Novel Brominated Flame Retardants
NI-CIMS: Negative Ion-Chemical Ionization Mass Spectrometry
OPs: Organophosphorus
OpenFOAM: Open Source Field Operation and Manipulation
OPFRs: Organophosphorus Flame Retardants (RFOP in French)
OQAI: Indoor Air Quality Observatory
PAHs: Polycyclic Aromatic Hydrocarbons
PBBs: Polybrominated Diphenyls
PBDEs: Polybrominated Diphenyl Ethers
PCBs: Polychlorinated Biphenyls
PDMS: Polydimethylsiloxane
PFRs: Phosphorus Flame Retardants
PFS: Passive Flux Sampler
PUF: Polyurethane Foam
PVC: Polyvinyl Chloride
PTR-MS: Proton Transfer Mass Spectrometry
R, R', R1, R2, R3: Alkyl Radicals
Re: Reynold's Number
REACH: Registration, Evaluation, Authorization, and Restriction of Chemicals
RH: Relative Humidity
RoHS: Restriction of Hazardous Substances

RSD: Relative Standard Deviation
RT: Retention Time
SD: Standard Deviation
SIM: Single Ion Monitoring
Sh: Sherwood Number
SPME: Solid-Phase Microextraction
STDC: Symmetrical Thin Diffusion Chamber
SVHC: Substance of Very High Concern
SVOCs: Semi-Volatile Organic Compounds (COSV in French)
TBP: Tributyl Phosphate
TBEP: Tri(2-butoxyethyl) Phosphate
TiBP: Triisobutyl Phosphate
TCEP: Tri(2-chloroethyl) Phosphate
TCP: Tricresyl Phosphate
TCPP: Tri(2-isochloropropyl) Phosphate
TDCPP: Tris(1,3-dichloro-2-propyl) Phosphate
TD-GC-MS: Thermal Desorption-Gas Chromatography-Mass Spectrometry
TEP: Triethyl Phosphate
TEHP: Tri(2-ethylhexyl) Phosphate
THPS: Tetrakis(hydroxymethyl) Phosphonium Sulfate
TMPP: Tris(methylphenyl) Phosphate
TPP: Triphenyl Phosphate
TSVOCs: Total Semi-Volatile Organic Compounds
TVOCs: Total Volatile Organic Compounds
TXP: Trixylenyl Phosphate
VOCs: Volatile Organic Compounds
VUV: Vacuum Ultraviolet
VVOCs: Very Volatile Organic Compounds
WHO: World Health Organization (OMS in French)
 μ -CTE: Thermal Extractor

List of Symbols

A: Emission Surface Area (m^2)

A_S : Sorption Surface Area (m^2)

B_{im} : Mass Transfer Biot Number

C_a : Equilibrium Concentration of the Compound in Air ($\mu g/ m^3$)

C_{dust} : Equilibrium Concentration of Compound in Dust ($\mu g/ g$)

C_{hum} : Equilibrium Concentration of the Compound fixed in Organic Matter on Human Skin ($\mu g/ m^3$)

C_{part} : Equilibrium Concentration of the Compound fixed on Particles ($\mu g/ m^3$)

C_m : Concentration of Compounds Sorbed on Clothes ($\mu g/ m^3$)

C_{surf} : Equilibrium Concentration of the Compound fixed in Organic Matter on a Fixed Surface ($\mu g/ m^3$)

C_0 : Initial Concentration of Compounds in the Material ($\mu g/ m^3$)

C2: Constant

$D = D_a$: Diffusion Coefficient of the compound in the air (m^2/ s)

d: Diffusion Distance (m)

E: Emission Rate ($\mu g/ m^2 \cdot h$)

$F_{om-Dust}$: Volume Fraction of Organic Matter Associated with Settled Dust

$F_{om-Part}$: Volume Fraction of Organic Matter Associated with Particles

h_m : Mass Transfer Coefficient (m/ s)

h_s : Convective Mass Transfer Coefficient near the Sorption Surface (m/ s)

i.d: GC-Column Internal Diameter (m)

K: Material/ Air Partitioning Coefficient (m)

K_{dust} : Dust/ Air Partitioning Coefficient ($m^3/ \mu g$)

K_{glass} : Glass/ Air Partitioning Coefficient (m)

K_{hum} : Human Skin/ Air Partitioning Coefficient (m)

K_{OA} : Octanol/ Air Partitioning Coefficient

$K_{part} = K_P$: Particle/ Air Partitioning Coefficient ($m^3/ \mu g$)

$K_{surf} = K_S$: Surface/ Air Partitioning Coefficient (m)

K_{SS} : Stainless Steel/ Air Partitioning Coefficient (m)

l: Characteristic Length over which the air flows (m) or the Length of the GC Column (m)

L: Thickness of the Material (m)

M_a : Air Molecular Weight (g/ mol)

M_g : Phthalate Molecular Weight (g/ mol)

P: Atmospheric Pressure (atm)
q: Surface Concentration of the Compound ($\mu\text{g}/\text{m}^2$)
Q: Air Flow Rate in the Chamber (m^3/s)
SER: Specific Emission Rate ($\mu\text{g}/\text{m}^2 \cdot \text{h}$)
t: Time (s)
T: Temperature (K)
TSP: Total Mass Concentration of Suspended Particles ($\mu\text{g}/\text{m}^3$)
v: Air Velocity on the surface of the Material (m/ s)
V: Chamber Volume (m^3)
 V_a : Air Molar Volume (cm^3/mol)
 V_g : Phthalate Molar Volume (cm^3/mol)
 V_p : Vapor Pressure of a Compound (Pa)
 y : Gas-Phase Concentration of the Compound in the Chamber ($\mu\text{g}/\text{m}^3$)
 y_0 : Gas-phase Concentration of the Compound in Equilibrium with the Material Surface ($\mu\text{g}/\text{m}^3$)
 y_s : Gas-phase Concentration of the compound immediately adjacent to the Sorption Surface ($\mu\text{g}/\text{m}^3$)
 y_{ss} : Gas-phase Concentration of the Compound in the Chamber at Steady State ($\mu\text{g}/\text{m}^3$)
 δ : Thickness of the Clothing Material (m) or of the used GC Column (μm)
 ΔH_{vap} : Enthalpy of Vaporization (KJ/ mol)
 μ : Viscosity of Air (kg/ m. s)
 ρ : Density of Air (kg/m^3)

Note de Synthèse

De nos jours, nous passons environ 90% de notre temps dans des environnements intérieurs [1]. Selon l'Organisation Mondiale de la Santé (OMS), environ 4,2 millions de personnes décèdent dans le monde chaque année à cause de la pollution de l'air intérieur. Depuis ces dernières années, la qualité de l'air intérieur (QAI), devenue un problème de santé publique majeur, a reçu une attention croissante du fait des effets sur la santé humaine de certains des polluants spécifiques [2].

Plusieurs polluants intérieurs tels que les fibres, les particules, les polluants biologiques et chimiques contribuent à dégrader la qualité de l'air intérieur. Les composés organiques volatils (COV) et les composés organiques semi-volatils (COSV) sont deux classes importantes de polluants chimiques identifiés fréquemment à l'intérieur des bâtiments. Cependant, les études sur les COSV restent encore moins nombreuses que celles sur les COV. Les COSV ont récemment attiré une attention particulière en raison de leur présence dans les environnements intérieurs et de leurs propriétés toxicologiques de certains de ces composés. Parmi les COSV, les phtalates et les retardateurs de flamme organophosphorés (RFOP) font partie des composés identifiés le plus fréquemment dans les environnements intérieurs.

Les phtalates et les RFOP entrent dans la composition de nombreux matériaux de construction et produits de consommation courante. En effet, ils confèrent à ces produits des caractéristiques techniques spécifiques. En raison de leur mode d'incorporation dans les matériaux, ces composés peuvent être émis au fil du temps dans les environnements intérieurs. Les émissions des matériaux sont ainsi, une des principales sources de pollution intérieure de ces composés. Du fait de leurs propriétés physico-chimiques, phtalates et RFOP peuvent être présents à la fois en phase gazeuse, mais également en phase adsorbée sur les surfaces et les poussières intérieures [3]. Par conséquent, la population générale est fortement exposée à ces composés dans les environnements intérieurs, ce qui peut se traduire par des effets négatifs sur la santé. Ainsi, il est nécessaire d'évaluer le risque d'exposition humaine aux phtalates et aux RFOP. La caractérisation des émissions de ces composés est donc une étape nécessaire et une condition préalable à une meilleure compréhension de leur répartition dans les différents compartiments des environnements intérieurs.

Certaines méthodes de mesure et d'analyse ont été développées pour fournir des informations sur la présence de ces composés dans l'air intérieur, les poussières et les particules. Cependant, les méthodes de mesure et d'analyse des émissions par les matériaux sont encore peu nombreuses.

La plupart des méthodes analytiques disponibles ont été initialement développées pour caractériser les émissions de phtalates, et notamment de phtalate de 2-éthylhexyle (DEHP), par les matériaux de construction et de consommation. Très peu de méthodes sont disponibles pour caractériser les émissions de RFOP. Cependant, ces méthodes présentent encore certaines limites et ne peuvent pas être utilisées comme méthodes de routine pour la caractérisation des sources intérieures. L'adsorption sur les parois dans les chambres d'essai d'émission est considérée comme la principale limite pour la plupart des méthodes développées et se traduit par un temps d'expérimentation relativement long, en particulier à température ambiante. De plus, la récupération de la masse adsorbée de ces composés sur les surfaces internes de la chambre est généralement complexe. L'évaluation de la concentration en phase gazeuse en équilibre avec la surface du matériau (γ_0) est donc longue et imprécise. Or cette concentration est considérée comme le paramètre clé dans la caractérisation des émissions de COSV par les matériaux de construction puisque la diffusion des COSV dans le matériau est considérée comme négligeable [4]–[6]. Par conséquent, le développement d'une nouvelle méthode de mesure rapide et robuste pour déterminer le γ_0 des phtalates et des RFOP émis par les matériaux à température ambiante est nécessaire.

La norme ISO 16000-25 recommande l'utilisation de micro-chambres pour caractériser les émissions de COSV des matériaux de construction [7]. Les avantages de ce type de chambres d'essai sont : sa faible surface d'adsorption potentielle par rapport à la surface d'émission et la possibilité de chauffer le système pour une meilleure récupération des COVS adsorbés sur les surfaces internes. Les micro-chambres à extraction thermique ou μ -CTE, fabriquées par Markes International, ont été utilisées dans cette étude (Figure 1) [8]. Le matériau est placé dans la micro-chambre et l'échantillonnage de l'air extrait se fait en continu jusqu'à ce que les émissions atteignent un état stationnaire. Puis les échantillons d'air prélevés sont analysés par désorption thermique et chromatographie en phase gazeuse couplée à la spectrométrie de masse (TD-GC-MS).



Figure 1: Micro chambre à extraction thermique

Par conséquent, les objectifs de cette thèse sont organisés en deux grandes parties :

- Le développement d'une méthode TD-GC-MS unique et sensible pour caractériser les émissions de phtalates et de RFOP par les matériaux
- La mesure des émissions des matériaux, par le développement d'une méthode innovante, rapides et robuste pour l'estimation des γ_0 de ces composés émis à température ambiante

Pour le premier objectif, huit phtalates et six RFOP ont été sélectionnés du fait de leur abondance dans les environnements intérieurs et de leurs effets potentiels sur la santé humaine. Une méthode TD-GC-MS spécifique a été développée en optimisant les différents paramètres de désorption et d'élution chromatographique des phtalates, tels que le temps et la température de désorption du tube de prélèvement, les divisions de flux (splits) au niveau du thermodésorbeur et la programmation de la température du four GC. Cette méthode a ensuite été validée pour les deux familles de composés (phtalates et RFOP) en termes de linéarité, de répétabilité et de limites de détection (LD) et de quantification (LQ).

Les résultats obtenus ont montré que la méthode mise au point est reproductible avec un écart-type relatif moyen (RSD) inférieur à 15 % pour les deux familles de composés. Cette méthode a été validée en quantifiant les émissions de phtalates et de RFOP d'échantillons réels tels que des revêtements de sol en PVC et des mousses de polyuréthane (PUF). Pour un volume d'échantillonnage d'environ 80 L, les LD moyennes sont de 0,01 $\mu\text{g}/\text{m}^3$ pour les phtalates et de 0,04 $\mu\text{g}/\text{m}^3$ pour les RFOP. Les LD obtenues pour cette méthode sont 2 et 5 fois inférieures à celles d'autres méthodes décrites dans la littérature. Par conséquent, cette méthode TD-GC-MS qui permet la caractérisation conjointe des émissions de phtalates et de RFOP par les matériaux est également la plus sensible.

Pour estimer les γ_0 des phtalates et RFOP à température ambiante, deux approches ont été proposées dans cette étude en utilisant deux configurations différentes des μ -CTE.

Pour la caractérisation des émissions de COSV par les matériaux, certaines études ont fait l'hypothèse que la valeur de γ_0 à température ambiante était proche de celle de la pression de vapeur saturante de chaque composé, et ont donc considéré que l'émission de ces composés se produisait principalement par vaporisation. Par conséquent, γ_0 est grandement affecté par l'augmentation de la température. Dans une étude menée en 2015 en collaboration entre la direction Santé Confort du CSTB et la Division de l'Exposition et de la Biosurveillance de Santé Canada, une relation linéaire a été établie entre la concentration de DEHP émise dans l'air de la μ -CTE (γ) par les revêtements de sol PVC et l'inverse de la température [9].

Cette relation a permis de déterminer la valeur γ du DEHP à température ambiante par extrapolation à partir de températures plus élevées en utilisant l'équation de Clausius-Clapeyron, puis l'estimation de γ_0 selon l'équation fournie par Xu et al. [3]. Inspirée de ces résultats, une méthode alternative a été développée dans cette thèse pour déterminer le γ_0 des phtalates et des RFOP par extrapolation à partir des températures plus élevées (Figure 2). Cette méthode a été validée en comparant la valeur expérimentale mesurée du γ_0 des phtalates à 25 °C avec la valeur estimée par calcul. Les résultats obtenus ont montré que la détermination de γ_0 par extrapolation était une méthode encourageante, l'erreur moyenne entre les deux valeurs mesurée et calculée étant inférieure à 10%.

Après avoir pu déterminer les γ_0 des phtalates à température ambiante, la méthode a été appliquée aux RFOP. Le pourcentage moyen d'erreur entre les valeurs expérimentales et extrapolées des γ_0 pour les RFOP est de 18%, ce qui indique que cette méthode est robuste et peut s'appliquer simultanément à différentes familles de COSV, comme les phtalates et les RFOP.

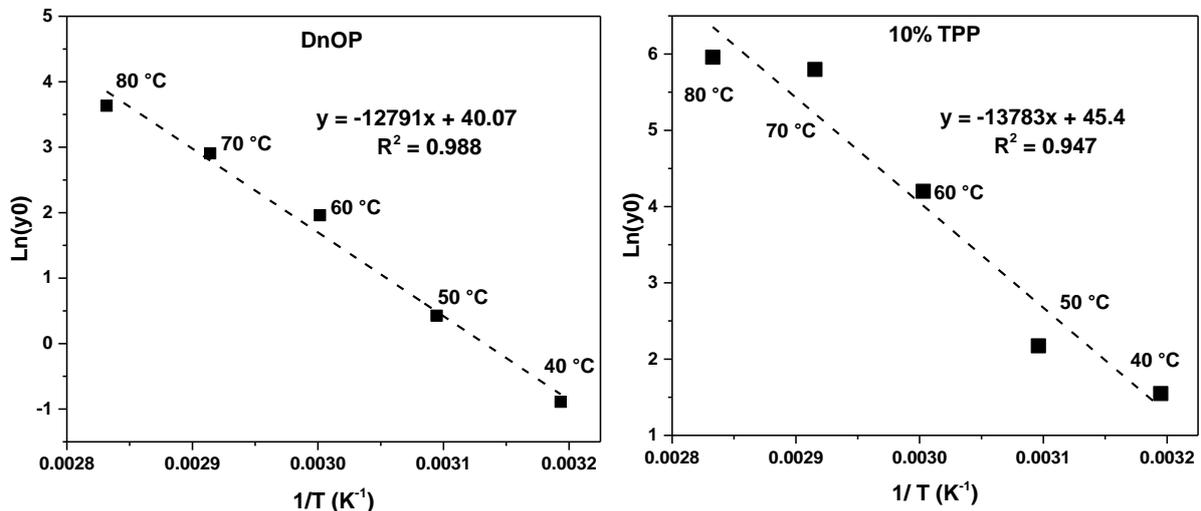


Figure 2: Ln(γ_0) en fonction de l'inverse de la température pour di-n-octyle phtalate (DnOP) et triphényl phosphate (TPP) émis par le matériaux

Une autre approche novatrice a ensuite été proposée dans le cadre de cette étude pour une détermination rapide et précise de γ_0 des COSV à température ambiante. En s'inspirant des méthodes de mesure des émissions en mode statique, il a été supposé que γ_0 pouvait être mesuré directement à l'équilibre dans la μ -CTE en réduisant au minimum le volume de la cellule des μ -CTE. Dans ce travail, la hauteur de la cellule de la μ -CTE au-dessus de l'échantillon a été réduite de 36 à 3 mm en surélevant le matériau avec des entretoises. Dans cette configuration, la concentration en phase gazeuse à l'équilibre des phtalates et des RFOP était égale aux valeurs de γ_0 mesurées dans la configuration conventionnelle de la μ -CTE, ce qui confirme l'hypothèse de la possibilité d'une mesure directe du γ_0 avec les μ -CTE. De plus, le temps nécessaire pour arriver à l'équilibre a été réduit de quelques jours à quelques heures à 40 °C.

Dans la plupart des études portant sur les phtalates, γ_0 est supposé constant en raison d'une concentration initiale (C_0) constante de ces composés dans les matériaux [10]. Par conséquent, la diffusion interne de ces composés dans le matériau est considérée comme négligeable [4], [6]. Cependant, les mesures réalisées sur des mousses PUF ont montré que les γ_0 des RFOP avaient diminué d'environ 70% en trois ans. Cette observation peut s'expliquer par un processus de vieillissement de la mousse PUF, augmentant la taille des pores et par conséquent la diffusion des OPFRS dans le matériau et se traduisant par une diminution de la concentration initiale (C_0) [11]. Cette diminution a été confirmée par une expérience similaire réalisée sur le même matériau avec une autre technique analytique par une équipe de l'IMT Mines Alès. Par conséquent, il ne semble pas possible de négliger le phénomène de diffusion interne pour toutes les familles de COSV.

Enfin, l'adsorption des phtalates et des RFOP sur les surfaces de la μ -CTE a été étudiée en calculant le coefficient de partage surface/ air (K_{SS}). Les valeurs de K_{SS} obtenues pour les phtalates sont conformes aux valeurs rapportées dans la littérature. Pour les RFOP, des coefficients de partage surface/ air ont été déterminés pour le verre par Ghislain et al. [12]. Les valeurs de K_{SS} obtenues dans cette étude sont les premières données expérimentales sur l'inox. Une relation linéaire entre K_{SS} et la pression de vapeur saturante (V_p) des RFOP a été déterminée à partir de nos expériences (Figure 3). Cette relation, similaire à celle obtenue pour le verre, indique que l'adsorption des COSV semble être indépendante de la nature de la surface adsorbante.

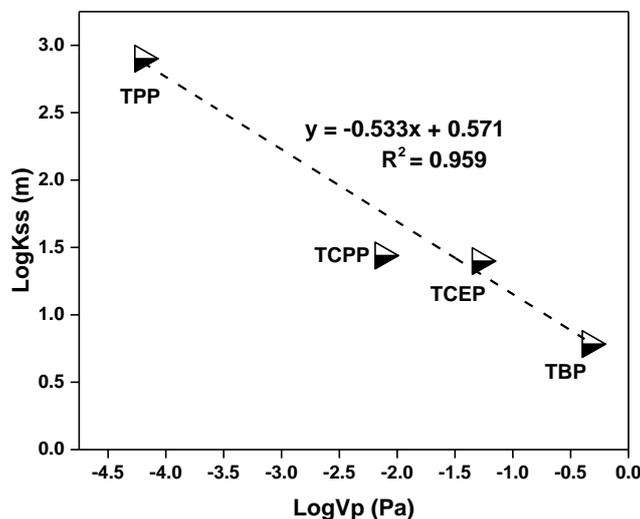


Figure 3: $\text{Log}(K_{SS})$ en fonction de $\text{log}V_p$ de RFOP

Les effets de la température, du débit d'air et de l'humidité sur l'émission de phtalates ont été étudiés. Pour les RFOP, l'effet de la température a été étudié. L'augmentation de la température est associée à une augmentation significative de l'émission des phtalates et des RFOP.

Cependant, pour le phosphate de triéthyle (TEP), qui est le composé le plus volatil parmi les RFOP, l'augmentation de la température se traduit par son épuisement rapide dans le matériau. Comme pour la température, l'augmentation du débit d'air a augmenté l'émission des phtalates par les matériaux. Cependant, la variation de l'humidité relative ne se traduit pas par des variations des à 40 °C, mais cette variation est plus importante à des températures élevées (80 °C).

Pour conclure, des méthodes d'analyse et de mesure sensibles et robustes pour caractériser les émissions de COSV des matériaux ont été élaborées dans le cadre de cette étude. Il sera intéressant de tester ces méthodes pour la caractérisation des émissions d'autres COSV que les phtalates et les RFOP ainsi que d'appliquer cette méthode à différents types de matériaux de consommation courante.

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➤ National Conference

Braish T., Nicolas M., Maupetit F., Desauziers V.

Development of a novel method for the characterization of the emission of phthalates from building and consumer materials

Atmos'Fair, 5-6 June 2019, Lyon

➤ International Conferences

Braish T., Nicolas M., Maupetit F., Desauziers V.

Development of new analytical and measurement methods for characterizing the emission of semi-volatile organic compounds (SVOCs) from building and consumer materials

ISES ISIAQ, 18-22 August 2019, Lithuania

❖ **Best poster award**

Braish T., Nicolas M., Maupetit F., Desauziers V., "Development of new analytical and measurement methods for characterizing the emission of phthalates from building and consumer materials into indoor air", *IOP Conf. Ser.: Mat. Sci. Eng.*, 609, 042009, 2019. doi:10.1088/1757-899X/609/4/042009

IAQVEC, 5-7 September 2019, Italy

Achille J., Braish T., Codaccioni M., Desqueyroux H., Glorennec P., Hanoune B., Hulin M., Mandin C., Nicolas M., Pourchet M., Raffy G., Regrain C., Wei W., "Conférence sur les environnements bâtis, naturels et sociaux 18-23 août 2019, Kaunas (Lituanie)", *Environnement, Risques & Santé*, vol. 19, no. 1, pp. 51-57, 2020. doi:10.1684/ers.2019.1392

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General Introduction

People spend about 90% of their times in indoor environments. According to the World Health Organization (WHO) an estimated 4.2 million worldwide deaths are caused annually by indoor air pollution which has received a great attention in the last 20 years. This attention was after considering its effects on indoor air quality (IAQ) that became a major health issue.

Several indoor pollutants such as fibers, particulate matter, and biological and chemical pollutants contribute to the quality of indoor air. Volatile (VOCs) and emerging semi-volatile organic compounds (SVOCs) are considered two important classes of chemical pollutants. However, studies on SVOCs are still limited compared to VOCs. These compounds are recently receiving raised attention because of their occurrence and toxicological properties. A group of families belongs to SVOCs with phthalates and organophosphate flame retardants (OPFRs) being two of the most abundant indoor toxins.

To enhance the properties of materials, phthalates are usually added as plasticizers to polymeric materials while OPFRs are used as flame retardants in different consumer products. Because of their incorporation mode, these compounds can be emitted over time from the material into indoor environments, which is considered one of the major indoor sources of indoor pollution. However, due to their physico-chemical properties, phthalates and OPFRs have the ability to partition after emission among the gaseous phase, particulate matter, and indoor settled dust. Therefore, they are considered ubiquitous indoor pollutants that make people, especially children, greatly exposed to these compounds in indoor environments through inhalation, dermal contact, or dust ingestion. This may lead to adverse human health effects ranging from asthma and allergy to growth, reproduction, and neurological problems in addition to cancer. Thus, it is necessary to evaluate the risk of human exposure to phthalates and OPFRs indoors in order to prevent their consequential health effects. Characterizing the emissions of these compounds is a necessary step and a prerequisite for a better understanding of their partitioning among the different indoor compartments. Some measurement and analytical methods have been developed to provide information on their presence of these compounds in indoor air, dust, and particulate matter. However, measurement and analytical methods on their emission from materials are still scarce.

Available methods are based on active or passive measurements. Most of the available methods were initially developed to characterize the emissions of phthalates, especially di(2-ethylhexyl phthalate) (DEHP), from building and consumer materials while few were applied to characterize the emissions of OPFRs. However, these methods present some limitations and cannot be used, as such, as routine methods for source control. Similar to their partitioning in real indoor environments, the emitted

amounts of phthalates and OPFRs from materials are partitioned in two phases: the gaseous phase of the test chamber and the adsorbed phase on inner surfaces. Adsorption in the emission test chambers is considered as the main limitation for most of the developed methods and is leading to long experimentation time to reach steady-state conditions, especially at ambient temperature. In addition, the recovery of the sorbed mass of these compounds from the inner surfaces of the chamber is usually complex. This all leads to long and inaccurate estimation of the gas-phase concentration in equilibrium with the material surface (y_0). This concentration is considered the key parameter in characterizing emissions of SVOCs from building and consumer materials. Therefore, the development of a new rapid and robust measurement method to determine y_0 of phthalates and OPFRs emitted from building and consumer materials at room temperature is the main objective of this thesis.

ISO 16000-25 standard recommended the use of micro-chambers for characterizing SVOCs emissions from building and consumer materials [1]. The advantages of this type of chambers are summarized by its small sorption surface compared to the emission surface in addition to the ability to heat them for better recovery of SVOCs sorbed on inner surfaces. One type of micro-chambers is the thermal extractor or μ -CTE.

Several studies have been reported in literature for understanding the emission of SVOCs from materials. Some of these assumed that y_0 of SVOCs at room temperature is close to their vapor pressure, and thus considered that the emission of these compounds from materials occurs by vaporization; therefore, it is greatly affected by the increase in temperature. In a collaborative study done in 2015 between the Health and Comfort Division at CSTB and the Exposure and Biomonitoring Division of Health Canada, a linear relationship has been established between the chamber air concentration of DEHP (y) emitted from vinyl floorings and the reciprocal of temperature by using the μ -CTE [2]. This relation enabled the determination of y of DEHP at room temperature by extrapolation from higher temperatures according to Clausius-Clapeyron equation, then the estimation of y_0 according to the equation provided by Xu et al. [3]. This innovative method evidenced the suitability of the μ -CTE in determining y_0 of SVOCs. However, it was only applied to DEHP. This thesis was proposed for further developments of the extrapolation concept in order to establish a rapid method for estimating y_0 of phthalates and OPFRs at room temperature using the μ -CTE.

Analytical methods are used to quantify the collected samples of SVOCs in the above mentioned test chambers. The air samples collected on adsorbent tubes are analyzed by thermal desorption coupled to gas chromatography-mass spectrometry (TD-GC-MS) which is the most used technique for the characterization of these compounds [1]. The efficiency of the used analytical technique is very important for accurate estimation of y_0 . Because of their wide range of volatility and boiling temperatures, it is challenging to have one analytical method applicable to multiple families of SVOCs.

Up to now, and to our knowledge, no available, or at least tested, TD-GC-MS method has been reported in literature for characterizing the emissions of both, phthalates and OPFRs, from materials. Therefore, the development of a sensitive TD-GC-MS method able to characterize the emission of both families is a necessity.

The objectives of this thesis are divided into two main parts:

- Analytical, through the development of a single sensitive TD-GC-MS method for characterizing the emission of phthalates and OPFRs from materials
- Material emission measurement, by developing a robust and innovative method for rapid estimation of y_0 of these emitted compounds at room temperature

This document is divided into 4 chapters. In the first chapter, a general introduction to indoor air pollution and IAQ followed by an overview of SVOCs are presented to concentrate after on phthalates and OPFRs. A detailed literature review on the properties, sources, partitioning in indoor environments, and indoor human exposure to these compounds is shown. Since characterizing the emission of these compounds from materials is the main objective of this thesis, their mechanism of emission with the relation among the different parameters is thoroughly explained. Finally, a presentation of the different available measurement and analytical methods with their advantages and disadvantages is presented.

Chapter 2 will focus on the development of a sensitive TD-GC-MS method for characterizing the emission of phthalates from materials and the validation of this method for the emissions of both families of SVOCs, phthalates and OPFRs. It will also present the used experimental setup and the followed protocols in developing a rapid method for the estimation of y_0 of phthalates at room temperature.

To achieve this goal, two measurement approaches will be presented in chapter 3. The first one, based on characterizing the emissions of phthalates at high temperatures, aims to estimate their y_0 at room temperature by extrapolation from higher temperatures, which is the main element of this thesis. The second method is by reducing the volume of the test chamber which is assumed to enable direct measurement of y_0 of emitted phthalates.

After well developing a rapid and robust method for determining y_0 of emitted phthalates at room temperature, the efficiency of this method will be tested on the emissions of OPFRs from materials and which it will be presented in the last chapter of this document.

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Chapter 1.

Semi-volatile organic compounds: Emission from materials and effects on indoor air quality

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1. INDOOR AIR QUALITY (IAQ)

1.1. General definition

Air pollution is the presence of toxic contaminating substances, such as chemicals, in the atmosphere. People spend an average of about 85% of their times in indoor environments [1] during which they are exposed to a wide range of pollutants. Indoor air pollution began in the rudimentary life where people used fire for warmth, cooking, and light [2], and is nowadays present in every indoor space [3]. However, it has not received a great attention until the early 2000s opposite to outdoor air pollution that is well-known and regulated [1]. This attention was after considering its negative effects on indoor air quality (IAQ) and consequently on human health. IAQ is the quality of air within buildings and structures [4], and is responsible for more than 1 million worldwide deaths each year due to acute respiratory infections [5]. Therefore, it is necessary to characterize IAQ in order to estimate the risk of human exposure to the different indoor pollutants.

The main sources of indoor air pollutants, as shown in Figure 4, are not only interior such as anthropogenic activities and emissions from building and consumer materials (e.g. household products), but also exterior due to the infiltration of outdoor air polluted by emissions from transportation, factories, or natural source [6], [7]. However, in order to enhance the properties and reduce the cost of indoor building materials and consumer products, considerable changes have occurred over the past 50 years through the introduction of synthetic polymers and new manufacturing lines leading to increased emissions of pollutants from these materials and worse IAQ [8]. Indoor air is therefore much more polluted than outdoor air where the concentration of some pollutants, such as formaldehyde, is higher indoors than outdoors [9], [10]. In addition, 76% of particulate matter, relative to outdoor concentrations, is found indoors in developing countries [2].

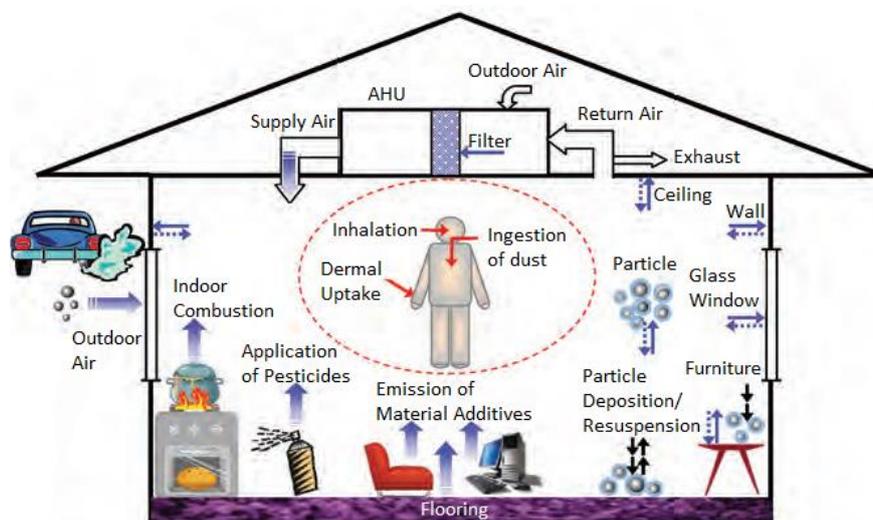


Figure 4: Sources of indoor air pollution [11]

There are different types of indoor air pollutants including particulate matter, fibers, biological, and chemical pollutants. As part of the chemical pollutants, volatile and semi-volatile organic compounds (VOCs and SVOCs, respectively) are pollutants that are increasingly being studied due to their toxicology and severe health effects they cause. These effects are of different severity ranging from allergy, asthma, headaches, flu-like symptoms, nausea, skin and eyes irritations to lung cancer [12]. Some of these health effects such as headaches, tiredness, and dizziness constitute the symptoms of sick building syndrome (SBS). No exact cause for SBS has been identified since 1970s; however, unhealthy indoor environments play an important role [13]. The most important factors that describe this latter are insufficient ventilation, high or low temperature and humidity, and low indoor air quality [14]. Therefore, to reduce the health effects caused by indoor air pollutants, it is necessary to improve IAQ.

1.2. How to improve IAQ?

In order to improve IAQ, the Environmental Protection Agency (EPA) in the United States suggests improving ventilation systems, addition of air cleaners, and controlling indoor emission sources of pollutants [15]. In France, several regulations and pollutants measurement campaigns have been established to fulfill these goals.

1.2.1. VENTILATION

Air is exchanged in buildings through natural ventilation, infiltration of outdoor air through openings and cracks, and mechanical means such as mechanical ventilation and air conditioning systems [15]. It is believed that increasing ventilation rates lowers concentrations of indoor air pollutants [15]. The French government established a number of orders and decrees for mandatory evaluation of the average ventilation rates in dwellings.

The first order was issued in 1982 specifying the ventilation rates based on the number of pieces of a dwelling, particularly those accommodating children [16]. Then two decrees were declared in 2012 and 2015 for obligatory evaluation of the average ventilation rates and measurement of pollutants indoor air concentrations in some establishments receiving people (nurseries and primary schools) every 7 years [17], [18].

1.2.2. SOURCE CONTROL

Emissions from indoor materials is considered the major source of indoor air pollutants; therefore, the most effective way to reduce the concentrations of indoor air pollutants is by eliminating the emission source or reducing its emission. Therefore, continuous monitoring of the concentrations of indoor pollutants is necessary. A group of standards was found to provide measurement protocols for indoor air pollutants either present in indoor air or emitted from building and consumer materials [19]–[25]. Moreover, an Indoor Air Quality Observatory (OQAI) was created in 2001 in France. This observatory aims to compensate for the ignorance of public exposure to indoor air pollution, and to create a permanent device for data collection on indoor pollutants in order to prevent consequent health risks and thus improve IAQ [9]. In addition, some decrees were also established for monitoring IAQ by setting guideline values for pollutants concentrations in indoor air. According to these decrees, the guide indoor air concentrations of benzene and formaldehyde are 2 and 10 $\mu\text{g}/\text{m}^3$ starting from the years 2016 and 2023, respectively [26]. Another order, established in 2009, declared that construction and decoration products cannot be placed on market if the emitted concentrations of some carcinogenic, mutagenic, or reproduction toxic (CMR) substances, benzene, trichloroethylene, Dibutyl phthalate (DBP), and Di(2-ethylhexyl) phthalates (DEHP), exceed 1 $\mu\text{g}/\text{m}^3$ after 28 days of testing in an emission test chamber [27].

Moreover, a group of European labels, schemes, and regulations has been established to determine the emissions of different pollutants from several materials into indoor air for protecting consumers. These include the German Committee for Health-related Evaluation of Building Products (AgBB) scheme, M1 Finnish Label, Indoor Climate Label (ICL), Natureplus, Blue Angel, the French guideline protocol AFSSET, and many others [28], [29]. Most of these deal with the emission of VOCs and total volatile organic compounds (TVOCs), but few among them that include the less volatile compounds, SVOCs.

1.2.3. USAGE OF AIR CLEANERS

Air cleaners or purifiers are devices that remove contaminants from indoor air. There are many types of air cleaners. The efficiency of these latter depends on how much air it draws through the cleaning filter and the strength of the pollutants source [15]. However, not all air purifiers are efficient. Two standards, XP-B44-013 and XP-B44-200, were issued in France in 2009 and 2011, respectively to evaluate the performance of standalone air purifiers and purifiers based on photocatalysis of indoor air VOCs for tertiary and residential application [30], [31]. Costarramone et al. classified air purifiers according to XP-B44-013 into two classes according to their efficiency in removing VOCs from indoor air [32].

The use of air cleaners is an expensive and energy consuming technique; therefore, it is considered a complementary method to improve IAQ compared to ventilation and indoor source control. However, in order to control indoor sources, it is necessary to characterize the indoor emissions of pollutants from these latter.

1.3. Evaluation of indoor emissions of pollutants

Organic chemicals constitute a major class of indoor pollutants. Among these there exist very volatile (VVOCs), volatile (VOCs), and semi-volatile (SVOCs) organic compounds. Compounds belonging to these three classes have different physico-chemical properties such as boiling temperature (Table 1) [19]. However, VVOCs are not well defined at which there is still no internationally accepted definition for these compounds [33].

Table 1: Classification of organic compounds according to their boiling temperature [19]

Class	Boiling temperature (°C)
Very volatile organic compounds (VVOCs)	< 0 to 50-100
Volatile organic compounds (VOCs)	50-100 to 240-260
Semi-volatile organic compounds (SVOCs)	240-260 to 380-400

1.3.1. VOLATILE ORGANIC COMPOUNDS (VOCs)

Volatile organic compounds (VOCs) are the most common organic air pollutants of the hydrocarbon class in indoor environments [34] with a vapor pressure greater than 10 Pa [6]. These compounds are usually emitted into indoor environments as gases from solids or liquids such as wood, lubricants, cleaners, solvent thinners, and degreasers [35].

VOCs have been of great concern due to their toxicological properties and the severe human health effects they cause including: irritations, allergies, malfunctions of lungs, asthma, children leukemia, neurological symptoms as fatigue, headaches, and depression as well as cancer through inhalation, ingestion, or dermal contact [36], [37].

In addition to the primary VOCs emissions, secondary emissions result from the reaction of ozone with some unsaturated hydrocarbons producing by-products such as free radicals, alcohols, aldehydes, carboxylic acids, ketones, and fine particles at which most of them are volatile compounds and are of greater harm to human health than the primary reactants [38]. A group of the most common VOCs is

shown in Table 2. However, formaldehyde is the most abundant aldehyde-VOC in indoor environments where it can be formed both naturally and due to anthropogenic activities [39].

Table 2: Common VOCs present in schools [34]

VOCs	Source(s)
Toluene	Cleaners, construction materials
Xylenes	Cleaners, construction materials
Siloxanes	Waxes, polishes, deodorants, furniture
Formaldehyde	Furniture, ceiling tile, wood, cabinetry
Hexane	Markers, cleaners
Acetone	Markers, art supplies
1,4-Dichlorobenzene	Cleaners, deodorizers
Hexanal	Cleaners, adhesives, deodorizers, cabinetry
2-Butoxyethanol	Wood cabinetry, cleaners, paints
Ethanol	Cleaners, disinfectants
Trimethyl Pentanyl Diisobutylrate (TXIB)	Plastics, paints
Acetaldehyde	Plastics, paints, foam insulations
Longifolene	Cleaners, wood products, flooring
Naphthalene	Adhesives, art supplies, rubber flooring

1.3.2. REGULATION AND STANDARDS

As previously stated (§1.3.1), VOCs emission from materials is a major source of indoor air pollution. A group of international standards is available for characterizing the emissions of VOCs, especially formaldehyde, in indoor environments. Some of these standards are found to characterize the presence of VOCs in indoor air and others for the characterization of their emissions from building and consumer products using emission test chambers. In 2001, ISO 16000-3 was established proposing a method for active sampling of formaldehyde and other carbonyl compounds present in indoor air and analyzing these samples by high performance liquid chromatography (HPLC) [24]. Then, in 2004, ISO 16000-6 was found to characterize indoor air VOCs collected by Tenax TA tubes using gas chromatography [25]. For the emissions of VOCs from building products, ISO 16000-9 and 10, found in 2006, specify methods for determining the emission rates of these compounds from building products and furniture using different emission test chambers and cells, respectively [21], [22]. ISO 16000-11 was also declared in the same year to provide procedures for storage and preparation of test specimen in addition to sampling techniques [23]. Then in 2017, EN 16516 was established for providing a reference method for determining the emissions of dangerous substances such VOCs, aldehydes, and SVOCs from building and consumer products [40].

In France, starting from January 2012, decorative and construction products had a mandatory label indicating their emission levels of VOCs into indoor environments (Figure 5). The terms of this label are issued by the French Ministry of Ecology [41], [42]. This label covers the compounds present in which allows consumers to select their products based on their emission of VOCs (Table 3). Emission levels ranged from A⁺ indicating very little or no emissions of VOCs to C meaning high levels of VOCs emissions. However, most of the manufactured materials are classified as A⁺ nowadays.



Figure 5: Label on decorative and construction products indicating the level of VOCs emission in indoor environment [41]

Table 3: Concentration ($\mu\text{g}/\text{m}^3$) of VOCs covered by the emission labeling [42]

Compounds	C	B	A	A ⁺
Formaldehyde	> 120	< 120	< 60	< 10
Acetaldehyde	> 400	< 400	< 300	< 200
Toluene	> 600	< 600	< 450	< 300
Tetrachloroethylene	> 500	< 500	< 350	< 250
Xylene	> 400	< 400	< 300	< 200
1,2,4-Trimethylbenzene	> 2000	< 2000	< 1500	< 1000
1,4-Dichlorobenzene	> 120	< 120	< 90	< 60
Ethylbenzene	> 1500	< 1500	< 1000	< 750
2-Butoxyethanol	> 2000	< 2000	< 1500	< 1000
Styrene	> 500	< 500	< 350	< 250
TVOCs	> 2000	< 2000	< 1500	< 1000

2. SEMI-VOLATILE ORGANIC COMPOUNDS (SVOCS)

SVOCs are considered as emerging indoor pollutants since studies and regulations on their emissions indoors are still not well developed compared to VOCs.

2.1. Overview on SVOCs

2.1.1. DEFINITION AND INDOOR SOURCES

Semi-volatile organic compounds (SVOCs) are an important class of indoor pollutants [11]. Their properties are different than those of VOCs starting from their higher molecular weight and lower vapor pressure. SVOCs, as their names imply, are organic molecules of vapor pressure ranging between 10^{-9} and 10 Pa [43] or 10^{-5} to 10 Pa at room temperature and boiling temperature between 240 to 400°C [19].

SVOCs are ubiquitous indoor pollutants. Weschler and Nazaroff defined them as abundant organic molecules found in both gaseous and condensed phases and that are emitted over time from their original source into indoor air, house dust, and other indoor surfaces [43].

These compounds are known for their slow emission rates from sources, adsorption on different surfaces, which is known as sink effect, and severe health effects they may cause [44], [45]. Therefore, the behavior of these compounds make studies, especially the analytical ones, challenging and not well developed as those of other indoor air pollutants [43]. Studies on SVOCs have greatly increased between the 1980s and 2000 [46]. For example, organophosphate esters and phthalates, two families of SVOCs, have been identified for the first time in indoor environments in the 1980s [47], and in the early 2000s phthalates started to receive considerable attention as endocrine disruptors [48].

In 2002, the OQAI has proposed a method for health ranking of more than 70 chemical substances based on more than 70 parameters of interest [49]. However, this method was updated in 2005 to include 29 additional substances classified as SVOCs and belonging to five major families: phthalates, alkyl phenols, brominated flame retardants, organotins, and short-chain chlorinated paraffins [50]. This update was after the significant detection of SVOCs in house dust as part of a campaign done in 100 dwellings in the United Kingdom (UK) and then a similar investigation was performed in May 2003 in about 50 houses in France [50], [51]. Moreover, these five families were selected based on their large production volumes and dangerous health properties and are ranked from substances with high health priority, like di(2-ethylhexyl) phthalate (DEHP), to unclassifiable, such as certain alkyl phenols, due to the lack of information on the exposure to these compounds or their toxicology.

Based on their physico-chemical properties, diverse compounds and families are classified as SVOCs. These include: brominated (BFRs) and phosphorus flame retardants (PFRs), phthalate esters, polycyclic aromatic hydrocarbons (PAHs), alkylphenols, organotin compounds, polychlorinated biphenyls (PCBs), perfluorinated compounds (PFCs), alkaloids, dioxins and furans, parabens, chlorinated paraffins, pesticides, etc. [11]. Some of these compounds are usually used as additives to enhance the properties of materials and products in terms of stability, fire resistance, or durability [11], [52] (Table 4).

Moreover, these compounds are greatly detected in indoor environments which increases exposure and the potential of severe health effects. According to the results obtained by the OQAI in French houses, diisobutyl phthalates (DiBP), dibutyl phthalate (DBP), and DEHP are detected in all collected dust samples while benzyl butyl phthalate (BBP) and diethyl phthalate (DEP) are present in more than 90% of house dust; moreover, the highest mass concentrations are for DEHP and diisononyl phthalate (DiNP). In addition to phthalates, four polybrominated diphenyl ethers (PBDEs) are also found in all dust samples [53]. However, these compounds are not only widely detected in indoor dust, but also in indoor air and airborne particles. The frequency of detection of DiBP, dimethyl phthalate (DMP), and DEP is 100% in French indoor air while that of DEHP, DBP, BBP, DiNP, and tributyl phosphate (TBP) is 100% in airborne particles [54].

Table 4: Different families of SVOCs, uses, and sources [11]

SVOCs	Use(s)	Sources	Potential health effect(s)
Alkylphenols	Nonionic surfactants	Detergents, disinfectants, and surface cleaners	May interfere with, mimic or block hormones
Organochlorines	Pesticides, termiticide, and bactericide	Outdoor and indoor air, tracked in dust, and disinfecting products	Neurotoxicity, effects on developing reproductive systems and on lactation, cancer
Organophosphorus Compounds (OPs)	Plasticizers, antifoaming agents, flame retardants, and pesticides	Polymeric materials, fabrics, polyurethane foams, electronics, outdoor and indoor air, and dust	Effects on neurodevelopment and growth in developing tissue, relate to respiratory disease in children through dysregulation of the autonomic nervous system
Polybrominated Diphenyl Ethers (PBDEs)	Flame retardants	Carpet padding, wall coverings, electronics, and furniture	Effects on the development of brain and nerve tissues, permanent learning and memory impairment, behavioral changes, delayed puberty onset, fetal malformations, thyroid hormone disruption
Phthalates	Plasticizers, solvents, fixing fragrances	Flexible PVC, PVC flooring, wall covering, electrical cable and casings, and personal care products	Effects on the development of male reproductive tract, prenatal mortality, reduced growth and birth weight, may relate to asthma and allergies in children
Polychlorinated Biphenyls (PCBs)	Heat transfer fluids, stabilizers, and flame retardants	Floor finishes, foam, cushioning and mattresses, oil-filled transformers, and capacitors	Developmental neurotoxicants, effects on immune, reproductive, nervous, and endocrine systems, cancer (including breast cancer)
Polycyclic Aromatic Hydrocarbons (PAHs)	Combustion by-products	Outdoor air, cooking, and smoking	Cataracts, kidney and liver damage, jaundice, increased risk of skin, lung, bladder, and gastrointestinal cancers
Pyrethroids	Insecticides	Outdoor and indoor air, tracked in dust, and cleaning products	Weak anti-androgenic, anti-estrogenic, or estrogenic effect
Parabens	Bactericides, antimicrobial agents, and preservatives	Personal care products, canned food, and fabrics	Weak environmental estrogens

2.1.2. PARTITIONING OF SVOCs IN INDOOR ENVIRONMENT

Semi-volatile Organic Compounds (SVOCs) are ubiquitous and highly detected in indoor environments [54]. Due to the increased use of commercial products and construction of buildings, the sources, amounts, and exposure to different SVOCs indoors are increasing as well. The emission and persistence of SVOCs in indoor air are many-factors dependent. They are mostly affected by the air mixing near the surface of the material [55], indoor humidity, and temperature [56].

The fate, transportation, and settlement of these compounds in the atmosphere is determined by their partitioning and partitioning coefficients (Figure 6) [57]. Based on their physico-chemical properties, especially their low vapor pressure and high molecular weight, SVOCs are usually partitioned after emission among different compartments in indoor environments including gas phase, airborne particles, dust, and other indoor surfaces including residents bodies [43], [54], [58], [59]. House settled dust is considered a strong repository for SVOCs and particle-bound organic matter in indoor environments [60]. However, few studies are available on the presence of SVOCs in indoor air compared to the extensive studies in literature on their presence in settled dust [45].

High volatile SVOCs are normally found in air while less volatile ones are found in particulate phase and dust. These compounds are not only found in air or adsorbed on airborne particles and dust, but they are also adsorbed on different indoor surfaces [61].

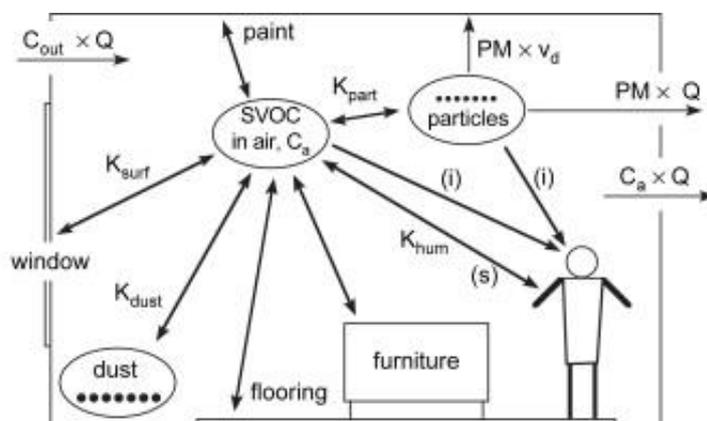


Figure 6: Partitioning of SVOCs among the different indoor compartments (i: inhalation; s: skin permeation) [43]

Partitioning coefficients of SVOCs are usually represented as their distributions between air and settled dust (K_{dust}), airborne particles (K_{part}), fixed surfaces (K_{surf}), and human occupants surfaces (K_{hum}), and can be described either as function of vapor pressure or the octanol-air partitioning coefficient (K_{oa}) of the SVOCs [43].

Distributions of SVOCs among the different indoor compartments and phases are correlated. The concentration of SVOCs in each phase and its corresponding partitioning coefficient can be estimated based on the following equations [43], [59]:

$$K_{\text{part}} = \frac{C_{\text{part}}}{C_{\text{a}}} = f_{\text{om-part}} K_{\text{oa}} \quad (1)$$

$$K_{\text{dust}} = \frac{C_{\text{dust}}}{C_{\text{a}}} = f_{\text{om-dust}} K_{\text{oa}} \quad (2)$$

Weschler and Nazaroff assumed that the affinity of an SVOC for an organic matter, present on any surface or on human skin, is similar to its affinity for octanol [43]:

$$K_{\text{surf}} = \frac{C_{\text{surf}}}{C_{\text{a}}} = K_{\text{oa}} \quad (3)$$

$$K_{\text{hum}} = \frac{C_{\text{hum}}}{C_{\text{a}}} = K_{\text{oa}} \quad (4)$$

Where C_{a} , C_{part} , C_{dust} , C_{surf} , C_{hum} are the equilibrium concentrations of SVOCs in air, particles, dust, organic matter on a fixed surface, and organic matter on human skin, respectively and $f_{\text{om-part}}$ and $f_{\text{om-dust}}$ are the volume fraction of organic matter associated with airborne particles and settled dust, respectively. Moreover, Wei et al. obtained an empirical relation between K_{part} and K_{dust} at which the ratio of these two parameters is equal to 8.32 [62]:

$$K_{\text{part}} = 8.32 K_{\text{dust}} \quad (5)$$

However, few studies are carried on accurately determining these coefficients.

Some SVOCs do not persist outdoors since they are exhibited to photo degradation, biodegradation, and anaerobic degradation [63], [64]. However, SVOCs stay for a long time in indoor environments even after the removal of the source material [11]. The persistence of SVOCs depends on their sorption strength or K_{oa} of each compound. Compounds of $K_{\text{oa}} > 10^{10}$ stay indoors for hundreds of hours while compounds with $K_{\text{oa}} > 10^{12}$ might persist for hundreds of years [43].

Studies on SVOCs partitioning in indoor environments focus on the partitioning between air and particles, but neglect the fraction of SVOCs present within the material which might have a great effect on the distribution and persistence of SVOCs in indoor environments [43]. Moreover, air/ particles partitioning coefficients of SVOCs are well determined in literature, but few are those that determine material/ air partitioning coefficient. Therefore, more research should be done on the partitioning of SVOCs between air and the surface of the hosting material.

Understanding the partitioning of SVOCs in indoor environments helps understanding humans' exposure risk to these compounds and estimating their potential health effects.

2.1.3. INDOOR EXPOSITION OF SVOCs

Due to the partitioning of SVOCs among the different indoor compartments and their sorption ability, humans, especially children, are greatly exposed to these compounds. Exposure pathways are diverse including inhalation of indoor air and airborne particles, dermal absorption of the gas and settled dust containing SVOCs (e.g. through clothes), and oral ingestion of suspended particles or of SVOCs sorbed to food in contact with indoor air [43], [65] (Figure 7).

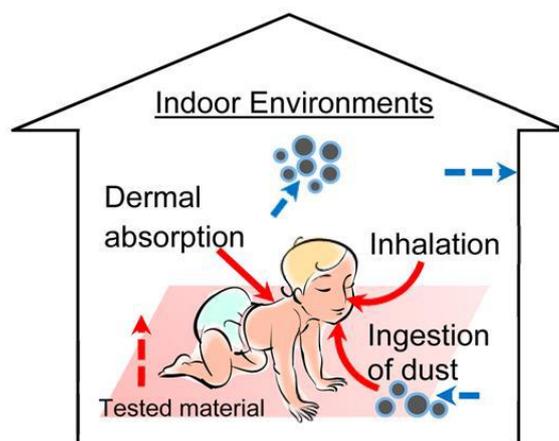


Figure 7: Exposure pathways of Humans to SVOCs in Indoor Environments [65]

Exposure to SVOCs can be monitored in different ways: by modeling the daily consumption of SVOCs or their emissions from materials into indoor environments, by monitoring the concentrations of their biomarkers in humans' urine, blood, or breast milk, or by determining the concentrations of SVOCs in indoor air or dust [66], [65], [67]. Knowing the toxicological properties of SVOCs and predicting the risk of humans' exposure to these compounds allow us to assess the health effects they might cause. However, since risk exposure data on humans are not always available, studies on experimental animals (e.g. mice) are usually performed and results are compared to humans exposure estimates [66].

Infants (< 1year old), toddlers (1-3 years old), and children (4-10 years) are more exposed to SVOCs than adults (> 19 years old) because of the higher hand-to-mouth contact, mouthing of soft plastic toys, and immature systems of their organisms [20], [54], [75].

The exposure to the different families of SVOCs can cause severe health effects including reproductive, nervous, and growth problems as previously mentioned. However, over the past 20 years, a group of chemicals used in building and consumer materials started to be considered as endocrine disruptors i.e. they interfere in the function of endogenous hormones [68]. These include phthalates, PCBs, brominated and chlorinated flame retardants, pesticides, alkylphenols, and parabens [63].

2.1.4. REGULATION

The European Union regulation concerning the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) was created in 2006 to address the production and use of chemicals in addition to their potential health effect on human health and environment [69]. It has issued a list of substances of very high concern (SVHCs) that includes chemicals with serious and irreversible effects on human health and environment such as CMR, persistent, and bioaccumulative substances [70]. 10 new substances were added in June 2018 to this list to have a new SVHCs list of 191 substances among which phthalates, flame retardants, paraffins, alkylphenols, furans, and many other SVOCs are included [70], [71].

A directive was issued in 1967 in Europe putting laws for the classification, labelling, and packaging (CLP) of dangerous substances placed on the market and was replaced by regulation no. 1272/2008 [72], [73]. This CLP regulation issued in 2008 completes REACH regulation and aims to ensure high level of protection of human health and the environment. According to this latter, substances that are irritant, toxic, and harmful upon consumption, inhalation, or dermal sorption are classified as dangerous. Therefore, the packaging and labelling of materials should follow specific procedures such as mentioning the name, origin, danger symbol, and nature of the potential risk of the dangerous substance on the packaging. This regulation defines 28 classes from which 16 are physical, 10 are health, and one is environmental hazard [74].

However, phthalates and flame retardants include chemicals that are considered from the most dangerous substances to human health. These compounds are considered endocrine disruptors [63]. Besides, most of the mentioned phthalates in the CLP regulation are considered presumed human reproductive toxins while some organophosphate flame retardants (OPFRs) are potentially carcinogenic [73]. Therefore, concentration in this chapter will be only on phthalates and flame retardants due to their toxicity and severe health effects they cause in addition to their abundance in indoor environments.

2.2. Phthalates

2.2.1. DEFINITION AND PROPERTIES

Phthalates or non-halogenated phthalic acid esters are a group of synthetic chemical compounds (Figure 8) that are commonly and widely added to daily used building and consumer products to enhance their properties [51], [75], [76].

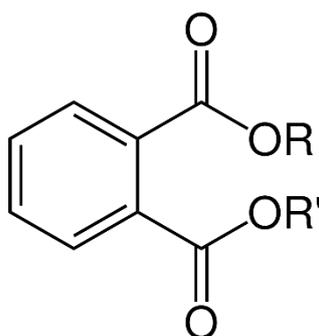


Figure 8: General structural formula of phthalates, R and R' are alkyl radicals

These compounds are used as plasticizers to enhance the properties of materials, especially plastics [66]. They constitute 10-60% by weight of many plastics because they improve flexibility, transparency, durability, and other physical properties [77].

The first identification of phthalates in indoor environments was in 1980s, and exposure to these compounds highly increased in 1950s [47], [48]. This is because after World War II, polyvinyl chloride (PVC) floorings began to replace asphalt tile and flexible PVC insulation replaced rubber and textile insulations on wiring and cables used in residential and commercial buildings [78]. PVCs are greatly produced at which their rate of production was about 163 thousand tons per year in 1950 and increased to 3.44 billion pounds per year in 1971 [79]. Therefore, starting from the 1950s, levels of phthalates in indoor environments increased and stayed high [78].

Phthalates are physically (no covalent bonds) bound to the polymers to which they are added and thus are susceptible to leach from their hosting materials and be emitted into indoor environments [75]–[77]. The different physico-chemical properties of the most encountered phthalates in indoor environments are presented on Table 5.

Table 5: Physico-chemical properties of phthalates (NA = not available) [59], [75]

Phthalate	Acronym	Molecular formula	Molecular weight (g/ mol)	V _P at 25 °C (Pa)	Boiling temperature (°C)	LogK _{OA}
Dimethyl phthalate	DMP	C ₁₀ H ₁₀ O ₄	194	2.6 x 10 ⁻¹	282	7.0
Diethyl phthalate	DEP	C ₁₂ H ₁₄ O ₄	222	6.5 x 10 ⁻²	298	7.6
Diisobutyl phthalate	DiBP	C ₁₆ H ₂₂ O ₄	278	4.7 x 10 ⁻³	327	8.5
Dibutyl phthalate	DBP	C ₁₆ H ₂₂ O ₄	278	4.7 x 10 ⁻³	340	8.5
Benzyl butyl phthalate	BBP	C ₁₉ H ₂₀ O ₄	312	2.5 x 10 ⁻³	379	8.8
Di-n-hexyl-phthalate	DnHP	C ₂₀ H ₃₀ O ₄	334	3.5 x 10 ⁻⁴	359	NA
Di(2-ethylhexyl) phthalate	DEHP	C ₂₄ H ₃₈ O ₄	390	2.5 x 10 ⁻⁵	386	10.5
Di-n-octyl phthalate	DnOP	C ₂₄ H ₃₈ O ₄	390	2.5 x 10 ⁻⁵	380	10.5
Diisononyl phthalate	DiNP	C ₂₆ H ₄₂ O ₄	418	5.0 x 10 ⁻⁷	370	NA
Diisodecyl phthalate	DiDP	C ₂₈ H ₄₆ O ₄	446	5.3 x 10 ⁻⁷	482	NA

2.2.2. INDOOR SOURCES

The application of phthalates depends on their structure: short-chain phthalates are usually used in the formulation of perfumes, cosmetics, nail polishes, and baby lotions while long-chain ones are added as plasticizers to PVC plastics (i.e. toys, electronic cables, decorating and building products, etc.), adhesives, food packaging, medical products, shoes, furniture upholstery, etc. [75], [77].

Eight thousand tons of phthalates were produced in 2003 in western Europe [66]; however, the annual consumption of these compounds increased to reach about 8 million tons worldwide and 1 million tons in Europe in 2015 [80]. From these 24% are for Di(2-ethylhexyl) phthalate (DEHP) and about 50% of Diisononyl phthalates (DiNP) and Diisodecyl phthalates (DiDP). DEHP accounts for about 50% of the overall worldwide production [81].

More than 95% of the consumed DEHP is used as plasticizer in polymers, especially in the production of flexible PVC due to its ease of transformation and good quality value compared to price [82]. It constitutes 30% by weight of PVC floorings [81]. The other 5% of DEHP production is used in non-polymer products such as paints, inks, adhesives, etc. However, nowadays, new nontoxic DEHP-free PVC plastics are being manufactured [83]. DEHP percentages in different applications are presented on Table 6.

Table 6: Percentage of consumed DEHP in different applications in 2005 (NA = absence of data) [82]

Application	Consumed DEHP with respect to the total DEHP consumption (%)	Consumed DEHP with respect to the total phthalate consumption (%)
Polymer		
Cables	17	20
Movies and Calender Sheets	15	60
Fabrics/ Coated Papers	4.4	70
Extruded Products and Tubing	13	60
Coated Floor Coverings	15	50 to 60
Wall Protection	21	
Roofing Materials and Coatings	1.3	NA
Automobile	1.5	NA
Shoes Soles	8.4	60
Other Polymers	NA	NA
Non-polymer		
Seals/ Adhesives	2.3	
Lacquers and Paints	0.3	
Inks	0.3	
Ceramics	0.006	
Paper	NA	

Di-n-octyl phthalate (DnOP) is used in paper lacquers and in lacquers suitable for water resistance [79]. The productions of benzyl-butyl phthalate (BBP) and di-n-butyl phthalate (DBP) are 1/10 that of DEHP [81]. BBP is used as a plasticizer in PVC floorings, tiles, carpets, and artificial leather while DBP is used in latex adhesives, plasticizer in cellulose plastics, solvent of certain dyes, and sometimes a plasticizer in PVC [81]. Diisobutyl phthalate (DiBP) has the same properties as DBP, and is used as a substitute to it in glues, inks for paper and food packaging, toys, and many other consumer products [84]. However, the use of these four compounds is decreasing with time.

A directive RoHS 2 (restriction of hazardous substances) that refers to the directive 2011/65/EU on the restriction of certain hazardous substances in electrical and electronic equipment has replaced the first RoHS of directive 2002/95/EC after limiting the use of DEHP, BBP, DBP, and DiBP to 0.1% [84]. In order to decrease toxic emissions of phthalates from materials, DiNP and DiDP are used as substituents for DEHP in plastics for their lower volatility [85]. However, REACH limited the concentration of these two compounds to less than 0.1% by weight in children's toys that can be placed in mouth [86]. Moreover, a directive was issued in 2007 by the European Union obliging manufacturers of medical devices to label on the device and/ or its packaging if it contains phthalates classified as CMR substances of category 1 or 2 [87]. The different uses of the most encountered phthalates in indoor environments are summarized on Table 7.

Table 7: Application of phthalates [66]

Phthalate ester	Uses
Di-ethyl-phthalate (DEP)	Personal care products and cosmetics
Di-n-butyl phthalate (DBP)	PVC plastics, latex adhesives, cosmetics, personal care products, cellulose plastics, solvent for dyes
Butyl benzyl phthalate (BBP)	Vinyl tiles, food conveyor belts, artificial leather, automotive trim, traffic cones
Di-n-hexyl-phthalate (DnHP)	Dipmolded products, such as tool handles, dish-washer baskets; flooring, vinyl gloves, flea collars, conveyor belts used in food processing
Di(2-ethylhexyl) phthalate (DEHP)	Building products (wallpaper, wire and cable insulation), car products (vinyl upholstery, car seats), clothing (footwear, raincoats), food packaging, children's products (toys, grip bumpers), medical devices
Di-n-octyl-phthalate (DnOP)	In mixtures C6–C10 phthalates: garden hoses, pool liners, flooring tiles, tarps Seam cements, bottle cap liners, conveyor belts
Di-isononyl phthalate (DiNP)	Garden hoses, pool liners, flooring tiles, tarps, toys
Di-isodecyl phthalate (DiDP)	PVC plastics, covering on wires and cables, artificial leather, toys, carpet backing, pool liners

2.2.3. INDOOR PARTITIONING

Phthalates are one of the most encountered SVOCs in indoor environments. Blanchard et al. studied the indoor concentrations of 57 compounds in 30 French dwellings [54]. They found that the median concentrations of phthalates were the highest among all compounds at which highly volatile phthalates (DEP, DiBP, and DBP) are the most abundant in indoor air while the least volatile phthalates (BBP, DEHP, and DiNP) are more detected in settled dust.

Another nationwide survey, carried out by the OQAI between 2003 and 2005 in 567 French dwellings, was launched to study the distribution of SVOCs in indoor environments [45]. In this study 35 compounds were detected in almost all the dwellings among which phthalates are one of the most abundant pollutants in particulate phase with a median concentration greater than 1 ng/ m^3 . Mercier et al. have developed an analytical method to determine the concentration of 55 SVOCs in indoor suspended particles in thirty French houses [88]. The maximum concentration of DiBP, DBP, BBP, DEHP, and DiNP in suspended particles were 115, 52, 3, 113, and 57 ng/ m^3 , respectively.

Analysis on the presence of SVOCs, especially phthalates, in indoor air and dust in 30 French nurseries and primary schools was investigated by Raffy et al. in 2017 [89]. This work was done to study the effect of SVOCs on children spending 16% of their lives in schools. Concentrations of SVOCs in schools were correlated with those obtained by Blanchard et al. in the 30 French dwellings except for phthalates [54]. The concentrations of most phthalates in schools' indoor air were up to twice higher than those in air of homes which can be explained due to the enhanced presence of PVC floorings in schools and the need to apply more floor care chemicals.

A summary of the concentrations of phthalates in indoor air, particulate phase, and dust obtained from these studies are shown in Table 8 and Table 9.

Li et al. developed a model based on the lattice Boltzmann method for studying the transport process of indoor SVOCs, particularly DEHP emitted from vinyl flooring, and obtaining their concentration distribution in the gaseous and particulate phases [90]. They found that emission rates of DEHP from vinyl flooring are enhanced in the presence of airborne particles.

Studies in different parts of the world on the presence of SVOCs in indoor settled dust were also investigated. Results were similar to those obtained in France. Phthalates were detected in almost all dust samples and are the most concentrated compounds with a median concentration of above $100 \text{ } \mu\text{g/ g}$ of dust (Table 10) [91]. DEHP was the most detected phthalate in settled house dust in almost all countries with concentrations up to 416, 1091, 2350 ng/ g in the United Kingdom (UK), Canada, and Texas, respectively and 4843 and 980 $\text{ } \mu\text{g/ g}$ in Stockholm and Denmark, respectively. DiNP and DiDP were the second two phthalates with the highest concentrations due to the frequent usage of these two compounds as substituents for DEHP as previously mentioned.

Wei et al. developed recently a method to predict the gas- and particulate-phase concentrations of 48 SVOCs from their measured concentrations in indoor dust at a nationwide scale in 3.6 million French dwellings [92]. They found that phthalates are the SVOCs with the highest concentrations, more than 1 ng/ m^3 , in both gaseous and particulate phases.

Table 8: The partitioning of phthalates (ng/ m³) between gaseous and particulate phases in indoor air of homes in France

Compound	Gaseous phase					Particulate phase				
	n = 30 [89]		n = 30 [54]			n = 30 [54]			x 10 ⁻³ , n = 567 [45]	
	P5	P95	Minimum	Maximum	Frequency (%)	Minimum	Maximum	Frequency (%)	P5	P95
DMP	6.7	> 50	1.7	50.8	100	< 0.1	< 0.1	0	< 0.02	0.07
DEP	85	515	39.4	711	100	< 1	3.7	53	< 0.4	9.8
DiBP	352	> 800	42.5	2690	100	< 5	115	93	< 0.4	22.9
DBP	66	744	< 10.4	234	23	2.9	57.8	100	< 0.4	25.2
BBP	3.7	> 50	< 1.3	6.5	23	1.1	14.6	100	< 0.4	31.9
DEHP	49	417	< 10	20.2	10	21.7	158	100	9.1	25.2
DiNP	8.2	214	< 25	35.6	10	3.4	57.1	100	2	50.1
DMEP			< 0.6	< 0.6	0	< 0.02	< 0.02	0	< 0.04	< 0.08

n: number of dwellings; *PX*: percentile *X*; *DMEP*: Di(methoxyethyl) phthalate

Table 9: Values of some phthalates ($\mu\text{g}/\text{g}$) present in indoor settled dust in French homes

Compound	n = 30 [89]		n = 25 – 30 [54]				n = 7 [93]		n = 1 [51]
	P5	P95	n	Minimum	Maximum	Frequency (%)	Minimum	Maximum	
DMP	< 0.07	1.7	25	< 0.08	2.3	88	0.1	0.46	ND
DEP	0.7	6.6	28	< 0.7	93.6	89	1.7	29.6	43.6
DiBP	41	> 52.6	30	8.1	227	100	9.3	574	68.4
DBP	11	> 52.6	29	< 0.7	59.7	97	5.7	20	22.1
BBP	11.4	468	29	0.2	79.5	100	3.8	138	9.3
DEHP	275	5830	30	13.7	1520	100	138	785	185.4
DiNP	258	4100	30	< 2.9	537	97	80	149	312.4
DMEP			30	< 0.06	< 1.8	0	ND/ NQ	ND/ NQ	

n: number of dwellings; ND and NQ: not detected and not quantified, respectively

Table 10: Levels of phthalates ($\mu\text{g/g}$) in indoor settled dust in different homes over the world.

Compound	$\times 10^{-3}$, UK* n = 29 [51]	Stockholm n = 62 [94]	Denmark n = 500 [48]		Canada n = 38 [60]	Texas n = 14 [95]	
	Range	Range	P5	P95	Range	P10	P90
DMP	ND-1.1	ND-2.3			<MDL*-0.01	< LOD	< LOD
DEP	0.6-114.8	ND-323	0.3	200	<MDL-0.01	< LOD	0.1
DiBP	0.2-157.4	2.7-1080	0.1	140	0.002-0.06		
DBP	0.1-106.4	1477681	0.2	74	0.01-0.5	< LOD	0.6
BBP	ND-238.9	3.4-397	0.7	50	0.005-0.7	< LOD	0.5
DnOP		ND-30				< LOD*	0.2
DEHP	0.5-416.4	33-4843	63	980	0.06-1.1	0.02	2.4
DiNP	ND-337.2	ND-5740			0.02-0.6		
DiDP	ND-156.6	ND-2388			0.01-0.2		

*UK: United Kingdom, LOD: Limit of detection, MDL: Method detection limit, and *n*: number of dwellings

2.2.4. EXPOSURE IN INDOOR ENVIRONMENTS

People are greatly exposed to these compounds where phthalate metabolites have been detected in almost all tested human urine [63]. Liang and Xu have estimated by modeling the risk of human exposure to some phthalates emitted from vinyl floorings into indoor environments through the different exposure pathways. They found that infants and toddlers are the most exposed to DEHP emissions from vinyl floorings into indoor environments: 65.4 and 91.5 $\mu\text{g}/\text{kg}\cdot\text{day}$, respectively (Table 11) [65].

Table 11: Overall daily estimated humans' exposure levels ($\mu\text{g}/\text{kg}\cdot\text{day}$) to phthalates emitted from vinyl floorings into indoor environments [65]

Compound	Infants (< 1 year)	Toddlers (1-3 years)	Children (4-10 years)	Teenagers (11-18 years)	Adults (≥ 19 years)
DBP	25.7	21.2	13	9.7	9.1
BBP	10.2	9.4	5.1	3.7	3.4
DEHP	65.4	91.5	25.3	15.8	12.6
DiNP	5.7	7.9	2.2	1.4	1.1

Inhalation of phthalates is a minor exposure pathway while diet is the most exposure path to these compounds [63]. People are exposed to phthalates added to food packaging and teething toys, through ingestion of dust, and dermal absorption of phthalates in personal care products. Wormuth et al. estimated the exposure risk of Europeans of different ages to 8 phthalates by modeling their daily consumptions through food, air, water, household products, etc. [66] (Table 12). The highest exposure risk was for infants and toddlers as well, with the highest exposure dose to DEHP (about 135 $\mu\text{g}/\text{kg}\cdot\text{day}$) and DiNP (about 65 $\mu\text{g}/\text{kg}\cdot\text{day}$). The results emphasize the large usage of DEHP in PVC plastics and the use of DiNP as its substituent.

In addition to being endocrine disruptor chemicals, phthalates are mainly known for their great effect on male reproductive system, fertility, and sperm quality in addition to causing asthma and allergy in children. For example, exposure of mice to DBP at doses of 1.5-3, 50, 100, and 700 $\text{mg}/\text{kg}\cdot\text{day}$ affects mammary gland and spermatocyte development, testosterone levels, fetus male masculinization, and testicular toxicity, respectively [63]. The health effects of a group of the most present phthalates in indoor environments are summarized in Table 13.

Table 12: Daily exposure ($\mu\text{g}/\text{kg}\cdot\text{day}$) of different ages of humans to some phthalates present in different indoor compartments [66], [96]

Compound	Infants 0-12 month (5.5 kg)		Toddlers 1-3 years (13 kg)		Children 4-10 years (27 kg)		Female adults 18-80 years (60 kg)		Male adults 18-80 years (70 kg)	
	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
DMP	1.8	234.5	0.8	9.7	0.5	6.3	0.2	2.5	0.2	2.7
DEP	3.5	19.7	1.5	8.3	0.8	4.4	1.4	64.9	1.2	50.9
DBP	1.6	5.6	0.7	2.6	0.3	1.3	0.4	1.5	0.5	1.6
DiBP	7.6	44.9	2.6	25.4	1.2	17	3.5	38.6	3.6	18.6
BBP	0.8	7.6	0.3	3.7	0.06	1.2	0.3	1.7	0.3	1.9
DEHP	16.2	135.3	6.3	62.1	1.97	17.4	2.5	14.7	2.9	16.3
DiNP	22	135	7.1	67.2	0.2	5.6	0	0.3	0	0.3
DiDP	1.4	9	0.5	4.2	0.03	0.5	0	0.08	0	0.09

Table 13: Health effects of some phthalates present in indoor environments on humans [58], [59], [62], [97]

Compound	Acronym	Potential health effect(s)
Diethyl phthalate	DEP	Reduced growth rate, food consumption and increased organ weights
Di-n-butyl phthalate	DBP	Hepatic and renal effects, developmental and reproductive effects, reduced fetal weight, cryptorchidism, hypospadias, reduced anogenital distance in males
Butylbenzyl phthalate	BBP	Testicular toxicity, cryptorchidism, reduced anogenital distance, teratogenic, modulates steroid hormone levels, Effects perinatal sexual differentiation
Di(2-ethylhexyl) phthalate	DEHP	Hepatocellular carcinoma, testicular toxicity, anovulation, teratogenic at high doses, affects fetal growth, affects perinatal sexual differentiation, female reproduction problems, reduces hydrolysis of body lipids, accumulates triglyceride, and causes obesity
Diisononyl phthalate	DiNP	Effects perinatal sexual differentiation

2.3. Flame retardants

2.3.1. DEFINITION AND PROPERTIES

Flame retardants (FRs) are chemical substances that are added to different household products, such as textile, to delay or inhibit the spread of fire after ignition by suppressing chemical reactions or by forming a protective layer on the surfaces of the material [98], [99]. The composition of these compounds is variable. Some FRs are halogenated (chlorinated or brominated) or might contain phosphorus, nitrogen, metallic compounds, minerals based on aluminum and magnesium, or nanoparticles [99]. The consumption of FRs reached 498,000 tons in Europe in 2007 (Figure 9) [100].

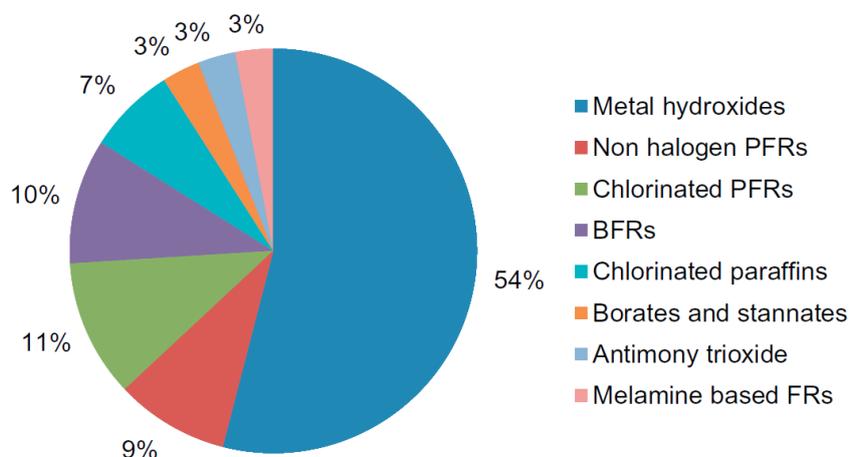


Figure 9: Consumption of flame retardants in Europe in 2007 [100]

Based on their composition, FRs include several sub-families: polychlorinated biphenyls (PCBs), polybrominated diphenyl (PBBs), polybrominated diphenyl ethers (PBDEs), and phosphorus flame retardants (PFRs). However, due to their health and environmental effects, it was prohibited to place on the market new PCBs-containing materials based on a decree issued by the European Union in 1987 and that was modified in 2001 to put plans for getting rid of already available PCB products [101]. Another decree was issued in 2011 limiting the maximum concentration of PBBs and PBDEs to 0.1% by weight in materials [102]. Therefore, the demand of alternative flame retardants (AFRs) such as phosphorus flame retardants (PFRs) and novel brominated flame retardants (NBFRs) had risen [103].

PFRs are of three groups: inorganic, organic, and halogenated flame retardants that differ in terms of structure, reaction, and application [98], [99]. Organic PFRs include in their turn three subgroups: organophosphate esters (OPFRs, Figure 10), phosphonates, and phosphinates [99].

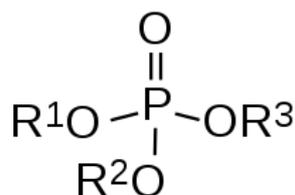


Figure 10: General structural formula of organophosphate flame retardants, R^1 , R^2 , and R^3 represent chloroalkyl radicals for some OPFRs

FRs are classified according to their mode of incorporation in the material into either additive FRs, just added or mixed in a polymer, or reactive FRs, covalently bound to the hosting polymer; however, most FRs are additive [104]. Being additive, FRs can be also emitted from the material into indoor environments, decreasing their concentration with time, and leading to decreased flame retardancy properties [99]. Physico-chemical properties of some OPFRs are listed in Table 14.

Table 14: Physico-chemical properties of some organophosphate flame retardants (OPFRs) [105]

OPFRs	Acronym	Molecular formula	Molecular weight (g/ mol)	V_p at 25 °C (Pa)	Boiling temperature (°C)	Log K_{OA}
Triethyl phosphate	TEP	$C_6H_{15}O_4P$	182	2.2×10	233	6.6
Tributyl phosphate	TBP	$C_{12}H_{27}O_4P$	266	4.7×10^{-1}	327	8.2
Tri(2-chloroethyl) phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	286	5.2×10^{-2}	352	5.3
Tri(2-ischloropropyl) phosphate	T CPP	$C_9H_{18}Cl_3O_4P$	328	7.5×10^{-3}	365	8.2
Tricresyl phosphate	TCP	$C_{21}H_{21}O_4P$	368	8.0×10^{-5}	476	9.6
Triphenyl phosphate	TPP	$C_{18}H_{15}O_4P$	326	6.3×10^{-5}	441	8.5
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	$C_9H_{15}Cl_6O_4P$	431	3.8×10^{-5}	459	10.6

2.3.2. INDOOR SOURCES

Flame retardants (FRs) are used in a wide range of products such as insulating materials, electronic and electrical goods, upholstered furniture, carpets, etc. to decrease the risk of fire or sometimes as plasticizers [10], [98]. Several groups of flame retardants are present in indoor environments. PCBs were used in heat transfer fluids and joint sealants while PBDEs were used as flame retardants in foams, cushioning, mattresses, and electronic devices [89]. The principal uses of PBDEs are presented in Table 15. However, after the European Union banned the use of PCBs in 1987, penta- and octa-BDE mixtures in 2004, and deca-BDE in 2008 [101], [106], [107], the use of PFRs emerged as substituents for these banned compounds.

Table 15: The uses of PBDEs in resins/ polymers and their destined applications [97]

Resin/ Polymer	Deca-BDE	Octa-BDE	Penta-BDE	Application
Acrylonitrile-butadiene styrene		X		Molded and automotive parts of electric devices
Epoxy	X		X	Circuit boards, protective coatings
Paints/ Laquers	X		X	Coatings
Phenolics	X		X	Printed circuit boards
Polyacrylonitrile	X			Panels and electrical components
Polyamide	X	X		Electrical connectors and automotive interior parts
Polybutylene terephthalate	X	X		Electrical components and connectors
Polyethylene/ Cross-linked polyethylene	X			Cross-linked wire cable, foam tubing, weather protection, moisture barriers
Polyethylene terephthalate	X			Electrical components
Polypropylene	X			Conduits and electronics devices
Polystyrene/ High impact polysterene	X	X		Television cabinets and back covers, and electrical housing
Polyvinyl Chloride	X		X	Cable sheets
Polyurethane			X	Cushioning/ packaging materials
Rubber	X		X	Transportation
Textiles	X		X	Coatings
Unsaturated polymers	X		X	Circuit boards, and coatings

Halogenated phosphorus flame retardants act in the gaseous phase and are usually used as flame retardants whereas non-halogenated ones mainly act in the solid phase of burning materials and are mostly used as plasticizers [99]. The use of PFRs as flame retardants is preferred over BFRs. This is because toxic by-products are formed from BFRs during a fire whereas when using PFRs emissions of toxic gases is reduced due to the formation of char [99]. The consumption of PFRs, especially OPFRs,

increased after banning the use of BFRs to constitute 20% of the total FRs consumption in Europe in 2006 [99]. The different applications of OPFRs are listed in Table 16.

Many OPFRs have replaced deca-brominated diphenyl ethers (deca-BDE). Tris(2-chloroisopropyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) are considered good substituents for BFRs; however, not only replacement of BFRs by PFRs took place, but also the substitution of halogenated PFRs with non-halogenated ones, for example the replacement of tris(2-chloroethyl) phosphate (TCEP) and tris(chloropropyl) phosphate (TCPP) by resorcinol bis(diphenylphosphate) (RDP) due to its lower volatility [99].

Table 16: Applications of PFRs in indoor environments [99]

Name	Abbreviation	Application
Tris(2-butoxyethyl) Phosphate	TBEP	Antifoam agent, floor polish, lacquers, plastic, rubber, solvent
Tributyl Phosphate	TBP	Antifoam agent, hydraulic fluids, lacquers, extractant for metal complexes, plastic, solvent
Tricresyl Phosphate	TCP	Hydraulic fluids, PVC, cellulose, cutting oils, plastic, polystyrene, thermoplastics, transmission fluids, solvent
Tris(2-chloroethyl) Phosphate	TCEP	PVC, cellulose, coatings, polyester resins, textile, polyurethane foam
Tris(chloroiso-propyl) Phosphate	T CPP	Polyurethane foam
Tris(1,3-dichloro-2-propyl) Phosphate	TDCPP	Plastic, textile, polyurethane foam
Tris(2-ethylhexyl) Phosphate	TEHP	PVC, cellulose, paints and coatings, rubber, solvent, polyurethane foam
Triethyl Phosphate	TEP	PVC, polyester resins, polyurethane foam
Tetrakis(hydroxymethyl) Phosphonium Sulfate	THPS	Biocide, cellulose, cotton
Triphenyl Phosphate	TPP	Hydraulic fluids, PVC, electronic equipment such as video display units cables, casting resins, glues, engineering thermoplastics, phenylene-oxide-based resins, phenolics resins
Tris(hydroxymethyl) Phosphine Oxide		Polystyrene
Tris(isopropyl-phenyl) Phosphate		PVC, engineering thermoplastics
Trioctyl Phosphate		PVC, paints and coatings, rubber, solvent, polyurethane foam
Trixylenyl Phosphate	TXP	Hydraulic fluids, PVC

2.3.3. INDOOR PARTITIONING

Similar to phthalates, flame retardants are partitioned between the different indoor compartments.

Even if the use of PCBs and some PBDEs was banned in newly manufactured materials, these compounds are still present indoors due to their thermal stability, resistance to microbial degradation, and chemical inertness [63]. Thus, some PCBs and PBDEs are still detected in indoor air, particulate phase, and dust due to their slow emission rates from materials and sorption properties. Studies on the presence of PFRs in indoor environments in French dwellings are not as frequent as those done worldwide. However, TBP was more detected in the particulate phase and settled dust than in indoor air (Table 17 and Table 18) [45], [89], [54].

A study on PFRs present in indoor and outdoor airs was conducted in Rhine/ Mine in Germany. The concentrations of 9 organophosphate flame retardants (OPFRs) was determined in 56 indoor and 9 outdoor samples [10]. The total concentration of these compounds in indoor air ranged from 3.3 to 751 ng/ m³ which is significantly higher than their total concentration in outdoor air: 1.7 to 21.1 ng/ m³. Another study on OPFRs present in indoor air was conducted in 12 locations in and around Zurich in Switzerland [108]. They found that TCPP is more detected where polyurethane foams usage is dominant but not in the electronic stores. While TBP and TCEP are detected in almost all samples indicating their variable application compared to TCPP. The results of the two studies are shown in Table 19.

The concentrations of PBDEs and OPFRs in settled dust in countries all over the world was determined in a group of studies (Table 20 and Table 21). These concentrations are comparable in almost all the listed countries TCEP, TCPP, TPP, and TDCPP have the highest concentrations in settled dust; however, OPFRs levels are higher in Japan.

Table 17: Levels (ng/ m³) of flame retardants in indoor air in French dwellings

Compound		Gaseous Phase					Particulate Phase				
		n = 30 [89]		n = 30 [54]			n = 30 [54]			x 10 ⁻³ , n = 567 [45]	
		P5	P95	Minimum	Maximum	Frequency (%)	Minimum	Maximum	Frequency (%)	P5	P95
PBDEs	BDE-28			< 0.6	< 0.6	0	< 0.002	< 0.002	0	< 0.4	1.9
	BDE-47			< 0.6	< 0.6	0	< 0.002	0.134	90	< 2.1	0.13
	BDE-85			< 0.6	< 0.6	0	< 0.002	< 0.002	0	< 4.2	< 4.2
	BDE-99	< 1	4.9	< 0.6	< 0.6	0	< 0.002	0.082	90	< 2.1	0.06
	BDE-100			< 0.6	< 0.6	0	< 0.002	0.019	53	< 2.1	0.014
	BDE-119			< 0.6	< 0.6	0	< 0.002	< 0.002	0	ND	ND
	BDE-153			< 0.6	< 0.6	0	< 0.002	< 0.002	0	< 4.2	< 4.2
	BDE-154			< 0.6	< 0.6	0	< 0.002	< 0.002	0	< 4.2	< 4.2
	BDE-209			<2.5	4.5	3	< 5	< 20	0		
PCBs	PCB-28	< 26.3	< 26.3	< 0.03	0.07	4	< 0.002	< 0.002	0	< 0.4	2.2
	PCB-31	< 26.3	< 26.3	< 0.03	< 0.7	0	< 0.002	0.006	3	< 0.4	2.2
	PCB-52	< 26.3	48	< 0.03	0.2	8	< 0.002	0.004	3	< 0.4	11.5
	PCB-77			< 0.03	< 0.7	0	< 0.002	< 0.002	0	< 0.4	1.5
	PCB-101	< 26.3	107	< 0.03	0.3	21	< 0.002	0.028	3	< 0.4	29.9
	PCB-105			< 0.03	0.1	14	< 0.002	0.04	3	< 0.4	18.5
	PCB-118			< 0.03	0.2	28	< 0.002	0.07	3	< 0.4	47.9
	PCB-126			< 0.03	< 0.7	0	< 0.002	< 0.002	0	ND	ND
	PCB-138	< 26.3	79	< 0.03	0.4	12	< 0.002	0.1	3	< 0.4	53.6
	PCB-153			< 0.03	0.3	26	< 0.002	0.05	13	< 0.4	40.2
	PCB-180			< 0.03	0.3	13	< 0.002	0.03	13	< 0.4	25.1
OPFRs	TBP	2	12.4	< 0.6	5.4	63	0.3	7.3	100		

n: number of dwellings

Table 18: Levels ($\mu\text{g/g}$) of flame retardants in settled dust in French dwellings

Compound		n = 30 [89]		n = 19 – 30 [54]			n = 7 [93]		
		P5	P95	n	Minimum	Maximum	Frequency (%)	Minimum	Maximum
PBDEs	BDE-28			30	< 0.6	<1.8	0		
	BDE-47			22	< 0.6	0.23	18		
	BDE-85			30	< 0.6	<1.8	0	NQ	0.001
	BDE-99	< 0.07	0.3	21	< 0.6	0.28	14	< 0.07 x 10 ⁻³	0.002
	BDE-100			30	< 0.6	<1.8	0	< 0.2 x 10 ⁻³	0.47 x 10 ⁻³
	BDE-119			30	< 0.6	<1.8	0		
	BDE-153			30	< 0.6	<1.8	0		
	BDE-154			30	< 0.6	<1.8	0		
	BDE-209			16	<0.5	1.7	44		
PCBs	PCB-28	< 0.03	< 0.03	23	< 0.03	0.07	4		
	PCB-31	< 0.03	< 0.03	30	< 0.03	< 0.7	0		
	PCB-52	< 0.03	0.05	24	< 0.03	0.2	8	ND	0.095
	PCB-77			30	< 0.03	< 0.7	0		
	PCB-101	< 0.03	0.1	24	< 0.03	0.3	21	ND	0.3
	PCB-105			22	< 0.03	0.1	14	ND	0.1
	PCB-118			18	< 0.03	0.2	28	ND	0.3
	PCB-126			30	< 0.03	< 0.7	0		
	PCB-138	< 0.03	0.08	25	< 0.03	0.4	12	ND	0.3
	PCB-153			19	< 0.03	0.3	26	ND	0.2
	PCB-180			23	< 0.03	0.3	13	ND	0.06
OPFRs	TBP	< 0.07	0.4	21	< 0.09	1.3	90	NQ	NQ

n: number of dwellings; ND: not determined; NQ: not quantified

Table 19: Concentrations of organophosphate flame retardants (OPFRs) (ng/ m³) in indoor and outdoor airs in Rhine/ Mine (Germany) and limits of detection (LOD) (ng/ m³) of these compounds in indoor air in Zurich (Switzerland)

Compound		Indoor Air n = 56 [103]		Outdoor Air n = 9 [103]		Indoor air LOD n = 12 [108]
		Mean	Range	Mean	Range	
Non-chlorinated organophosphates (non-Cl-OPFRs)	TEP	1.29	<MDL-27.13	< MDL	<MDL	
	TPP	0.26	<MDL-8.91	0.57	<MDL-4.29	0.15
	TIBP	26.41	<MDL-663	1.55	<MDL-4.35	
	TBP	10.2	<MDL-112.1	1.4	<MDL-8.66	0.073
	TBEP	0.74	<MDL-17.51	< MDL	<MDL	0.3
	TEHP	0.36	<MDL-9.55	0.08	<MDL-0.42	0.11
Chlorinated organophosphates (Cl-OPFRs)	TCEP	1.04	<MDL-9.24	< MDL	<MDL	0.15
	TCPP	38.99	1.19-496.9	2.66	<MDL-11.06	0.12
	TDCPP	2.61	<MDL-29.86	1.07	<MDL-7.07	0.11

n: number of sites; MDL: method detection limit

Table 20: Levels ($\mu\text{g/g}$) of polybrominated diphenyl ethers (PBDEs) in indoor dust in countries all over the world

Compound	UK n = 10 [51]	Singapore n = 31 [109]	Barcelona n = 5 [110]	Texas n = 14 [95]	
	Range			P10	P90
BDE-28	< 0.0001-0.03	< LOD-0.006		< LOD	7.7
BDE-47	0.01-2	< LOD-1.5	0.007-0.1	< LOD	0.7
BDE-85				< LOD	2.1
BDE-99	0.02-2.1	< LOD-6.3	0.005-0.02	< LOD	1.6
BDE-100		< LOD-1.2	ND-0.006	< LOD	0.9
BDE-119					
BDE-153	< 0.0001-0.2	< LOD-1.4	0.008-0.01	< LOD	2.5
BDE-154		< LOD-1	ND-0.003	< LOD	0.2
BDE-183	< 0.0001-0.09	0.002-0.2		< LOD	0.2
BDE-209	3.8-19.9	0.07-13	1.1-13.8	0.1	12.8

n: number of sites; *LOD*: limit of detection

Table 21: Levels ($\mu\text{g}/\text{g}$) of organophosphate flame retardants (OPFRs) in indoor settled dust in different homes in worldwide countries

Compound	Stockholm n = 62 [95]	Barcelona n = 5 [110]	Netherlands n = 8 [111]	Japan n = 120 [112]	Canada n = 134 [113]	New Zealand n = 16 [103]
	Range					Concentration
TMPP	ND-31	0.1-0.5	< 0.05-0.2	ND-193.1		
TEHP	ND-46	0.2-0.7		ND-73.1		
TPP	ND-1.6			ND-<MDL		
TDCPP	ND-12	0.2-1.4	0.07-3.2	<MDL-593.1	0.1-77	0.1
TCPP	1.2-98	1.9-7.2	0.5-3.8	1.3-462.4	<MDL-56	0.3
TCEP	ND-808	0.1-13.2	0.2-6.9	<MDL-2320	<MDL-33	0.04
TBP	0.12-162	0.09-0.1	0.01-0.2	ND-42.8	<MDL-7.1	0.07
TiBP	ND-47	0.09-0.2	0.03-0.2			
TPP	0.7-38	0.6-2.6	0.7-11	<MDL-889.2	0.3-63	0.2

n: number of dwellings; ND: not detected; MDL: method detection limit; TMPP: Tris(methylphenyl) Phosphate

2.3.4. EXPOSURE IN INDOOR ENVIRONMENTS

Indoor exposure to PCBs is considered to be more significant than outdoor one due to the 10 to 100,000 times higher air concentration of PCBs indoors than outdoors [63]. Exposure to these compounds affects the immune, reproductive, nervous, and endocrine systems and causes breast cancer [11].

Similar to PCBs, exposure of humans to PBDEs is higher indoors than outdoors. Exposure pathways to these compounds are variable including indoor air, dust, and food [63]. In addition to PBDEs, OPFRs are widely present in indoor environments nowadays due their usage as substituents for PBDEs and PCBs. These compounds are greatly present in both indoor air and dust as previously mentioned. People are thus greatly exposed to these compounds through inhalation and dust ingestion.

A study was conducted in the United States to estimate the daily indoor intake of PBDEs and OPFRs from dust by firefighters [114]. Exposure doses ranged from 0.017 to 20.1 ng/ kg. day for PBDEs depending on the compound (Table 22). Moreover, toxicity values of some PBDEs and OPFRs were also estimated in this study (Table 23). BDE-209, TCPP, and TDCPP were shown to cause liver, kidney, or testes cancer for 0.014, 5×10^{-4} , and 7.7×10^{-5} mg/ kg. day, respectively.

Inhalation exposure risk to PBDEs and OPFRs was estimated by another study done also in the United States in 18 different indoor spaces [115] (Table 24). The mean inhalation exposure dose was about 1 ng/ kg. day for the studied PBDEs and OPFRs. In France, 17 FRs, including PBDEs and OPFRs, have been recently identified in 12 upholstered furniture present in the French market [116]. This study shows that these compounds, particularly PFRs, have the ability to migrate into indoor air increasing human risk of exposure to these compounds by inhalation.

PBDEs and OPFRs have similar health effects to those of PCBs: nervous, reproductive, growth, and hormonal problems in addition to respiratory problems for OPFRs. The CLP regulation classified some OPFRs according to the health effects they might cause [73]. TBP, TCEP, and TDCPP were classified as potentially carcinogenic substances in addition to TBP and TCEP being skin irritant and reproductive toxic, respectively. The health effects caused by some halogenated and non-halogenated OPFRs are summarized in Table 25.

Table 22: Daily intake of PBDEs from indoor dust by firefighters in the United States [114]

PBDEs	28	47	99	100	153	154	183	196	197	206	207	208	209
Intake from Dust (ng/ kg. day)	0.017	2.22	3.96	0.74	0.52	0.39	0.033	0.033	0.022	0.48	0.25	0.16	20.1

Table 23: Toxicity doses due to the intake of some PBDEs and OPFRs by firefighters in the United States (NA = not available) [114]

Toxicity Value	BDE-47	BDE-99	BDE-153	BDE-197	BDE-209	TCEP	TCPP	TDCPP
Oral (mg/ kg. day)	3×10^{-6}	3×10^{-6}	3×10^{-6}	3×10^{-6}	2×10^{-4}	0.067	0.014	1.9×10^{-3}
Inhalation (mg/ m ³)	0.006	0.006	0.006	0.006	NA	≤ 0.2	NA	NA
Dermal Absorption (%)	62	NA	1.9	4.5	0.34	100	40	30
Cancer (mg/ kg. day)	NA	NA	NA	NA	0.014 (liver cancer)	5×10^{-4} (kidney cancer)	NA	7.7×10^{-5} (liver, kidney, and testes cancer)

Table 24: Inhalation exposure doses of occupants to some PBDEs and OPFRs in 18 indoor spaces in the United States [115]

Compound	BDE-47	BDE-85	BDE-99	BDE-100	BDE-153	TCEP	TCPP	TDCPP
Mean inhalation exposure dose (ng/ kg. day)	1.1	0.9	1.1	1.1	1.1	1.2	1.1	1.1

Table 25: Health effects of some phosphorus flame retardants (PFRs) present in Indoor environments on humans [10], [99]

Compound	Acronym	Health Effect(s)
Triethyl phthalate	TEP	Nervous and male reproductive problems
Tris(2-chloroethyl)phosphate	TCEP	Toxic for kidneys, liver, and brain Causes health damage and potentially cancer, neurotoxin, reproductive problems
Tris(1,3-dichloroisopropyl)phosphate	TDCPP	Decreases semen quality in me, carcinogenic category 2
Tris(2-chloroisopropyl)phosphate	T CPP	Potential concern for carcinogenicity, irritating to skin and eyes
Tributyl phosphate	TBP	Neurotoxic, causes asthma and allergic rhinitis
Tris(2-butoxyethyl)phosphate	TBEP	Suspected to be carcinogenic
Triphenyl phosphate	TPP	More toxic to aquatic organisms than humans Neurotoxic, sensitizer of allergies, causes contact dermatitis, affects immunological defense system, potent human blood monocyte carboxyl esterase inhibitor
Tricresyl phosphate	TCP	Reproductive toxin, neurotoxic based on its different isomers

3. EMISSIONS OF SVOCs FROM MATERIALS

The emissions of SVOCs from materials into indoor air is considered one of the major sources of indoor air pollution, as previously mentioned, and results in severe human health effects. To limit the indoor concentrations of toxic emitted SVOCs, certain regulations are imposed on materials before they are placed on the market.

The French government established an order in 2009 declaring that construction and decoration products cannot be placed on market if the emitted concentrations of carcinogenic, mutagenic, or reproduction toxic (CMR), including DBP and DEHP, exceed $1 \mu\text{g}/\text{m}^3$ [27]. This value is calculated according to the protocols defined in the ISO 16000 series [21]–[23], [25]. Moreover, $0.1 \text{ mg}/\text{m}^3$ is the acceptable concentration of SVOCs emitted in total (TSVOCs: C6-C22) set by AgBB within 28 days of emissions in test chambers according to EN 16516 [40], [117]. But regulations on the emissions of flame retardants from indoor materials are still rare. Moreover, the generalization of the use of flame retardants in upholstered furniture in the European Union is still under discussion [118]. For this reason, the French Agency for Food, Environmental and Occupational Health & Safety (ANSES) was chosen in 2011 to carry out an appraisal for identifying the used flame retardants in upholstered furniture put on the French markets, in addition to evaluating the benefits and risks associated with their use [119].

However, in order to be able to study the emission of SVOCs from building and consumer materials, it is important to understand the behavior and transfer of these compounds upon emission which are still not fully defined.

3.1. Emission mechanism

3.1.1. MASS TRANSFER OF SVOCs

Empirical and mass transfer models have been developed for describing the behavior of SVOCs in indoor environments or emission test chambers. However, mass transfer models are more relevant than empirical models since they are developed on clear physical basis [120]. These models are usually validated based on results obtained from emissions of compounds of interest in test chambers.

Modeling of SVOCs emissions follows the same procedure as that of VOCs except that adsorption into interior surfaces should be additionally taken into consideration [65], [120], [121]. Cox et al. developed a mass transfer model for predicting the emission rate of VOCs from vinyl floorings [122]. Xu and Little extended this model later to understand the emissions of SVOCs and predict their emission rates from

the same materials [121]. In this model SVOCs are considered uniformly distributed in the hosting material. Moreover, the initial material-phase concentration (C_0), material-air partitioning coefficient (K), convective mass transfer coefficient (h_m), and surface/ air partitioning coefficient (K_s) are considered the key parameters that control the emissions of these compounds.

The mechanisms controlling the emission and sorption of SVOCs are represented by the scheme in Figure 11 where the parameters shown in the figure are defines as follow: V is the volume of the chamber, y is the gas-phase compound concentration in the chamber air, Q is the air flow rate in the chamber, q_s is the sorbed compound concentration, y_s is the compound gas-phase concentration in the air adjacent to the sorption surface, h_s is the convective mass transfer coefficient near the sorption surface, K_p is SVOCs partitioning coefficient between air and particles, and TSP is the total mass concentration of suspended particles.

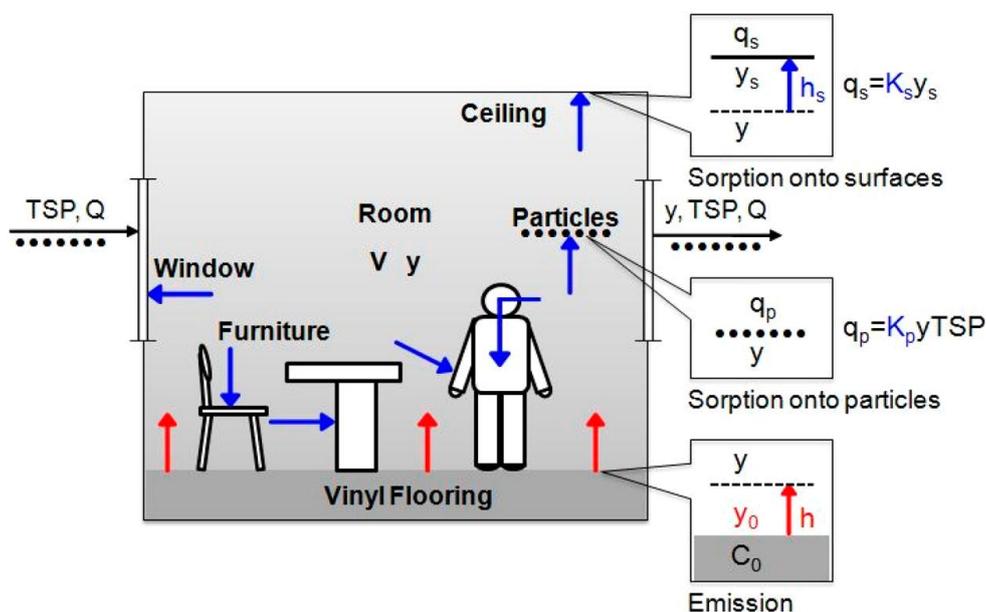


Figure 11: Schematic representation of the emission of SVOCs from material in a closed chamber with air exchange [67]

The emission of VOCs and SVOCs from solid hosting material is either internally or externally controlled. Internally controlled emission is through diffusion within the material while externally controlled emissions is via mass transfer between the material surface and the gaseous boundary layer existing above it [121]. The domination of one phenomenon over the other depends on the ratio of the mass transfer Biot number (Bi_m) to K which is representable of the ratio of internal diffusion (within the material) to the mass transfer (across the material surface). Bi_m can be determined according to the following equation [123]:

$$Bi_m = \frac{h_m L}{D} \quad (6)$$

Where L is the thickness of the source material.

So if Bi_m/K is larger than 1, emission is controlled by internal diffusion while if it is smaller, it is controlled by mass transfer [120]. For VOCs, emissions are mostly internally controlled while for SVOCs they are externally controlled.

Due to their high molecular weights and low vapor pressures, the emission rate of SVOCs from material is slow, so that their total emitted mass is negligible compared to their initial-material mass [120]. For example, Xu et al. found that 0.003% of the total mass of DEHP was emitted from vinyl floorings after one year [44]. As a result, in this case, the initial concentration (C_0) of SVOCs with very low volatility, like DEHP, is considered constant over time and thus diffusion of these compounds within the material is no longer important. Therefore, as most studies on the emission of SVOCs concern phthalates, internal diffusion within the material is neglected and SVOCs gas-phase concentration in equilibrium with the material surface (y_0) is the key parameter in estimating their emissions from building and consumer materials [65], [105], [124]–[127].

3.1.2. RELATION BETWEEN y_0 AND C_0

The relation between C_0 and y_0 of SVOCs and whether these two parameters can be considered constant or not for all SVOCs are still not well understood.

Cao et al. found an exponential relationship between C_0 and y_0 , but this relation was only applied for DEHP and is still not validated for other SVOCs [125]. Usually a linear partitioning exists between C_0 and y_0 of SVOCs when their concentration in the material is less than 1% [67], [120].

Liang et al. showed that y_0 and the mass fraction (proportional to C_0) of phthalates and organophosphate flame retardants in the material are linearly related [123]. However, this relation does not include SVOCs with high mass fraction (> 15%) due to the lack of data on these latter.

In most of the developed methods on phthalates, C_0 and y_0 are considered constant throughout the emission. This assumption is valid in case the material/ air partitioning coefficient (K) and C_0 are large [123], [128], [129]. However, Pei et al. found that y_0 of phthalates (DiBP and DBP) and OPFRs (TCPP) emitted from vinyl floorings and polyurethane foams (PUF), respectively decreased by 16 to 36% within 60 days in a ventilated test chamber, but that of DEHP decreased by 38% after about 1.5 years [130]. Based on their results, there are two reasons behind this: 1) due to the increased porosity of the PUF with time leading to an increase of diffusion within the material and a consequent decrease in C_0 of OPFRs or 2) due to the non-negligible internal diffusion of SVOCs within the material in the case of

vinyl floorings. To explain the second reason, they suggested that diffusion coefficients (D) used in the previously developed emission chambers and models to calculate B_{im}/K are overestimated and that the internal diffusion of phthalates cannot be always considered negligible. Thus, phthalates in the deeper layers of vinyl floorings will not diffuse to the surface due to small diffusion coefficients and thus surface C_0 will decrease leading to a decrease in y_0 as well. However, these suggestions are still not well developed and further studies should be conducted for accurate determination of D and K.

Liu et al. have developed a method to estimate these two parameters for PCBs by model fitting [131]. This method was later applied by Liang et al. to calculate D and K for OPFRs emitted from PUF to find that emissions of TCEP and TCPP might be both internally and externally controlled [123], but this hypothesis needs further validation.

3.1.3. SORPTION

Due to their sorption ability, another boundary layer exists between the gaseous phase of the chamber and its walls in the case of SVOCs (Figure 11). In this layer, accumulation rate of SVOCs on the sorption surfaces follows a convective mass transfer characterized by h_s , K_s , and y_s . Therefore, emission of SVOCs in chambers occurs by air diffusion of these compounds from the surface of the material into the air bulk of the chamber until reaching steady state, i.e. the emission rate of SVOCs from the material becomes constant and equal to their sorption rate on interior surfaces [132]. Once at steady state, y_s is assumed to be equal to y [65]. K_s is calculated by determining the amount of SVOCs adsorbed on the different surfaces of a chamber [65], [105], and h_s is determined based on empirical correlations and Sherwood number (Sh) or by model fitting [65], [67].

However, when the source of emission is depleted or removed, SVOCs adsorbed on the surfaces will act as the new source of emission to compensate for losses [67].

3.1.4. IMPORTANT PARAMETERS FOR CHARACTERIZING THE EMISSION OF SVOCs

The main objective behind characterizing the emission of SVOCs, in addition to understanding the mechanism of their emission, is to predict the risk of human indoor exposure to these compounds. Little et al. developed a simplified model to estimate the steady-state gas phase concentration of SVOCs (y_{ss}) using the following equation [67]:

$$y_{ss} = \frac{h_m \cdot y_0 \cdot A}{h_m \cdot A + h_s \cdot A_s + (1 + K_p \cdot TSP) \cdot Q} \quad (7)$$

This parameter is needed to apply in the different exposure-pathways dose equations: air inhalation, dust and gas dermal absorption, and dust ingestion [65], [67].

A and A_s , that are the areas of the used material and the sorption surfaces, respectively, are available. Up to know, there is no precise determination of h_m ; however, similar to h_s , it is estimated either based on empirical correlations and Sherwood number (Sh) [65], [123], [133] or by model fitting [134], [135]. TSP is available in literature and K_p can be estimated as previously mentioned in the above partitioning part. However, there is a need to find the value of y_0 for (7) to be applicable in estimating exposure risks to SVOCs.

Xu and Little developed a mass transfer model to understand and predict the emission of SVOCs, such as phthalates, flame retardants, from polymeric materials in closed ventilated chambers [121]. This model considers that SVOCs are uniformly distributed in the test material and that they are subject to external control. Later on this model was simplified by Xu et al. for determining y_0 of SVOCs emitted from building and consumer materials in test chambers [124]. This model suggested a group of equations that describe, emission, sorption and accumulation of SVOCs in the test chamber. According to the simplified model, the emission rate (E) ($\mu\text{g}/\text{m}^2\cdot\text{h}$) of SVOCs in the chamber is represented by the following equation:

$$E_{(t)} = h_m \cdot (y_0 - y_{(t)}) \quad (8)$$

Where $y(t)$ ($\mu\text{g}/\text{m}^3$) is the concentration of SVOCs in the chamber air at time t . Assuming that accumulation of SVOCs on sorption surfaces follows a linear isotherm, the surface/ air partitioning coefficient (K_s) (m) can be expressed as:

$$K_s = \frac{q}{y_s} \quad (9)$$

Where q is the surface concentration of SVOCs ($\mu\text{g}/\text{m}^2$) and y_s is the gas-phase concentration immediately adjacent to the sorption surface ($\mu\text{g}/\text{m}^3$).

Assuming a boundary layer exists next to the sorption surface, the amount of SVOCs accumulated on the surface can be represented as:

$$\frac{dq(t)}{dt} = h_s \cdot (y_{(t)} - y_s) \quad (10)$$

Where h_s is the convective mass transfer coefficient near the sorption surface (m/s). Therefore, the accumulation of SVOCs in the test chamber obeys the following mass balance:

$$\frac{dy(t)}{dt} \cdot V = E_{(t)} \cdot A - \frac{dq(t)}{dt} \cdot A_s - y_{(t)} \cdot Q \quad (11)$$

Once steady state is reached, y_s becomes equal to y and thus $\frac{dq(t)}{dt}$ in equation 10 becomes equal to zero. Therefore, by combining the above equations, they obtained the following equation at steady state:

$$y_0 = \frac{y_{SS} \cdot Q}{h_m \cdot A} + y_{SS} \quad (12)$$

Where y_{SS} is the steady-state gas phase concentration of SVOCs ($\mu\text{g}/\text{m}^3$).

Up to now, equation 12 has been the most used in estimating y_0 of emitted SVOCs in test chambers.

3.2. Available methods for characterizing the emissions of phthalates and OPFRs from materials

Classical laboratory emission chambers and cells were developed for characterizing the emission of VOCs from building materials. These include the 24 L (0.02 m³) glass desiccator, 203 L and 1 m³ test chambers, Chamber of Laboratory Investigations of Materials, Pollution, and Air Quality (CLIMPAQ), Field and Laboratory Emission Cell (FLEC), and the 1 L emission cell [136]–[140] (Figure 12). In order to understand the emissions of SVOCs and characterize this latter from building and consumer materials (e.g. floors, adhesives, and paints), emission tests were done using some of these chambers in early stages. The tested material is placed in the test chamber or the emission cell is placed on it and continuous sampling occurs using either glass tubes filled with polyurethane foams (PUF) [98], or adsorbent tubes (e.g. Tenax tubes) [141]. The air concentration of emitted SVOCs is thus determined in order to calculate their emission factor.

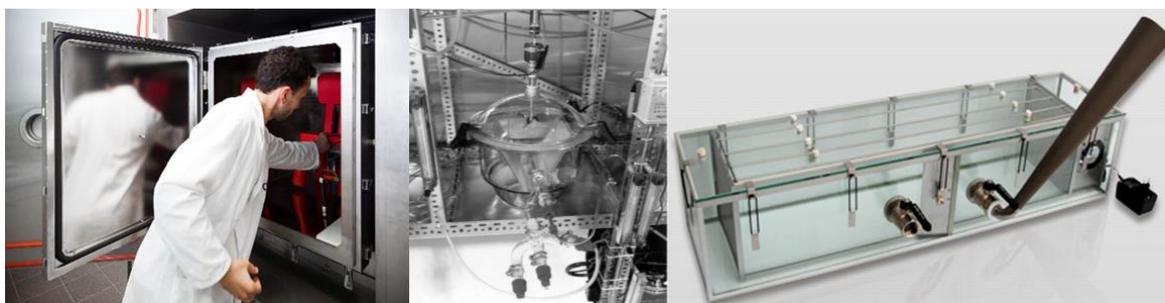


Figure 12: 1 m³ test chamber, 0.02 m³ glass desiccator, and CLIMPAQ emission test chambers

However, due to their high molecular weight and low vapor pressure, SVOCs are characterized by their slow emission rate and sorption capacity on the walls of the chamber. Therefore, the time of experimentation is so long in these chambers at which steady state is reached after 60 days using the 0.02 m³ test chamber [98] and 150 days in the CLIMPAQ and FLEC [138], [139]. In addition, contamination in laboratory facilities and the complexity of the experimental procedures are supplementary limitations [65], [124], [125]. Thus these types of chambers are not well suited for SVOCs measurements.

Therefore, adapted test chambers should be developed to characterize the emissions of SVOCs, particularly phthalates and OPFRs, from building and consumer materials. Maximizing the sample surface area and decreasing sorption surfaces are the key parameters for optimized emission chambers for SVOCs characterization [65]. These chambers include laboratory or on-site emission chamber and can be either dynamic (with air circulation over the material surface) or static (without air circulation in the chamber).

Most of the laboratory emission chambers include active sampling since they require air pumps to measure the overall concentration of emitted SVOCs. While on-site test chambers are divided into active and passive sampling methods at which the concentration of emitted SVOCs in the gaseous phase is determined by collecting samples that diffuse from the surface of the material into air and the sampling support.

Most of these methods are developed to determine y_0 of phthalates and OPFRs since it is the key parameter in estimating their emissions from building and consumer materials into indoor environments [65], [105], [124]–[127]. However, in most cases y_0 is determined by model fitting validated by experimental results obtained in these chambers.

A description of the different available measurement methods and test chambers developed to study the emissions of phthalates and OPFRs is listed below.

3.2.1. ON-SITE MEASUREMENT METHODS

3.2.1.1. Dynamic methods

Dynamic laboratory measurement methods are also known as chamber methods because they consist of a closed chamber with controlled conditions of temperature, relative humidity, and air flow rate inside.

Field and Laboratory Emission Cell (FLEC)

One of the active on-site measurement cells is the FLEC (Field and Laboratory Emission Cell). It is a small volume emission cell designed to study the emission of VOCs from building materials as recommended by ISO 16000-10 and was firstly used in 1991 [142], and was then adapted for measuring the emission rate of SVOCs [138]. It is a stainless steel circular cell, with an inner diameter of 150 mm and a volume of 35 mL (Figure 13), which is placed on the top of the material to measure the concentration of emitted volatile compounds under a constant air flow rate [141]. The interface between the material surface and FLEC is tightened by an O-ring silicon rubber and sampling occurs using adsorbent tubes (e.g. Tenax TA) after reaching equilibrium [143].

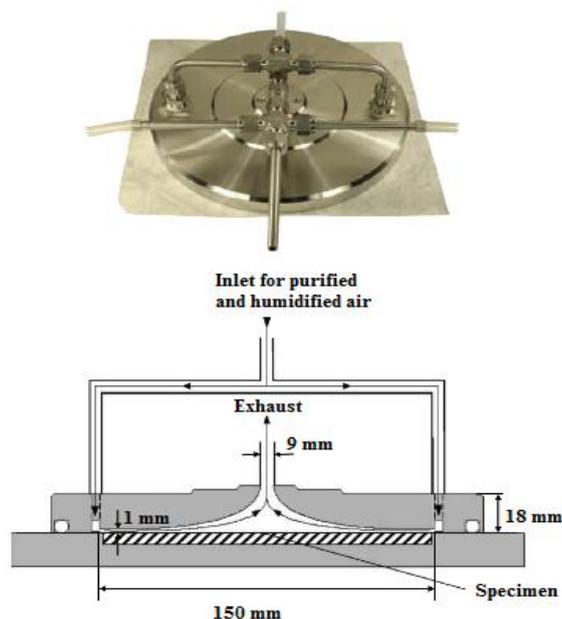


Figure 13: Field and Laboratory Emission Cell (FLEC®) and its Schematic Representation [144]

Clausen et al. found that at flow rates of 450 mL/min or less, y_{ss} is equal to y_0 and that y_0 is close to the vapor pressure of the pure compound [145]. However, steady state in the FLEC is reached after 150 days [138].

Since reaching steady state takes time in most of the developed methods, Xiong et al. developed a new model known as early stage C-history model to find y_0 and h_m of SVOCs [134]. This model was validated based on emission results obtained in the FLEC. The advantage of this model is that it is not necessary to reach steady state for determining y_0 ; it is sufficient to have early stage emission concentrations ($y(t)$) to determine h_m and y_0 from the slope of the linear relationship existing between y of SVOCs and time (t):

$$y(t) = y_0 \cdot h_m \cdot L \cdot t \quad (13)$$

Where L (s^{-1}) is the ratio of air flow rate to volume of the chamber and t is the time (s).

This model was well validated with a %RSD less than 10% between the obtained values of y_0 and h_m and those present in literature from the FLEC and sandwich-like chamber emission experiments. However, accurate h_m values should be known to use this model.

3.2.1.2. Static methods

Static on-site measurement chambers are easier to use and implement than dynamic emission chambers. Moreover, they are characterized by having their analytical sensitivity, shorter equilibrium time, and better recovery of SVOCs [146].

Adsorbent tubes

Wu et al. developed a passive on-site sampling method for estimating y_0 of SVOCs [127]. It consists of a thermal desorption tube (i.e. Tenax TA) inserted between two stainless steel cylinders, separated from the surface of material by a stainless-steel shim to prevent direct contact, and placed on the top of the material to be studied (Figure 14). In this method, emission of SVOCs occurs by diffusion from the surface of the material into the Tenax TA adsorbent present in the tube. However, it is not possible to distinguish between y_0 and the SVOCs sorbed on the tube walls when desorbing the collected SVOCs in the tube. Therefore, y_0 is then obtained by modeling of the sorbed amount in the adsorbent tube. Liang et al. applied recently this method also for estimating y_0 of organophosphate flame retardants emitted from polyurethane foams [123].

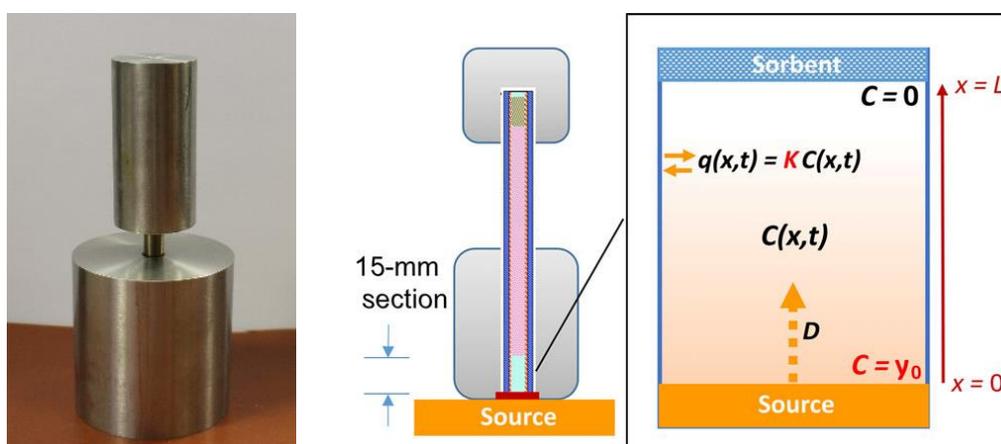


Figure 14: Diffusive adsorbent tube sampler and its schematic representation [127].

Passive flux samplers (PFS)

Passive Flux Sampler (PFS) is another passive on-site sampling method that was developed for measuring the emission rates of volatile organic compounds (VOCs), especially formaldehyde [147]. This type of samplers has been adapted to characterize the emissions of phthalates and organophosphate flame retardants [148], [149]. It is made of a Pyrex glass plate with an adsorbent glass filter or empore disk placed at its bottom (Figure 15). This device is placed directly on the material, emitted compounds are trapped on the filter by diffusion from the surface of the material into the adsorbent disk, and then are extracted using organic solvents for analysis.

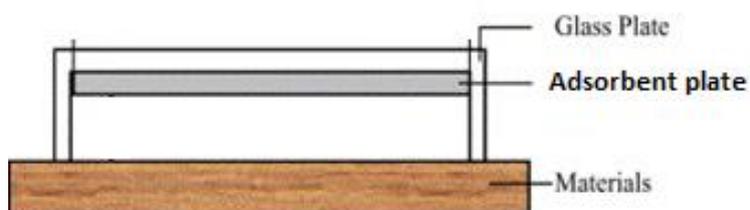


Figure 15: Schematic representation of the Passive Flux Sampler (PFS) [148]

This method is also applied to characterize the emission of SVOCs from building materials. Shinohara et al. used a PFS to determine the emission rate of DEHP from vinyl floorings according to Fick's law and then they estimated y_0 based on the following equation [135]:

$$E = D \cdot y_0 \cdot \frac{1}{d} \quad (14)$$

Where D is the compound diffusion coefficient in air (m^2/s) and d is the diffusion distance from the surface of the material to the PFS adsorbent (m).

Noguchi and Yamasaki also measured the amount of DEHP captured on a glass fiber in a PFS. They have then estimated y_0 from the slope and intercept of the obtained linear relation between their measured amount and time in their developed model [149]. Although the PFS method is easy to apply, errors from extractions of SVOCs adsorbed on filters is the limiting point.

SPME-emission cell

Another passive sampling emission cell coupled to a Solid-phase Microextraction (SPME) was developed by Ghislain et al. for studying the emission of organophosphate flame retardants from polyurethane foams [105] (Figure 16). Similar to the other static method chambers, y_{ss} is equivalent to y_0 in this emission cell where steady state is reached within 5 hours for the samples studied.

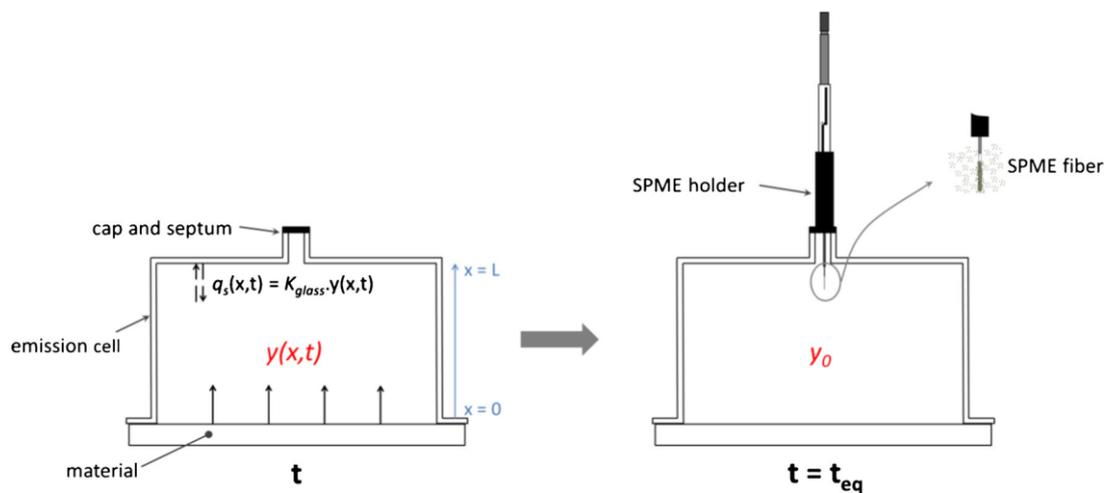


Figure 16: A schematic representation of the adapted SPME-emission cell [105]

3.2.2. LABORATORY MEASUREMENT METHODS

3.2.2.1. Dynamic methods

Micro-chambers

Maximizing the sample surface area and decreasing sorption surfaces are the key parameters for optimized emission chambers for SVOCs characterization [65]. The standard ISO 16000-25 was especially issued in 2011 for characterizing the emissions of SVOCs from building products [19]. It recommends the use of micro-chambers due to their relatively high loading factors (i.e. small internal volume and relatively big emitting surface). According to this norm, micro-chambers are made of airtight glass or stainless-steel chambers where the material is placed with a constant air flow rate traversing it. The characterization of SVOCs emissions occurs in two steps. In the first step, active sampling occurs using adsorbent tubes for the collection of the emitted SVOCs. While in the second step, the test material is removed and the chamber is placed in an oven at 220 °C for recovering the SVOCs adsorbed on its walls due to sink effect. Therefore, the actual amount of emitted SVOCs will be the sum of both emitted and desorbed compounds. Based on the recommendations of this standard upon characterizing the emissions of SVOCs from materials, a group of adapted test chambers and measurement methods has been developed later on for characterizing the emissions of phthalates and OPFRs from building and consumer materials, particularly floorings.

Markes International fabricated a commercial micro-chamber type thermal extractor (μ -CTE) [150]. It is a device made up of small cylindrical stainless steel cells placed in series with a constant flow rate of air traversing each cell and an integrated temperature control system (Figure 17). Two models of the μ -CTE exist: μ -CTE250 that is made up of four cells of 114 mL volume each and can be heated up to 250 °C and the other μ -CTE120 made up of six cells of 44 mL each and can be heated up to 120 °C.



Figure 17: The six- and four-cell thermal extractor (μ -CTE) [146], [150]

This device was intended to be a complementary tool for rapid screening and identification of VOCs in industrially manufactured materials (e.g. plastic) [146], [151]; moreover, it was used to determine the emission rates and study the behavior of VOCs emitted from different indoor materials [137], [152]. Recently, this device is being applied for characterizing the emission of SVOCs as well. It was also used to study the migration of brominated flame retardants into dust upon volatilization from the source [153]. Schripp et al. found that recovery rates of SVOCs emitted from plastic pellets in the μ -CTE are enhanced compared to those of the 1 m³ chamber [146]. This is because the small volumes of the cells of the μ -CTE reduces sink effect; in addition, SVOCs sorbed on the walls of the micro-chamber can be easily recovered by heating the μ -CTE after the removal of the material (up to 120 or 250 °C) without the need to place the cell in an oven as per ISO 16000-25.

Until the beginning of this thesis, no methods were reported in literature on the usage of this device for determining y_0 of SVOCs. A study done in 2015 at CSTB, France in collaboration with the Exposure and Biomonitoring Division of Health Canada was the first to use the μ -CTE120 for determining y_0 of DEHP emitted from vinyl floorings [154]. y_0 was calculated using equation 12. This study will be discussed in details throughout this chapter.

Sandwich-like chambers

A specially designed chamber, known as sandwich-like chamber, was developed in 2012 to measure the emission rate and study the sorption behavior of phthalates emitted from vinyl floorings [124]. A stainless steel emission chamber is placed between two flat sheets of homogeneous thickness of the to-be-studied vinyl flooring traversed by a constant flow rate of clean air entering the chamber through an inlet and another outlet where Tenax tubes are placed for sampling [65], [124], [126].

Using this method, the time required to reach steady state level of 0.8-0.9 $\mu\text{g}/\text{m}^3$ of DEHP emitted from vinyl flooring was about 20 days [124]. Later, Liang and Xu improved the design of the sandwich-like chamber in order to decrease sorption of SVOCs on the surface of the chamber [65]. This was done by maximizing the vinyl flooring emission area and minimizing that of the stainless steel chamber, in addition to enhancing the air flow inside the chamber by creating multiple inlets and outlets (Figure 18). This improved design enabled the emission of phthalates to reach steady state in 2 to 5 days instead of 20 [65].

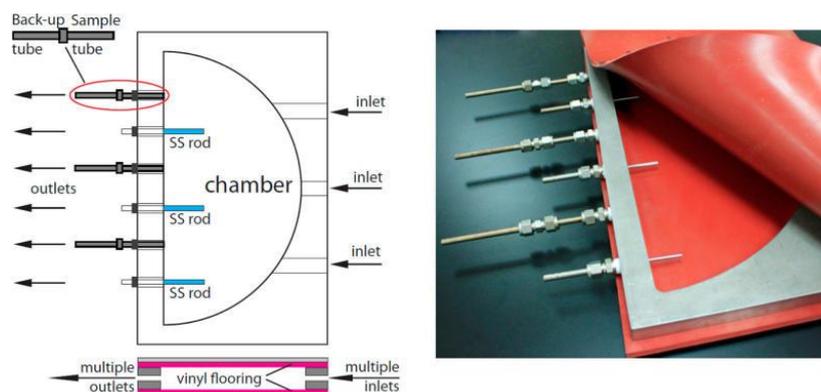


Figure 18: Improved model of the sandwich test chamber by Xu and Little [65]

Liang and Xu also designed another sandwich test chamber with the same form, but this time made up of wood instead of stainless steel to study the diffusion of phthalates emitted from vinyl flooring in wooden indoor furniture [126]. They have found that phthalates have the ability to diffuse within the wood material decreasing their chamber air concentration. This developed method decreased experimentation time to 2-5 days.

Yang et al. recently improved the sandwich-like chamber to determine y_0 and h_m of DEHP emitted from vehicle cabin materials [155]. Its design is similar to the chamber developed by Liang and Xu [125]; however, water baths are added to control temperature during emission (Figure 19). Moreover, sampling occurs by Solid-phase Microextraction (SPME) which consists of a stainless steel plunger and a fused silica fiber with a coating material [156]. The SPME is placed at the septum and DEHP emitted from the material into the air chamber are sorbed by the coating of the fiber.



Figure 19: A schematic representation of the improved sandwich-like chamber developed by Yang et al. [155]

In this study y_0 is determined from the slope and intercept of the linear obtained relationship between the reciprocal of y_{SS} and the ventilation rate (Q) according to the following equation:

$$\frac{1}{y_{SS}} = \frac{Q^{0.5}}{C_2 A y_0} + \frac{1}{y_0} \tag{15}$$

Where C_2 is a constant.

These types of chamber are of great advantage regarding the time of experimentation; however, they are only suitable for flat surface and uncertainties emerge from determining h_m .

Dual test chamber

y_0 was determined in a newly developed dual small chamber [123]. This method consists of two stainless steel chambers of 53 L volume connected in series: one acting as the source of OPFRs and the other one containing blank polyurethane foams (without OPFRs) acting as the sink surface for OPFRs coming from the first chamber [157], [158]. The amount of OPFRs adsorbed on the PUF is determined by extraction and the material/ air partitioning coefficient (K) is determined by modeling. y_0 is, then, estimated based on the following equation:

$$y_0 = \frac{C_0}{K} \quad (16)$$

However, the assumption of having a linear relationship between C_0 and y_0 is not always true as mentioned in part 3.1.2.

3.2.2.2. Static methods

For direct measurements of y_0 , test chambers can be improved by creating static test chamber. In this case, y_0 becomes equal to y_{ss} .

Cao et al. modified further the sandwich-like chamber into a sealed chamber [125] (Figure 20). Sampling occurs by SPME. Using this method, the experimental duration was reduced to 1 day due to the low value of A_s/A .

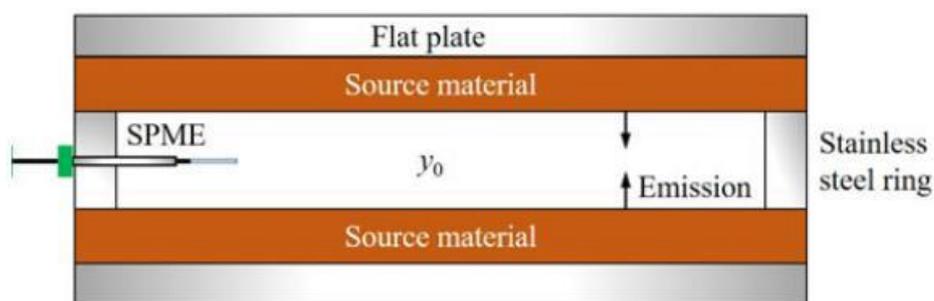


Figure 20: Schematic Representation of the SPME-based Chamber for Measuring Emission of SVOCs
[125]

They have also developed, in another study, another sandwich-like chamber known as symmetrical thin diffusion chamber (STDC) [159]. In this method, y_0 is determined by modeling the phthalates

concentration sorbed on a piece of cotton clothes (C_m) placed between two pieces of vinyl floorings (Figure 21) according to the following equation:

$$C_m = K \cdot y_0 \cdot (1 - e^{-D/\delta L K t}) \quad (17)$$

Where δ is the thickness of the clothing material (m), L is the thickness of the circular chamber (m), and t is the time (s). The used model is known as C_m -history model.

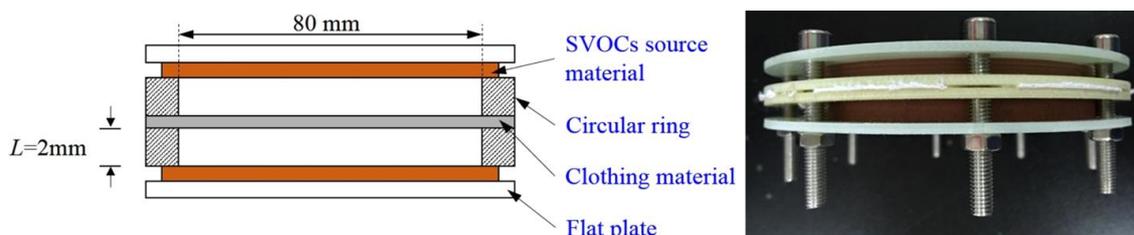


Figure 21: The symmetrical thin diffusion chamber (STDC) chamber developed for characterizing the sorption of phthalates emitted from vinyl floorings by clothes [159]

3.2.3. SUMMARY ON THE MEASUREMENT METHODS

Studies on the emission of SVOCs from materials is increasing day after day. Several experimental methods in addition to mass transfer models have been developed to understand the behavior of phthalates and OPFRs in indoor environments and determine their emission key parameter (y_0). However, each one of these methods has its advantages and disadvantages as previously mentioned. Table 26 shows a summary of all available methods with their advantages and disadvantages.

The main advantages and disadvantages vary among these different methods in terms of experimentation time, complexity of application, accuracy in determining y_0 and shape of tested material. Moreover, as shown in Table 26, most of the methods are developed to characterize the emissions of phthalates while methods that characterize the emission of OPFRs are still few.

Therefore, there is always a necessity to develop new test chambers and measurement methods for accurate determination of y_0 of phthalates and OPFRs, and this is why this thesis was proposed.

Table 26: The different developed methods for determining y_0 of SVOCs with their type, advantages, and disadvantages

Method (SVOCs)	Nature	Sampling support	Advantage(s)	Disadvantage(s)	Reference(s)
FLEC (Phthalates)	On-site Dynamic	Tenax TA	y_0 is directly measured at steady state	Time to reach steady state is long	[145]
Early C-history (SVOCs)	-	Model	Reduced experimentation time	h_m should be known to determine y_0	[134]
Diffusion adsorbent tube (Phthalates and OPFRs)	On-site Static	Tenax TA	Cheap and easy to apply	Reduced accuracy due to estimation of y_0 and h_m from the same data	[127]
PFS (Phthalates and OPFRs)	On-site Static	Glass or carbon filter	Cheap and easy to apply	Extraction of SVOCs might increase errors	[149]
Emission cell-SPME (OPFRs)	On-site Static	SPME	– Cheap and easy to apply – Direct measurement of y_0 – Experimentation time = 5 hrs	Only applied for flat surface materials	[105]
μ -CTE (phthalates)	Laboratory Dynamic	Adsorbent Tubes	Reduced experimentation time due to reduced chamber volume and ability to heat it	Uncertainties calculating h_m	[154]
Sandwich-like chamber (Phthalates)	Laboratory Dynamic	– Tenax TA – SPME	Experimentation time between 2 and 20 days	– Only suitable for flat surface materials – Uncertainties calculating h_m	[65], [124], [155]
Dual Chamber (OPFRs)	Laboratory Dynamic	PUF	Eliminated effect of h_m on the accuracy of y_0	Uncertainty assuming a linear partitioning exists between C_0 and y_0	[123]
Sandwich-like sealed chamber (Phthalates)	Laboratory Static	SPME	Experimentation time of 1 day	Only suitable for flat surface materials	[125]
– STDC – C_m -history (Phthalates)	Laboratory Static	– Clothes – Model	Reduced experimentation time	Extraction of SVOCs from clothes increase errors	[159]

3.3. Analytical methods for characterizing the emissions of phthalates and OPFRs from materials

Collected samples of SVOCs from indoor air, dust, and biological matrices or emitted from materials into indoor environments should be analyzed after for qualification or quantification. One of the first determination of DBP in air samples using liquid phase extraction and spectrophotometric analysis was in 1969 [75]. Later on, analytical procedures for characterizing these compounds have developed to include the use of solid phase extraction and gas chromatography with different detectors. Nowadays, several analytical methods exist for identifying SVOCs and determining their concentrations in indoor air, dust, and biological matrices; however, the analytical methods that characterize their emissions from materials into indoor air are scarce.

The most used methods to quantify phthalates and OPFRs emitted from materials is gas chromatography connected to mass spectrometry (GC-MS). GC is a fast, rapid, and sensitive technique [160]. Moreover, MS is an important detection technique for its high sensitivity and ability in excluding interference from impurities [160].

3.3.1. GC-MS

GC-MS methods is the only reported technique in literature for characterizing phthalates and OPFRs emitted from materials into indoor air. However, the difference between the used methods is in terms of sample introduction mode into the GC, detection modes, and nature of used columns.

Two modes of introduction of the analytes into the GC exist. The first one, known as thermal desorption (TD), is used when sampling of phthalates and OPFRs occurs via adsorbent tubes (e.g. Tenax TA) [65], [124], [127], [138], [146], or sometimes when these compounds are subjected to liquid extraction from the sampling support (e.g. empore disks) and spiked after into adsorbent tubes [149]. While the other mode, via direct introduction in the GC injector, is applied in the case of SPME thermo-desorption or also liquid extraction takes place [123], [125], [161], [105]. However, thermal desorption is more sensitive than liquid extraction. This is because all (or a major part) of the sampled compounds can be transferred to the GC depending on the set of splits, whereas only a small fraction of the liquid extract is injected upon direct injection [162]. Direct introduction into the GC will be abbreviated as DI throughout this chapter.

Thermal desorption is recently emerging as an alternative for solvent extraction [163]. Using TD avoids long sampling and extraction times and waste of solvent, and decreases contamination compared to direct injection [164]. Moreover, ISO 16000-25 recommended using TD-GC-MS for analyzing collected samples of SVOCs via adsorbent tubes [19].

Most of the applied GC-MS methods are used to determine the emission rates, y_{ss} , or y_0 of phthalates and OPFRs emitted from building and consumer materials in the emission test chambers listed previously. The characterization of phthalates, especially DEHP, emitted from materials into indoor air occurs by both DI/GC-MS and TD-GC-MS while that of OPFRs is rather by DI/GC-MS.

When using TD-GC-MS, Tenax TA tubes are the most used sampling support. Clausen et al. developed a TD-GC-MS/FID method to calculate the emission rate of DEHP from vinyl floorings [138]. The limit of detection (LOD) of this method is equal to 0.03 ng/ m³ for 288 L sampling volume. Another TD-GC-MS/FID method was developed by Xu et al. for the same purpose with an LOD of 0.01 µg [124]. Flame ionization detector (FID) is known for its wide measuring range of compounds compared to MS [165].

Other TD-GC-MS methods were used to determine y_0 of phthalates, especially DEHP, emitted from vinyl floorings. y_0 of DEHP is down to 0.02 µg/ m³ for 216 L of sampled air as determined by Liang and Xu [65] and 0.9 ng/ m³ by Wu et al. [127] using Tenax TA tubes and 55 µg/ m³ by Noguchi et al. when using glass fiber filters [149].

The DI/GC-MS method developed by Fujii et al. to characterize the emissions of phthalates from plastic materials has an LOD of 5 ng using active carbon disks as the sampling support [161] and that developed by Cao et al. to characterize their emissions from vinyl floorings using an SPME fiber has an LOQ equal to 0.05 ng [125], [159]. The difference in sensitivity between the two methods might be due to the analysis of only a fraction of the extracted phthalates from the carbon disks which leads to a higher method LOD compared to direct thermo-desorption of the SPME fiber.

The LODs of some DI/GC-MS methods developed to characterize the emissions of OPFRs from different indoor materials range from 3 to 10.5 ng/ m³ for an air sampling volume between 5 and 40 m³ collected on PUF as obtained by Kemmlein et al. [98] and 1.1 to 2.5 µg/ m³ by Ghislain et al. for static sampling using polydimethylsiloxane (PDMS) SPME fiber [105].

Flame photometric detector (FPD) is also used to specifically characterize the emission of OPFRs from building and consumer materials. This type of detectors increases the sensitivity and selectivity of the analytical method [166]. A GC-MS/FPD method of an LOD ranging between 15-30 ng was developed by Ni et al. for characterizing the emission of TCP from wallpapers [148].

MS acquisition or ionization modes contribute to increasing the sensitivity of an analytical method. Ionization modes vary between electron impact (EI) and chemical ionization (CI: positive or negative). Even if EI is the most used in studying phthalates and OPFRs, the use of CI is preferred for high-mass compounds, such as OPFRs, due to lower fragmentation [166]; however, to date, this ionization mode is still not applied in characterizing the emissions of phthalates and OPFRs from building and consumer

materials. Moreover, treating the data in selected ion monitoring (SIM) mode enhances selectivity and reduces LOD [166], [167].

Several types of GC columns are used to characterize phthalates and OPFRs present in indoor environments or biological matrices. Used columns differ in terms of stationary phase, length, and film thickness. These parameters have a great influence on the elution and chromatographic separation of analytes and their retention times. Non-polar GC columns with 5% phenyl and lengths varying between 15 to 60 m are the most used types of columns to characterize SVOCs. Thick-film columns are used for VOCs while thin-film ones (0.1-0.25 μm) are more convenient for high-molecular weight compounds, such as SVOCs. This is because columns with thinner film thickness have higher operating temperatures and reduced bleed [168].

3.3.2. OTHER METHODS

New analysis techniques are emerging for characterizing phthalates and OPFRs in indoor environments. Proton transfer mass spectrometry (PTR-MS) is an example of CI of chemical species that have a proton affinity higher than that of water [169]. This technique is exclusively developed for the detection of gaseous organic compounds in air and has been widely applied for the detection of VOCs [170], [171].

Recently, it is being used for identifying secondary SVOCs formed from the ozonolysis of isoprene in the gaseous and aerosol phases or vacuum ultraviolet (VUV) photolysis of naphthalene in indoor air [169], [172]. Moreover, it can be operated in both on- and off-line modes. Inomata et al. found that PTR-MS SVOCs spectra are consistent with the spectra of negative ion-chemical ionization mass spectrometry (NI-CIMS) [169]. However, for instance no studies are encountered on the use of PTR-MS for detecting and quantifying primary SVOCs (emitted from materials into indoor environments).

Membrane-introduction mass spectrometry (MIMS) is another on-line technique for identifying SVOCs. Continuous sampling of analytes in liquid, gaseous, or solid phase occurs through a semi-permeable membrane coupled to MS yielding selective and sensitive quantitation. The membrane is usually made of hydrophobic polymer materials.

Davey et al. reported the advancements done on the levels of the material membrane, heating system, and development of quadrupole MS in order to be able to monitor less volatile compounds such as SVOCs collected from different phases for obtaining quantitative data [173].

3.3.3. SUMMARY ON THE AVAILABLE ANALYTICAL METHODS

The developed analytical methods for characterizing the emissions of phthalates or OPFRs from indoor materials are limited to GC-MS and are very few. Table 27 summarizes all the methods reported in literature according to the used sampling supports, type of GC column, characterized compounds, measured parameter, and performance.

Three out of all the methods characterize OPFRs compared to phthalates with no method up to now is reported for characterizing both families of SVOCs at the same time. Moreover, no provided information on the performance of most of the below methods in terms of repeatability and limits of detection or quantification (LOD or LOQ).

Therefore, developing and validating sensitive GC-MS (TD or DI) methods for quantifying both, phthalates and OPFRs, is necessary for accurate characterization of the emissions of these compounds from indoor materials. This also is another objective of this thesis.

Table 27: Gas chromatography (GC) methods available in literature to characterize the emissions of phthalates and organophosphate flame retardants (OPFRs) from building and consumer materials into indoor air.

Method	Sampling support	GC column (l, i.d, δ)*	Compound(s)	Measured parameter	Limit of detection (LOD)	Limit of quantification (LOQ)	Reference(s)
DI/GC-MS	SPME	DB-5: 60 x 0.25 x 1	TEP, TBP, TCPP	γ_0	1.1-2.5 $\mu\text{g}/\text{m}^3$		[105]
		HP-5MS: 30 x 0.25 x 0.25	DEHP	γ_{ss}/γ_0		0.05 ng	[125], [159]
	PUF	Rxi-5 Sil MS: 30 x 0.25 x 0.25	TCEP, TCPP, TDCPP	γ_0			[123]
	PUF	HP-5MS: 30 x 0.25 x 0.25	OPFRs	SER	3-10.5 ng/m^3		[98]
	Active carbon disk	DB-5MS: 30 x 0.25 x 0.25	phthalates	ER	5 ng		[161]
DI/GC-MS/FPD	C18 disk	HP-1: 30 x 0.25 x 0.32	TCPP		15-30 ng	50-100 ng	[148]
TD-GC-MS/FID		CP Sil 8 CB: 60 x 0.25 x 0.25	DEHP		0.03 $\mu\text{g}/\text{m}^3$		[138]
		Rtx-1: 30 x 0.53 x	DEHP	0.01 μg		[124]	
TD-GC-MS	Tenax TA	DB-5MS: 30 x 0.25 x 0.25	DEHP, DBP, BBP, DiNP	γ_0			[65]
		DB-1, DB-5, Rtx-1	DEHP, DiBP, DBP	γ_0			[127]
	Glass fiber filters	NA	DEHP	γ_0			[149]

*l, i.d, δ : length (m), internal diameter (mm), and film thickness of column (μm)

SER: specific emission rate

ER: emission rate

NA: not available

4. CONCLUSION AND OBJECTIVES OF THESIS

Phthalates and organophosphate flame retardants (OPFRs) are added as plasticizers or flame retardants to different building and consumer materials to enhance their properties. As families of semi-volatile organic compounds (SVOCs), these compounds have high molecular weight and low vapor pressure. They are thus characterized by slow emission rates from the materials and the tendency to partition among the different indoor compartments: air, particulate phase, and settled dust. Hence, people, especially children, are greatly exposed to these compounds in indoor environments through inhalation, dust ingestion, and dermal contact. Depending on their specific toxicity, chronic exposure to SVOCs may cause severe growth, reproduction, and neurological problems and might in some cases cause cancer. Therefore, it is necessary to characterize the emissions of these compounds in indoor environments to reduce human exposure to these compounds and the associated potential health effects.

The gas-phase concentration of SVOCs on material surface (y_0) is the key parameter in estimating their emissions from building and consumer products. A group of analytical measurement methods has been developed to determine y_0 of phthalates and OPFRs emitted from materials. However, contamination, sorption into chambers surfaces, long experimentation time, cost, and installation complexity were the bottleneck in their analysis.

Therefore, the main objective of this thesis is to develop a new and rapid method for characterizing emissions of SVOCs, particularly phthalates and OPFRs, from indoor materials into indoor air by estimating their y_0 .

ISO 16000-25 standard recommends the use of micro-chambers to characterize emissions of SVOCs from building materials [19]. It is believed that the small volume of a micro-chamber reduces sorption to the chamber's internal surfaces and the time of experimentation. One type of micro-chambers is the thermal extractor (μ -CTE) fabricated by Markes International. The tested material is placed in the cells of the μ -CTE and adsorbent tubes (e.g. Tenax TA) are connected to the top of each cell for air sampling. The collected samples are then analyzed by TD-GC-MS as recommended by the standard.

A Collaborative study between the Health and Comfort Department at CSTB and the Exposure and Biomonitoring Division of Health Canada was initiated in 2015 to develop a new method for determining y_0 of DEHP emitted from vinyl floorings at room temperature [154]. In this study, Zhu et al. used the μ -CTE120 to determine the gas-phase concentration of DEHP at different temperatures ranging from 35 to 75 °C. A linear plot was obtained between the logarithm of air concentration and the reciprocal of temperature Figure 22.

This relation enabled the determination of the gas-phase concentration of DEHP at room temperature by extrapolation from higher temperatures according to Clausius-Clapeyron equation [145]. Then, y_0 was estimated by applying the obtained extrapolated values in equation 12. However, as a preliminary step, this method was only applied to DEHP emitted from a single material.

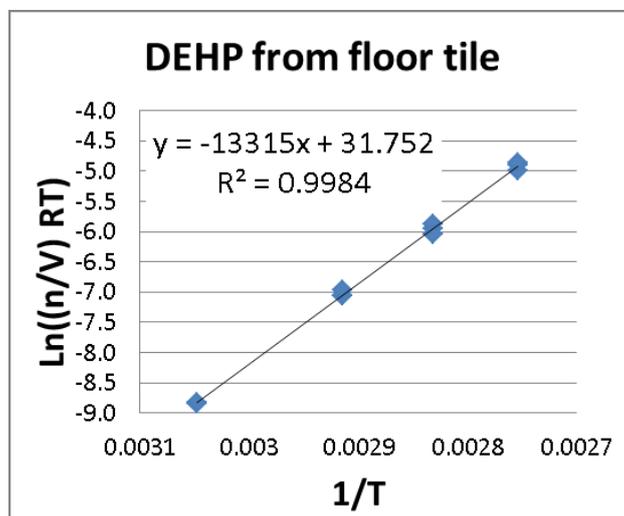


Figure 22: The obtained linear relation by Zhu et al. between the gas-phase concentration of DEHP emitted from vinyl floorings and the reciprocal of temperature [154]

The study done by Zhu et al. showed that the μ -CTE appears to be a promising device for characterizing emissions of SVOCs from indoor materials and estimating y_0 . Thus, the μ -CTE is chosen as emission test chamber in this study. Its large emission surface compared to potential sorption surfaces and the ability to heat the device at high temperatures help in reducing sink effect and the time for emissions to reach steady state. In addition, recovery rates of these compounds can be determined using the μ -CTE due to the ability to easily collect the sorbed amounts on surfaces by heating and calculate their surface/air partitioning coefficient (K_s).

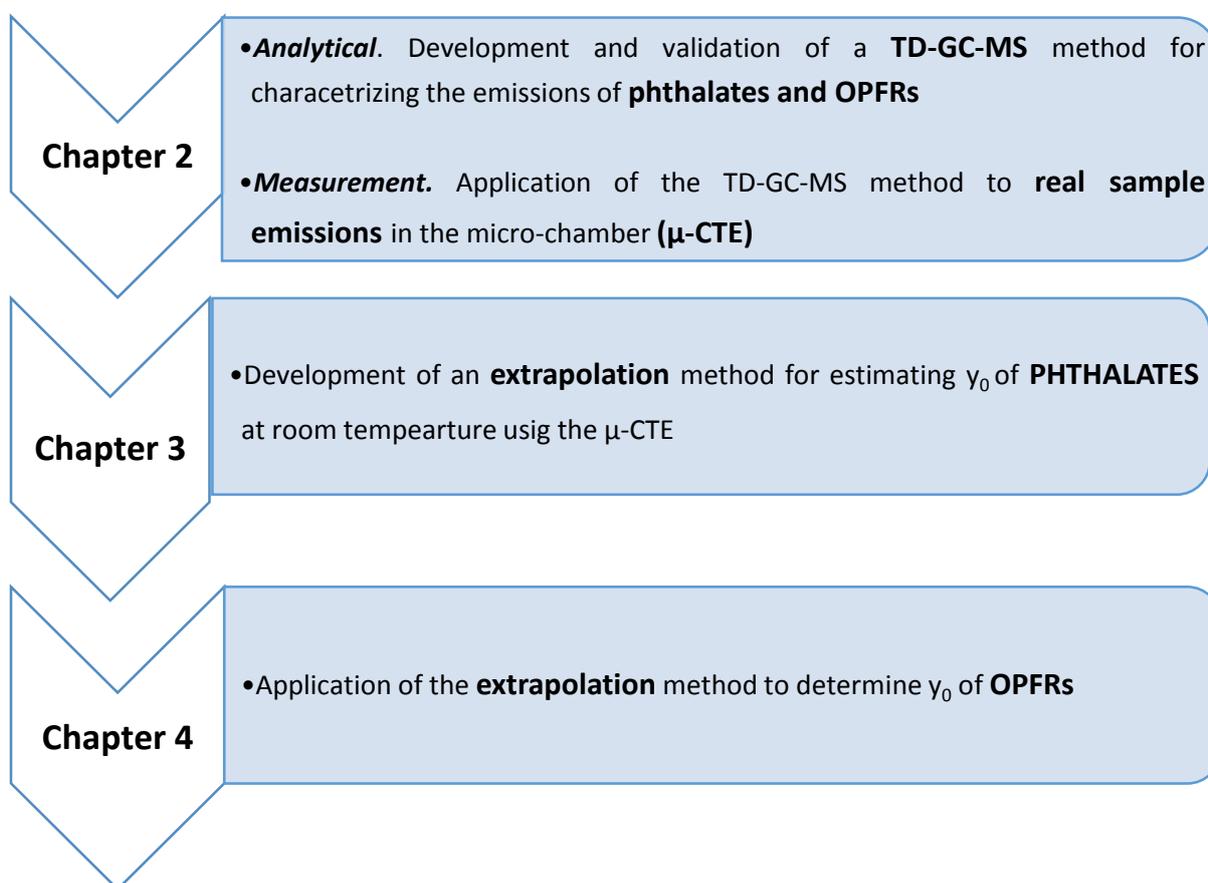
The development of the global method for characterizing emissions of SVOCs from indoor materials is divided into an analytical task and an emission measurement task.

The analytical part is discussed in chapter 2 of this document. It consists in the development of a sensitive TD-GC-MS for the characterization of the collected samples of emitted phthalates and OPFRs from building and consumer material. This method will be developed by optimizing its different key parameters, such as temperature and time programming. After development, it will be analytically validated for all selected phthalates and OPFRs. Then, its performance will be evaluated by testing real building materials using the μ -CTE. The development of this method and description of the used methodology for the μ -CTE are thoroughly explained in chapter 2.

In the second part, which is the motor of this thesis, using the μ -CTE, a rapid method will be developed to estimate y_0 of phthalates emitted from indoor building and consumer materials at room temperature. It is based on the previously mentioned study of Zhu et al. [154]. The concept of this method is to experimentally determine y_0 at several elevated temperatures and then estimate y_0 at room temperature according to a linear relationship established between these two parameters.

Moreover, the obtained linear relationship will also be used to study the effect of temperature dependence of phthalates emissions. In addition to temperature, the influence of relative humidity and air exchange rate on phthalates emissions will be also studied. Sorption of phthalates on the internal surfaces of the μ -CTE will be characterized by determining the sorbed quantity of these compounds and calculating the surface/ air partitioning coefficient (K_s). Therefore, chapter 3 of this document discusses thoroughly the obtained results on the extrapolation method and the effects of the above mentioned parameters on emissions of phthalates in the μ -CTE.

Once the extrapolation method is successfully developed for phthalates, it will be applied to OPFRs. Obtained extrapolation results for OPFRs in addition to the study of their adsorption on the inner surfaces of the μ -CTE are presented in chapter 4.



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Chapter 2.

Development of a sensitive
TD-GC-MS for characterizing
the emissions of SVOCs
from materials into air in the μ -CTE

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Analytical methods developed for characterizing the emissions of SVOCs from materials are still not well developed compared to methods that characterize their presence in indoor air and dust. ISO 16000-25 recommended the use of thermal desorption connected to gas chromatography and mass spectrometry (TD-GC-MS) when studying the emissions of SVOCs from materials in micro-chambers. TD-GC-MS are the most used among the few existing methods when adsorbent tubes are used as the sampling support. However, the majority of the TD-GC-MS methods reported in literature are used without validation to check their performance and efficiency in characterizing emissions of SVOCs from materials. Moreover, to our knowledge, up to date there exist no single method capable of characterizing the emissions of both families of SVOCs, phthalates and organophosphate flame retardants (OPFRs), or at least it was not tested. Therefore, there is a need to develop sensitive and validated TD-GC-MS method for characterizing the emissions of these compounds from building and consumer materials.

The first part of this chapter presents the development and validation of a sensitive TD-GC-MS for the characterization of phthalates and OPFRs emitted from materials. This method was developed by optimizing the different TD, GC, and MS parameters including splits and temperature and time programming. It was also validated by determining its linearity, repeatability, and limits of detection and quantification.

In the second part, the application of this method to emissions from real material samples in the μ -CTE together with the development of the emission procedure of this latter are shown.

1. ANALYTICAL METHOD

For micro-chambers, including the μ -CTE, the method recommended to analyze the gaseous emission from materials is based on air sampling using adsorbent tubes loaded on the cell output. The collected samples are then analyzed by thermal desorption connected to gas chromatography and mass spectrometry (TD-GC-MS) [1]. Existing TD-GC-MS methods normally characterize either phthalates or in rare cases OPFRs, but no available method characterizes both. This section describes the procedure followed to develop and validate a sensitive TD-GC-MS method for characterizing both compounds, phthalates and OPFRs, emitted from building and consumer materials.

1.1. Selection of compounds and adsorbents

As part of the development of the method, the selection of the compounds of interest and tube adsorbents took place.

1.1.1. COMPOUNDS

SVOCs integrated in the development method experiments are: eight phthalates and six OPFRs (Table 1).

Phthalates and OPFRs standards (purity > 99%) were used to prepare stock solutions of phthalates and OPFRs: BBP, DiBP, DBP, DEHP, DiNP, DiDP, TEP, TCEP, and TBP from Sigma Aldrich (Missouri, United States), DMP and TPP from Acros Organics (Geel, Belgium), DnOP from Alfa Aesar (Massachusetts, United States), and TCPP and TDCPP from ICL Products (Amsterdam, Netherlands). Tetradeuterium ring labeled DEHP (DEHP-d4) (purity > 99%) was used as internal standard from Sigma Aldrich as well. Methanol purchased from Honeywell (North Carolina, United States) and Sigma Aldrich (purity > 99,9%) was used as a solvent for the preparation of the stock and diluted solutions.

Stock solutions of DEHP or a mixture of either the eight phthalates or the six OPFRs are prepared with a concentration of about 5 g/ L for each compound. These solutions are then diluted to obtain daughter solutions with concentrations in the range of 1 to about 3000 ng/ μ L depending on the compound. A stock solution of the internal standard DEHP-d4 of concentration 2 g/ L is prepared as well and then a diluted solution of 24 ng/ μ L. Adsorbent tubes were spiked with 1 μ L of the diluted standard solutions, and they were spiked with 1 μ L of the diluted DEHP-d4 solution when validating the method.

Table 1: Physico-chemical properties and SIM acquisition ions of the studied phthalates and organophosphate flame retardants (OPFRs)

Compound	Acronym	CAS no.	Molecular formula	V _p (Pa) at 25 °C [2], [3], [4]	Boiling temperature (°C)	Ion for SIM acquisition (m/z)
Phthalates						
Dimethyl phthalate	DMP	131-11-3	C ₁₀ H ₁₀ O ₄	2.6 x 10 ⁻¹	282	163
Diisobutyl phthalate	DiBP	84-69-5	C ₁₆ H ₂₂ O ₄	4.7 x 10 ⁻³	327	149
Dibutyl phthalate	DBP	84-74-2	C ₁₆ H ₂₂ O ₄	4.7 x 10 ⁻³	340	149
Benzyl butyl phthalate	BBP	85-68-7	C ₁₉ H ₂₀ O ₄	2.5 x 10 ⁻³	379	149
Di(2-ethylhexyl) phthalate	DEHP	117-81-7	C ₂₄ H ₃₈ O ₄	2.5 x 10 ⁻⁵	386	149
Di-n-octyl phthalate	DnOP	117-84-0	C ₂₄ H ₃₈ O ₄	2.5 x 10 ⁻⁵	380	149
Diisononyl phthalate	DiNP	28553-12-0	C ₂₆ H ₄₂ O ₄	5.0 x 10 ⁻⁷	370	293
Diisodecyl phthalate	DiDP	26761-40-0	C ₂₈ H ₄₆ O ₄	5.3 x 10 ⁻⁷	482	307
Di(2-ethylhexyl) phthalate-3,4,5,6-d4	DEHP-d4	93951-87-2	C ₂₄ H ₃₄ O ₄ D ₄		281	153
OPFRs						
Triethyl phosphate	TEP	78-40-0	C ₆ H ₁₅ O ₄ P	2.2 x 10	233	99
Tributyl phosphate	TBP	126-73-8	C ₁₂ H ₂₇ O ₄ P	4.7 x 10 ⁻¹	327	211
Tri(2-chloroethyl) phosphate	TCEP	115-96-8	C ₆ H ₁₂ Cl ₃ O ₄ P	5.2 x 10 ⁻²	352	63
Tri(2-isochloropropyl) phosphate	TCPP	13674-84-5	C ₉ H ₁₈ Cl ₃ O ₄ P	7.5 x 10 ⁻³	365	99
Triphenyl phosphate	TPP	115-86-6	C ₁₈ H ₁₅ O ₄ P	6.3 x 10 ⁻⁵	441	326
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	13674-87-8	C ₉ H ₁₅ Cl ₆ O ₄ P	3.8 x 10 ⁻⁵	459	99

V_p: Vapor pressure

1.1.2. ADSORBENTS

To trap the emitted phthalates and OPFRs from materials during chamber emissions, adsorbent tubes are one of the most used supports. However, the choice of adsorbent is very important for efficient characterization of compounds. In a previous study on the emission of DBP and DEHP from vinyl floorings, stainless steel tubes packed with 420 mg of Carbopack C (60/ 80 mesh) were used as adsorbent tubes [5]. Multi-bed adsorbent tubes packed in laboratory were used in a preliminary collaborative study with Dr. Zhu from Health Canada during the first two months of this thesis. These tubes contained 250 mg of glass beads, 200 mg of Carbopack C (60/ 80 mesh), and 100 mg of Carbopack B (60/ 80 mesh). Carbopack adsorbents are hydrophobic non-porous graphitized carbon blacks were used to increase sorption strength [6]. However, this type of adsorbents, especially Carbopack B, is known to be a strong adsorbent due to its high surface area (Table 2). Aragon et al. showed that multi-bed adsorbent tubes, including Carbopack B, are not good adsorbents for both phthalates and organophosphate esters [7]. Therefore, Carbopack is more adapted to relatively small molecules such as VOCs rather than SVOCs (Table 2).

Tenax TA, on the other hand, is the most used adsorbent to characterize the emission of phthalates and OPFRs from materials as reported in literature [8]–[11]. This type of adsorbent is a porous hydrophobic polymer resin based on 2,6-diphenylene oxide [6]. It is suitable for the adsorption of organic compounds with carbon atoms ranging from 5 to 26 (Table 2). Therefore, Tenax TA (60/ 80 mesh) tubes packed with 250 mg of adsorbent are used in this study.

All adsorbent tubes contained glass wool at both ends of the tube to maintain the adsorbent beds. However, Melymuk et al. showed that glass fibers, as quartz fibers, are efficient in collecting SVOCs [12]. Moreover, Jo et al. demonstrated that combining glass wool with Tenax TA increases the adsorption capacity to phthalates [13].

Table 2: Properties of the different adsorbents used for packing tubes listed in order of decreasing sorption strength [6]

Adsorbent	Mesh size	Surface area (m ² / g)	Density (g/ mL)	Maximum T (°C)	Application
Carbopack B	60/ 80	100	0.36	> 400	C5-C12
Carbopack C	60/ 80	10	0.72	> 400	C12-C20
Tenax TA	60/ 80	35	0.25	350	C5-C26
Glass beads	50/ 70	<5		350	Very large hydrocarbons

1.2. Development and Optimization of the TD-GC-MS method for phthalates

A Perkin-Elmer system made of a thermal desorber (Turbomatrix TD) connected to a gas chromatograph (Autosystem XL) coupled with a mass spectrometer (Turbomass) was used. Specific experiments were done to determine the relevant parameters of each component of the analytical system, for a selective and sensitive detection of the selected SVOCs. DEHP is the most difficult to analyze using TD-GC-MS since it is one of the lowest volatile and most prevalent SVOCs in indoor environments. Therefore, the effects of the different TD parameters were first tested using only DEHP. Once the TD method was optimized for DEHP, further optimization of the GC-MS method was performed for the mixture of all the eight chosen phthalates. After development of the TD-GC-MS method for the eight selected phthalates, it was interesting to check if the same method can be used to characterize OPFRs or if there is a need to develop another TD-GC-MS for the characterization of OPFRs.

1.2.1. THERMAL DESORPTION (TD) PARAMETERS

A two-stage desorption was applied: desorption of adsorbent tube and desorption of cryogenic trap, used for compounds focalization before their introduction into the GC column. Helium (He) pressure was set at 33.2 psi. Due to the physico-chemical properties of SVOCs and the known contamination problem, tube desorption and transfer line temperatures (from the TD to GC) were set at 300 °C to avoid condensation and/ or adsorption of compounds. Tenax TA tube desorption time was tested for 15 and 30 min with a helium flow rate of 50 mL/ min without inlet split. The desorbed analytes are sent after to a cold Tenax TA trap. Trap desorption time was studied for 15 and 20 min. Moreover, two outlet splits of 14 and 7 mL/ min were also tested. The outlet split is manually adjusted.

Optimization of the TD method was done by spiking 1 μ L of DEHP diluted solutions of concentrations ranging from 28 to 809 ng/ μ L into Tenax TA tubes and using Tenax TA trap.

1.2.1.1. Inlet and outlet split

The inlet and outlet splits control the amount of analyte desorbed from the tube to the trap and sent from the trap to GC column, respectively. In order to improve the performance of the method and to make sure that the all desorbed quantity of analyte is well recovered, no inlet split was used. However, lower outlet split increases the sensitivity of the method being developed [14].

When studying the effect of outlet split, DEHP five-points calibration curves using the two tested outlet splits (7 and 14 mL/ min) are linear ($R^2 > 0.99$). However, since the difference between the desorbed

amount of DEHP at the two outlet splits is less than 15% (Figure 1), 14 mL/ min was chosen for further optimization of the method in order to prevent system contamination and saturation.

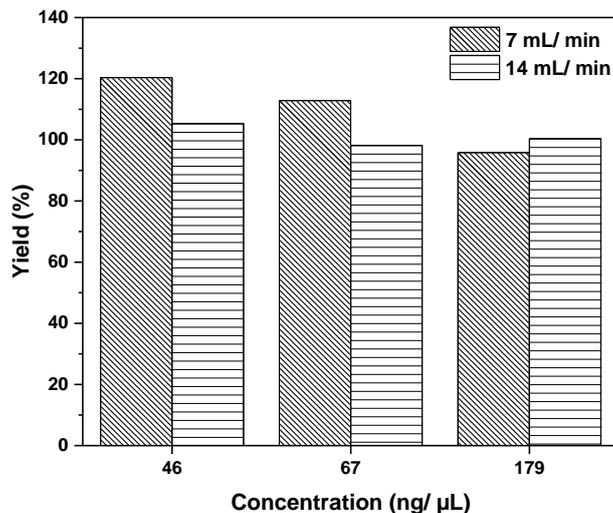


Figure 1: % Yield of desorbed DEHP from Tenax TA tubes for two different outlet split values and three concentration levels

1.2.1.2. Tube desorption time

Two tube desorption times (15 and 30 min) were tested using two concentration levels of DEHP standard solution spiked into Tenax TA tubes. Helium flow rate in the tube is set at 50 mL/ min. The time of tube desorption is an important parameter in characterizing phthalates. Tube desorption for 30 min enhanced the desorption of DEHP at which an increase of about 30 and 60% occurred at the concentration levels of 406 and 809 ng/ μ L, respectively (Figure 2). Therefore, 30 min was chosen as the tube desorption time.

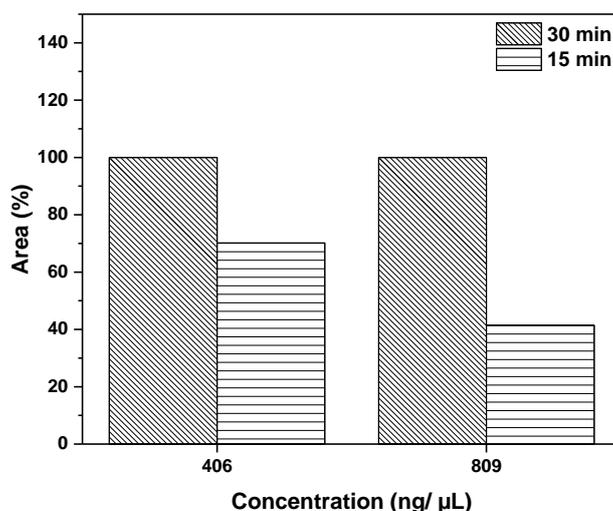


Figure 2: % Area of desorbed DEHP when desorbing Tenax TA tubes for 15 and 30 min at two concentration levels, taking 30 min as 100%

1.2.1.3. Trap desorption

The time of the secondary/ trap desorption is an important parameter to be studied as well when optimizing an TD method. The trap cold temperature is set at $-25\text{ }^{\circ}\text{C}$ since at low cold trap temperatures (down to -30 or $-40\text{ }^{\circ}\text{C}$), adsorbents in the trap have better strength to adsorb than at ambient temperature [15] while its highest temperature is set at $350\text{ }^{\circ}\text{C}$ to make sure that DEHP analyte is well desorbed. The temperature rate for the trap desorption was set at $20\text{ }^{\circ}\text{C}/\text{s}$.

However, when applying this method on another Perkin Elmer TD type (Turbomatrix 650 system), the trap temperature of $350\text{ }^{\circ}\text{C}$ was too high that it ruined the Tenax TA adsorbent in the trap. Therefore, a lower trap temperature of $330\text{ }^{\circ}\text{C}$ instead of 350 was also tested. Results showed that the difference of desorbed DEHP between both temperatures is about 15%. Therefore, since the difference is not so large, trap highest temperature of 330 or $350\text{ }^{\circ}\text{C}$ is to be applied depending on the used TD system.

When the trap highest temperature is reached, it is maintained for 15 or 20 min, which is the trap desorption time. The % yield is 20-40% higher when the trap is desorbed for 15 min than for 20 min at low concentration levels while it is almost the same at higher concentrations (Figure 3). The higher than 100 % yield at the lowest concentration levels can be explained due to condensation of DEHP in the system; however, this was obtained before full optimization of the method. This constraint was solved with full method development. Elorduy et al. showed that shorter times of trap desorption are more efficient than longer ones when optimizing the TD-GC-MS method for characterizing PAHs present in ambient air [14]. These results were also validated in this study for DEHP. Therefore, higher trap desorption durations do not necessarily result in better desorption of SVOCs, and thus trap desorption time was set at 15 min for further optimization of the method.

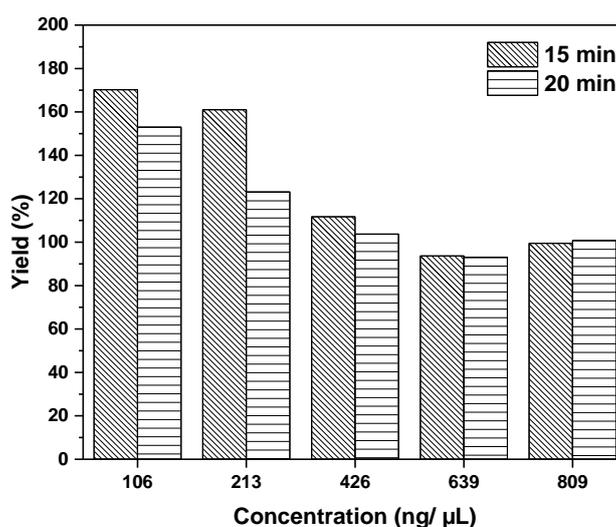


Figure 3: % Yield of desorbed DEHP from Tenax TA tubes at two different trap desorption times and five concentration levels

1.2.2. GAS CHROMATOGRAPHY (GC) PARAMETERS

After optimizing the TD method for DEHP, the GC-MS method was optimized using a mixture of the eight selected phthalates. 1 μ L of five levels of the diluted standard solutions of concentrations ranging from 1 to 200 ng/ μ L is spiked to Tenax TA tubes. Optimization occurred in terms of oven temperature and time programming.

A DB-5MS capillary column, supplied by Restek (Bellefonte, Pennsylvania, USA), of 60 m length, 0.25 mm internal diameter (i.d.), and 0.25 μ m film thicknesses was used. This type of column is made of 5% phenyl arylene polymer and 95% of dimethyl polysiloxane and is recommended for characterizing SVOCs [16]. Helium flow rate into the column is 1.7 mL/ min.

1.2.2.1. Temperature and time programming

Several GC temperature programs with different starting temperatures and ramps were tested (Table 3). Using GC methods of multiple ramps (methods 1 and 2) is not favorable for characterizing phthalates since calibration curves are not linear for almost all compounds, except BBP, with the lowest R^2 values for DEHP and DnOP. Therefore, high volatile compounds elute better at low temperatures (< 260 $^{\circ}$ C) than the lowest volatile phthalates that are better characterized at higher temperatures (260-330 $^{\circ}$ C). Therefore, other GC methods made up of a single ramp were tested for further optimization of the GC method (methods 3, 4, and 5).

Even if calibration curves are almost linear ($0.96 < R^2 < 0.99$) when testing method 3, setting the initial temperature at 50 $^{\circ}$ C with a temperature ramp of 10 $^{\circ}$ C/ min after, increased the total running time and the retention times of the analytes to have the first phthalate (DMP) eluting at about 19 min. Having the boiling point of DMP equal to 282 $^{\circ}$ C, it was better to start at a temperature of 85 $^{\circ}$ C for shorter running time. Moreover, this temperature is reasonable if a 5 min solvent delay is set at the beginning of the method in order to protect the MS filament against high concentrations of solvent vapor.

To further reduce the total running time of the GC method, temperature ramps of 15 and 20 $^{\circ}$ C/ min are tested starting from 85 $^{\circ}$ C (methods 4 and 5). Using method 5, calibration curves are more linear for low volatile compounds (DEHP and DnOP), $R^2 = 0.99$, and less linear for compounds of higher volatility (DMP, DiBP, DBP, and BBP), $R^2 = 0.98$. Similar to methods 1 and 2 at which low temperature ramps are better for more volatile compounds than the least volatile phthalates, high temperature ramps, on the contrary, are more suitable for low volatile phthalates. Using method 4, calibration curves are linear ($R^2 = 0.99$) for all compounds. Therefore, even if the two methods (4 and 5) have the

same running time of 27 min with acceptable linearity for all phthalates, method 4 was chosen since faster temperature ramps will decrease the resolution of peaks [17].

However, using the developed TD-GC-MS method, DiNP and DiDP were not detected since the method is too short for them to elute. Therefore, a hold time of 18 min instead of 10 min at 310 °C was applied to solve this problem.

Table 3: The different gas chromatography (GC) methods tested to characterize phthalates (DMP, DiBP, DBP, BBP, DEHP, and DnOP)

GC Method	Program	Total running time (min)	Linearity (R^2) and retention times (RT)
1	35 °C (1 min), 20 °C/ min to 200°C, 5 °C/ min to 260 °C, 20 °C/ min to 330 °C (5 min)	30	$0.85 < R^2 < 0.99$ with the lowest R^2 for DEHP and DnOP $12.6 < RT < 27.6$ min
2	35 °C (1 min), 20 °C/ min to 200°C, 10 °C/ min to 260 °C, 20 °C/ min to 330 °C (20 min)	39	$0.94 < R^2 < 0.99$ with the lowest R^2 for DEHP and DnOP $12.4 < RT < 22.3$ min
3	50 °C (4 min), 10 °C/ min to 300 °C (10 min)	39	$0.96 < R^2 < 0.99$ with the lowest for DiBP and DBP $19.9 < RT < 34.4$ min
4	85 °C (2 min), 15 °C/ min to 310 °C (10 min)	27	$R^2 = 0.99$ for all compounds $11.93 < RT < 22.1$ min
5	85 °C (2 min), 20 °C/ min to 310 °C (14 min)	27	$0.98 < R^2 < 0.99$ for all compounds $10.65 < RT < 19.01$ min

1.2.2.2. Transfer line temperature from GC to MS.

The transfer line temperature from the GC to MS is tested at 300 and 320 °C thinking that higher temperatures are better to avoid condensation of high boiling point compounds. However, increasing the temperature of the transfer line from 300 to 320 °C did not show a significant effect on the amount of DEHP eluted (Figure 4). Therefore, 300 °C was set as the temperature of the transfer line from the GC to the MS for longer life time.

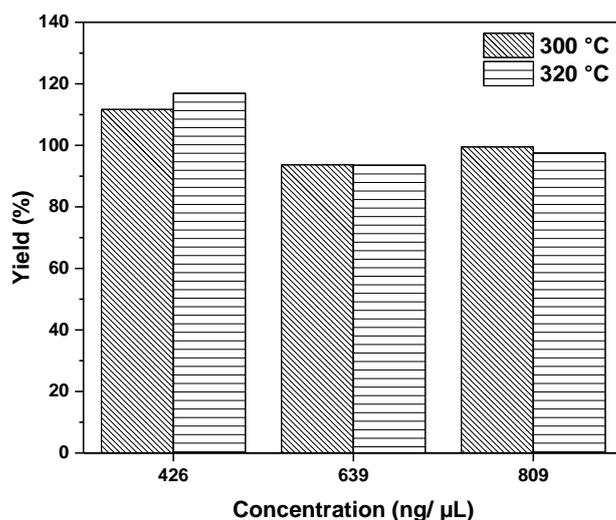


Figure 4: % Yield of DEHP upon changing the temperature of the transfer line from the GC to the MS at three different concentration levels

1.2.3. MASS SPECTROMETER (MS) DETECTOR PARAMETERS

The quadrupole MS was operated in electron impact ionization mode (EI) at 70 eV. The source temperature was set at 230 °C. Acquisition occurred in both modes: scan mode with a mass range from 33 to 450 amu and acquisition speed of 0.35 scan/ s for qualitative analysis and single ion monitoring (SIM) mode for quantitative analysis due to better sensitivity [18].

The used acquisition ions to quantify the compounds are shown in Table 3 and the optimized TD-GC-MS method is summarized in Table 4.

Table 4: The optimized parameters of the TD-GC-MS method for characterizing phthalates and OPFRs

Method	Parameter	Set value
TD	Adsorbent tubes	Tenax TA (m = 250 mg) with glass wool
	Tube desorption	300 °C for 30 min
	Helium tube desorption flow	50 mL/ min
	Trap desorption	-25 °C to 350 °C for 15 min at a temperature ramp of 20 °C/ s
	Valve temperature	300 °C
	Split flow	0 mL/ min inlet split 14 mL/ min outlet split
	Transfer line temperature to GC	300 °C
GC	Oven temperature program	2 min at 85 °C, raise to 310 °C at 15 °C/ min, and hold for 18 min
	Transfer line temperature to MS	300 °C
MS	Source temperature	230 °C
	Ionization mode	Electron impact (EI) at 70 eV
	Acquisition mode	Double acquisition mode: full scan and SIM

1.3. Application of the developed TD-GC-MS method to OPFRs

The developed analytical methods for characterizing the emission of phthalates and OPFRs from building and consumer products are scarce. Even if both families are classified as SVOCs, their physico-chemical properties are different in terms of volatility, boiling temperature, and partitioning in air and on different surfaces. Therefore, developing an analytical method that is sensitive for characterizing both families is challenging. To our knowledge, no TD-GC-MS method up to now has been reported in literature for characterizing both compounds simultaneously. Therefore, it is of great interest and added value if the developed TD-GC-MS for phthalates is applicable for OPFRs also.

Therefore, 1 μ L of a solution made up of the eight phthalates and another of the six OPFRs solution were spiked in a Tenax TA tube and analyzed by the developed TD-GC-MS method. The obtained chromatogram of the eluted compounds is shown in Figure 5 in SIM mode. The injected masses of phthalates ranged from 500 ng for DEHP, 1200 ng for DiNP and DiDP, and about 400 ng for all other phthalates while for OPFRs the injected masses are about 800 ng for TEP and TCEP, 600 ng for TPP, 1000 ng for TCPP and TDCPP, and 1500 ng for TBP.

All compounds are well separated. Even if the retention times of TDCPP and BBP are very close, their acquisition ions (m/z) are different enabling a good differentiation between the two compounds (Table 1). Moreover, TCPP, DiNP, and DiDP are made of isomers as shown in the chromatogram. So TCPP elutes in the form of three peaks [19] while DiNP and DiDP elute as multiple peaks.

After confirming that the method is convenient for the elution of both families, validation of the method for both families took place to check its sensitivity and repeatability.

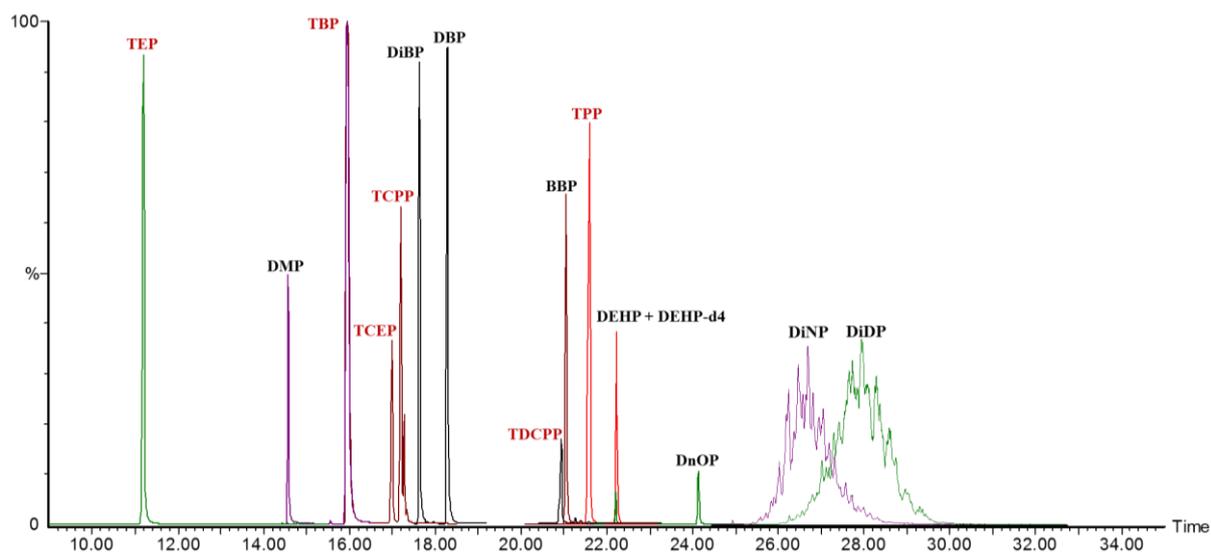


Figure 5: Gas chromatogram of all the selected phthalates (names in black) and OPFRs (names in red) using the optimized TD-GC-MS method

1.4. Validation of the optimized TD-GC-MS method for phthalates and OPFRs

The performance of the developed TD-GC-MS method for phthalates and OPFRs is characterized in terms of linearity and linearity range, repeatability or precision, and limits of detection (LOD) and quantification (LOQ).

The developed TD-GC-MS method was less sensitive to OPFRs than phthalates. For the same concentration of phthalates and OPFRs, the response factor of the method was about 4 times higher for phthalates than OPFRs. Therefore, in order to have comparable results, the outlet split was decreased from 14 to 7 mL/min when characterizing OPFRs. However, an outlet split of 7 mL/min can be used for analyzing both families simultaneously (see above part on the optimization of the outlet split of the TD method for DEHP) which is expected to further lower the LOD for phthalates.

The validation of the optimized TD-GC-MS for both families occurred by spiking Tenax TA tubes with 1 μ L of the diluted mixture of standard solutions of phthalates or OPFRs and 1 μ L of the internal standard (DEHP-d4).

1.4.1. LINEARITY RANGE AND LINEARITY

Calibration curves are represented as the ratio of analyte peak area to that of internal standard as function of the mass analyte injected into the adsorbent tube. The linearity range of each compound within the calibration curves was determined experimentally. The highest concentration values were removed consecutively until linear calibration curves are established [20]. Linearity was confirmed once the correlation coefficient (R^2) is equal to or higher than 0.99.

The concentrations at which calibration curves of phthalates and OPFRs remains linear with an R^2 value greater than 0.99 (linearity range) is determined. Calibration curves remained linear for all phthalates from 2 up to about 700 ng except for DiNP and DiDP at which the concentration range, 7 to 3300 ng, is about 4 to 5 times higher than that of the other phthalates [21]. For OPFRs, linearity ranges are more variable depending on the analyte. However, the highest concentration ranges are for the least volatile compound (TDCPP) and that made of isomers (TCPP). The optimized method is linear for all phthalates and OPFRs at which R^2 values are higher than 0.99 for all analytes (Table 6).

1.4.2. REPEATABILITY, LOD, AND LOQ

The repeatability or precision of the method was tested. It is represented by calculating the relative standard deviation (% RSD) of the analysis of five- to eight-points calibration curves with three points for each concentration level. The average % RSD value at the highest and lowest concentration levels was calculated according to the equation used by Kang et al. [22]:

$$\% \text{ RSD} = \frac{\text{SD}}{\overline{\text{CF}}} \quad (1)$$

Where SD is the standard deviation of the replicates (n) and $\overline{\text{CF}}$ is the mean calibration factor.

The limits of detection (LOD) and the limits of quantification (LOQ) are defined as three and ten times the standard deviation of the peak area obtained in SIM mode for the standard solution at the lowest value of the linear range (1-7 ng depending on the compound) for 4 replicates, respectively divided by the slope of the calibration curve [21], [22], [23]–[25].

The repeatability of the method is calculated by considering three replicates of each concentration level of the eight-points calibration for phthalates and the five-points calibration for OPFRs. The method is well repeatable since the average %RSD values range from 9 to 16% for the least volatile and more volatile phthalates, respectively and 7 to 18% variable between the least and more volatile OPFRs [26] (Table 5).

Table 5: Linearity range and linearity (R^2) of calibration curves of phthalates and OPFRs analyzed by the optimized TD-GC-MS method

Compound	Linearity range (ng)	Correlation coefficient (R^2)
Phthalates		
DMP	2-700	0.992
DiBP	2-700	0.993
DBP	2-700	0.993
BBP	2-760	0.992
DEHP	3-950	0.992
DnOP	2-700	0.992
DiNP	7-3300	0.999
DiDP	7-3300	0.998
OPFRs		
TEP	1-475	0.994
TBP	1-1200	0.992
TCEP	1-650	0.993
TCPP	5-1000	0.991
TPP	1-650	0.998
TDCPP	5-1200	0.994

As previously mentioned, this optimized TD-GC-MS method is used to characterize phthalates and OPFRs emitted from materials using the μ -CTE. Therefore, LOD and LOQ are calculated for these compounds in terms of: 1) injected mass into adsorbent tubes (ng) and 2) collected concentration ($\mu\text{g}/\text{m}^3$) for about 80 L of sampled air using the μ -CTE at 25 °C and 55 mL/ min air flow rate (Table 6).

Breakthrough of phthalates and OPFRs was checked by connecting two Tenax TA tubes in series at the outlet of the μ -CTE during their emission. No breakthrough of phthalates and OPFRs through the tubes has been observed for this sampling volume and at this temperature.

In the case of phthalates, LOD and LOQ are almost equal for 6 phthalates ranging from 0.4 to 0.9 ng and from 1.3 to 3.1 ng, respectively. However, since DiNP and DiDP are made of isomers as previously mentioned, and are the least volatile compounds among the others, their detection and quantification limits are about 3 times higher [21].

For OPFRs, the most volatile compounds (TEP, TBP, and TCEP) have the lowest LOD and LOQs ranging from 0.4 to 1.96 ng and 1.8 to 5.95 ng, respectively. TCPP, being made of isomers, and TDCPP, the least volatile OPFR, have higher LOD values of 11 and 22 ng, respectively. Even if TPP is the second least

volatile OPFR, its LOD and LOQ are close to those of the highly volatile compounds (TEP and TCEP), 0.42 and 1.28 ng, respectively.

The obtained LOD values of phthalates and OPFRs using this optimized method are much lower than values reported in the literature. Kang et al. obtained an LOD value of 4.1 ng for DBP [22] while those obtained by Ho et al. are 6.4, 2.62, 5.12, 7.4, and 6.95 ng for DMP, DBP, BBP, DEHP, and DnOP, respectively [27]. Fujii et al. showed a 5 ng LOD for a group of phthalates including DiBP, DBP, BBP, and DEHP [28]. For OPFRs, the LOD of the GC-MS/FPD method developed by Ni et al. is 15-30 ng for TCPP even if using a flame photometric detector (FPD) is expected to increase sensitivity [29]. While the LOD and LOQ of the TD-GC-MS method developed by Hayeck et al. are 15 and 32 ng for TCPP and TCEP, respectively [24].

Table 6: Limits of detection (LOD) and quantification (LOQ) for 4 replicates of phthalates and OPFRs in volume of solution (ng) and in air sampling volume of about 80 L at 25 °C ($\mu\text{g}/\text{m}^3$) in addition to the repeatability (% RSD) of the optimized TD-GC-MS method

Compound	LOD		LOQ		% RSD
	ng	$\mu\text{g}/\text{m}^3$	ng	$\mu\text{g}/\text{m}^3$	
Phthalates					
DMP	0.9	0.01	2.9	0.04	14
DiBP	0.9	0.01	2.9	0.04	13.8
DBP	1.04	0.01	3.2	0.04	16.5
BBP	0.9	0.01	2.8	0.04	14.4
DEHP	0.9	0.01	2.8	0.04	10.5
DnOP	0.4	0.006	1.3	0.02	10.3
DiNP	2.7	0.03	8.06	0.1	9.2
DiDP	2	0.03	6.04	0.08	9.9
OPFRs					
TEP	0.6	0.008	1.8	0.02	7.3
TBP	2	0.03	6	0.08	17.5
TCEP	0.4	0.005	1.1	0.01	18.4
TCPP	3.6	0.05	11.03	0.1	13.2
TPP	0.4	0.005	1.3	0.02	14.8
TDCPP	7.3	0.09	22.1	0.3	18.2

2. EMISSION EXPERIMENTS

2.1. Principle of the μ -CTE

2.1.1. DESCRIPTION OF THE DEVICE

The micro-chamber or thermal extractor (μ -CTE) is a commercial device fabricated by Markes International (Llantrisant, UK) with a built-in heating system. A μ -CTE250 model made up of four stainless steel cylindrical cells of 114 mL volume each with the ability to heat it up to 250 °C was used in this study. A constant flow rate of pure dry or humid air enters each cell where the tested samples are placed. Tenax TA tubes (60/ 80 mesh) with glass wool inside, supplied by Antelia (Dommartin, France), are then loaded at each cell outlet to collect samples of air. Collected samples are then analyzed by ATD-GC-MS. This device can be used in multiple configurations: i) materials placed at the bottom of the cell and ii) material lifted on spacer Figure 6.

Using the first configuration, the material is in direct contact with the cell of the μ -CTE. While to reduce the volume of the cells, materials can be lifted up on aluminum collar spacers provided also by Markes International.

Both configurations were tested in this study for characterizing the emissions of phthalates from materials. Spacers of 5 or 15 mm thickness were used to reduce the depth of the cell above the material surface from 3.3 cm to about 0.3 cm. This configuration was tested for direct determination of y_0 .

In addition, the effects of temperature and humidity on the emission of phthalates and OPFRs can be easily studied using the μ -CTE. A relative humidity value up to 50% is reached using the humidifier supplied by Markes International.

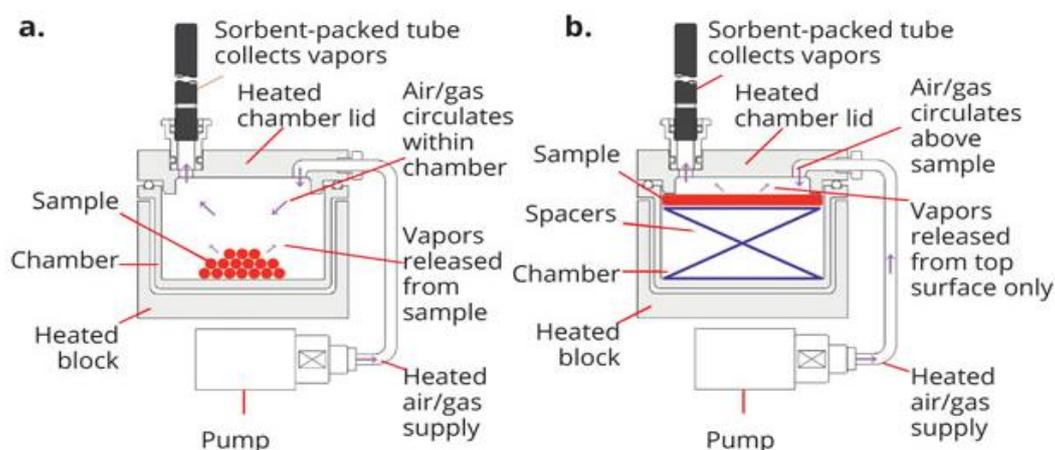


Figure 6: Operation of a micro-chamber system for characterizing the emissions of SVOCs in (a) bulk and (b) surface positions [30]

2.1.2. EMISSIVE MATERIALS AND SAMPLE PREPARATION

Vinyl floorings are chosen as the source of emission of phthalates since most of the consumed phthalates worldwide are used as plasticizers in polymers, especially in the production of flexible polyvinyl chloride [31], [32]. Flame retardants are added to the stuffing of 92% of upholstered furniture [33]. Polyurethane foam (PUF) is usually used as the cushioning materials in furniture [34]. Therefore, PUF are considered the source of emission of OPFRs in this study.

Nine different vinyl floorings (VF) were purchased from DIY store in France. These vinyl floorings were wrapped in aluminum foil and stored at room temperature. 2x2 cm piece of each was cut from random places and placed in the micro-chamber at 85 °C and 55 mL/ min air flow rate to qualitatively identify their emissions of phthalates. Collection of phthalates was performed during 45 min using Tenax TA tubes and were then analyzed by automated thermal desorption connected to gas chromatography and mass spectrometry (ATD-GC-MS). Among the nine VF, one product containing Di-n-octyl phthalate (DnOP) and another containing DiNP, were chosen as experimental specimens. To determine the percentage of DnOP and DiNP in the test material, extraction by ultrasonic was done following the same procedure as that proposed by Liang and Xu [10]. The percentage of DnOP and DiNP in the tested material was 3.3% and 9.1%, respectively.

Four soft polyurethane foams (PUF) with different OPFRs and of known % by weight in each are used in this study. These PUF were laboratory-made in 2015 as part of a previous project by mixing polyol mixture containing OPFRs with isocyanate [33], [35]. The content of OPFRs in the four PUF varied where one contained 10% of only TPP, one 10% of only TCPP, one 10% of only TDCPP, and one contained the six OPFRs: TEP, TBP, TCEP, TCPP, TDCPP, and TPP with individual concentration of 7.6%. They were wrapped in aluminum foils inside airtight polyethylene bags and stored at room temperature.

Test pieces were then cut into circular shape of about the same diameter as that of the micro-chamber cell ($d = 6.4$ cm) Figure 7. Backs and sides were covered with aluminum foil to limit the emission to the surface as recommended by ISO 16000-25. These pieces were placed at the bottom or top of the cell of the μ -CTE depending on the experiment. vinyl floorings had a thickness of 3 mm while PUF thickness was about 8 mm.

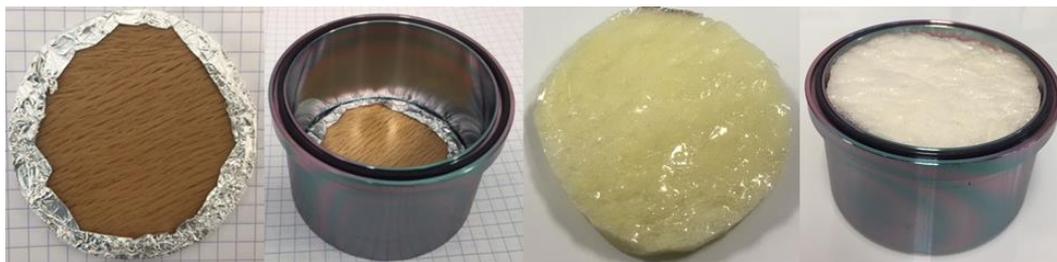


Figure 7: The used samples of vinyl floorings (to the left) and PUF (to the right) at both configurations: bottom of the cell and lifted on spacers

2.1.3. APPLICATION OF THE METHOD TO REAL MATERIALS

After validation, the developed TD-GC-MS method was applied to characterize phthalates, emitted from the previously mentioned vinyl floorings containing DnOP, and OPFRs, emitted from the PUF containing 7.6% of the six OPFRs.

Samples were collected via Tenax TA tubes at 25 °C and a flow rate of 55 mL/ min for 24 hours as per the calculation of LOD. The collected samples were analyzed after by the developed TD-GC-MS method. The resulting chromatograms are shown in Figure 8.

All phthalates and OPFRs were well detected and quantified, except for TDCPP which is below LOD at 25 °C due its low volatility. The intensity of the peak for each compound depends on its initial concentration in the material and volatility. The steady-state gas phase concentration (y_{ss}) of DnOP emitted from vinyl floorings is equal to 0.03 $\mu\text{g}/\text{m}^3$. TDCPP was below the LOD at 25 °C; however, y_{ss} of TEP, TBP, TCEP, TCPP, and TPP was equal to 33.7, 310.8, 33.2, 114.3, and 0.4 $\mu\text{g}/\text{m}^3$.

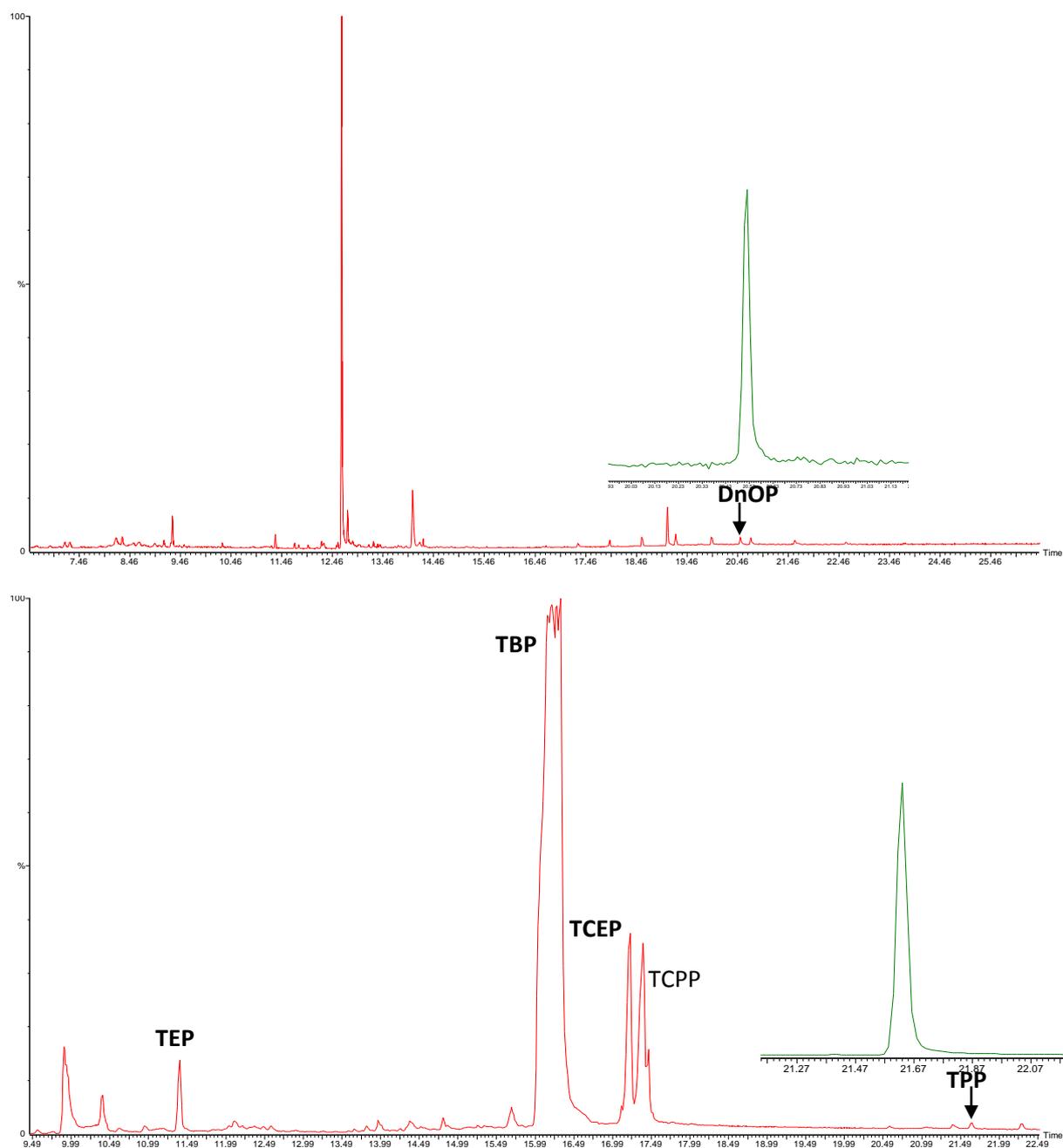


Figure 8: The chromatograms of the emission of DnOP from vinyl floorings (top) and OPFRs from PUF (bottom) in the μ -CTE at 25 °C and for a sampling volume of 80 L

3. MEASUREMENT METHOD

After developing and validating sensitive TD-GC-MS method for the characterization of the emissions of phthalates and OPFRs from vinyl floorings and PUF, the development of rapid measurement method for estimating their γ_0 at room temperature should be done.

The following sections present the followed experimental procedure for developing this method in addition to the equations used for calculating y_0 .

3.1. Protocol

Before each experiment, the micro-chamber was thoroughly cleaned. Its stainless-steel parts were dismantled, put in an oven at 300 °C for 3 hours, soaked overnight in tap water and alkali detergent, then in ethyl acetate for about two hours, and finally rinsed with nanopure water. Blank tests were performed before each experiment to ensure the absence of residual contamination. Moreover, recovery tests of the μ -CTE were performed using a standard prepared solution of the eight phthalates following the same procedure recommended by ISO 16000-25 [1]. Recovery rates were above 80% for all studied compounds.

The effects of temperature, air flow rate, and relative humidity on the emission of DnOP from VF were studied when the material is placed at the bottom of the cell while for DiNP, the effects of these three parameters were studied, following the same procedure, at two different material positions: i) placed at the bottom of the cell and ii) lifted on aluminum collar spacers.

For each emission test, a newly cut piece of vinyl flooring was used to ensure that the amount of the compounds of interest is not depleted. Sampling started after an equilibration time of 20 min. Samples were collected twice a day until reaching steady state which was considered when the difference in gas-phase concentration was less than 5% during 24 hours [36].

3.1.1. TEMPERATURE

The effect of temperature on the emission of DnOP and DiNP, placed at the bottom of the cell, was studied at 6 different temperatures: 25, 40, 50, 60, 70, and 80 °C. However, for the material lifted on spacers, only three temperatures were studied: 25, 40, and 80 °C. In both cases, dry air flow rate was set at 55 mL/ min. Sampling time ranged from 24 hours at 25 °C to 45 min at 80 °C. Sampling started after an equilibration time of 20 min. Once the gas-phase concentration in the micro-chamber reached steady state, the temperature was elevated to the next level. Backup tubes were connected to check for breakthrough, especially at high temperatures. No breakthrough was observed during the experiments.

3.1.2. AIR FLOW RATE

ISO 16000-25 recommended that the specific air flow rate in the micro-chamber should not be less than 0.15 m³/h [1]; moreover, Markes International recommended a minimum 50 mL/min flow rate when using the μ -CTE [37]. Therefore, two flow rates of 55 (1.3 m³/h) and 120 (2.9 m³/h) mL/min were chosen to study the effect of the change of flow rate on the emission of DnOP and DiNP. The experiment started at 120 mL/min of dry air with sampling for 45 min.

Once steady state was reached, the flow rate was decreased to 55 mL/min and after an equilibration time of 20 min, sampling took place again following the same manner. Temperature was set at 80 °C throughout the experiment to reduce sink effect and experimentation time.

3.1.3. RELATIVE HUMIDITY (RH)

A humidifier, also supplied by Markes International, was connected to the micro-chamber to provide humid air. The effect of relative humidity was studied at 0 and about 50% (the maximum value of the humidifier) at two different temperatures: 40 and 80 °C. The aim of this experiment is to verify the effect of RH on the emission of phthalates at moderate to extremely high temperatures. Similar to the flow rate experiment, experimentation started with dry air (0% RH) and after reaching steady state, humid air (50% RH) was supplied. Sampling time was 90 min at 40 °C and 45 min at 80 °C.

3.1.4. SORPTION EXPERIMENT

In order to estimate the quantity of phthalates adsorbed on the walls and different surfaces of the μ -CTE, a desorption test was performed. Since sorption is more important at low temperatures [38], desorption experiment was conducted after the emission experiment at 25 °C with an air flow rate of 55 mL/min. This experiment was conducted for both DnOP and DiNP (placed at the bottom of the cell and lifted on spacers). After reaching steady state, VFs were removed from the cells and the thermal extractor was heated after up to 240 °C as recommended by ISO 16000-25 standard [1]. Sampling in this experiment was performed consecutively for about 2 hours and a half using different Tenax TA tubes to ensure that all desorbed phthalates are collected. The sampling sequence was using two tubes 23 minutes/ each and then a tube each 10 minutes. The applied and used experimental conditions and parameters are presented in Table 7.

Table 7: Experimental conditions in the μ -CTE.

Parameter	Value
Air change rate (h^{-1})	28.9 at 55 mL/ min 63.2 at 120 mL/ min
Material surface area A (m^2)	0.0032
Sorption surface area A_s (m^2)	0.011 without spacers 0.019 with spacers

3.2. Calculation of y_0

y_0 is determined at the different studied temperatures. As explained previously in chapter 1, Xu and Little developed a mass transfer model to demonstrate the mechanisms of emission of different families of SVOCs including phthalates, brominated flame retardants, and biocides [39].

However, when steady state is reached y is assumed equal to y_s [9], [40]. Thus, based on equation 2, y_0 can be determined according to the following equation:

$$y_0 = y_{ss} \left(\frac{Q}{Ah_m} + 1 \right) \quad (2)$$

Where y_{ss} is its steady-state gas phase concentration in the chamber ($\mu g / m^3$).

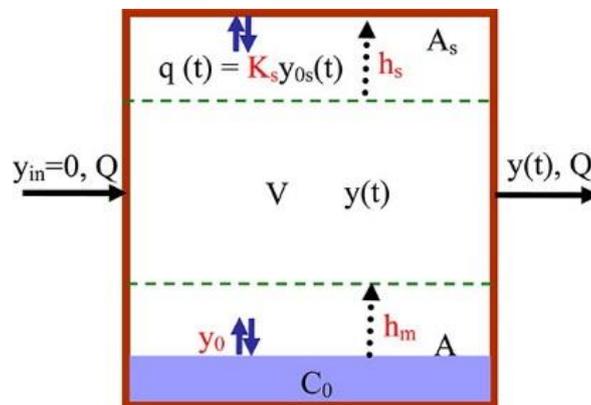


Figure 9: Schematic representation of the emission of SVOCs from VF in an emission test chamber based on the model developed by Xu and Little [39]

3.2.1. DETERMINATION OF THE CONVECTIVE MASS TRANSFER COEFFICIENT

The value of the convective mass transfer (h_m) was determined as function of air diffusivity and air velocity on the surface of the material [41], [42]:

$$h_m = 0.664 \frac{D_a}{l} \left(\frac{\mu}{\rho D_a} \right)^{1/3} \left(\frac{\rho v l}{\mu} \right)^{1/2} \quad (3)$$

where D_a is the diffusion coefficient of an SVOC in air (m^2/s), l is the characteristic length over which the air flows (m), μ is the viscosity of air ($kg/m \cdot s$), ρ is the density of air (kg/m^3), and v is the velocity of air (m/s).

3.2.1.1. Determination of the diffusion coefficient

The air diffusion coefficient (D_a) was determined at different temperatures based on the following equation [41], [42]:

$$D_a = \frac{10^{-7} T^{1.75} \sqrt{\frac{1}{M_a} + \frac{1}{M_g}}}{P(V_a^{1/3} + V_g^{1/3})^2} \quad (4)$$

where M_a and M_g are the air and the phthalate molecular weights, respectively (g/mol), P is the atmospheric pressure (atm) and was considered equal to 1 atm, and V_a and V_g are the air and the phthalate molar volumes at their boiling temperatures, respectively (cm^3/mol). The calculated values of D_a are shown in Table 8.

Table 8: The calculated values of $D_a \times 10^{-6}$ (m^2/s) for DnOP and DiNP at the different used temperatures

T (°C)	25	40	50	60	70	80
DnOP	4.2	4.57	4.83	5.1	5.37	5.65
DiNP	4.05	4.41	4.66	4.92	5.18	5.45

3.2.1.2. Determination of the air velocity

The determination of the air velocity on the surface of the material is important in characterizing the emission of SVOCs from building and consumer materials in the μ -CTE, especially for the determination of the convective mass transfer coefficient (h_m). Schripp et al. determined the velocity of air on the surface of the material in the six-cell μ -CTE120 model by CFD code [43]. The volume of the cells in this μ -CTE is 44 mL each. They found that air velocity in the empty micro-chamber is less than 0.1 m/s for an air flow rate of 100 mL/min. Liang et al. obtained an experimental average value of 0.09 m/s for an air flow rate of 195 mL/min for the same empty micro-chamber using an anemometer [44].

Since there are no available facilities to experimentally measure the air velocity on the surface of the material in the μ -CTE250 in our laboratory, it was determined by simulations. A CFD code was developed at CSTB using OpenFOAM (Open Source Field Operation and Manipulation) software programmed in C++ to determine the air velocity. The physical modeling of flows with heat transfer is based on mass, momentum, and energy conservation laws [45]. The cylindrical cell of the μ -CTE was divided into two symmetrical planes to simplify modeling (Figure 10). Moreover, its geometry was defined by Cartesian coordinates (x, y, z). Using existing OpenFOAM meshing tools, three different structured meshes were generated: 25000, 50000, and 90000 cells; however, results using the finest and the intermediary meshes showed no significant difference except for the computing time which was shorter for the intermediary mesh. Therefore, this latter was used for all simulations.

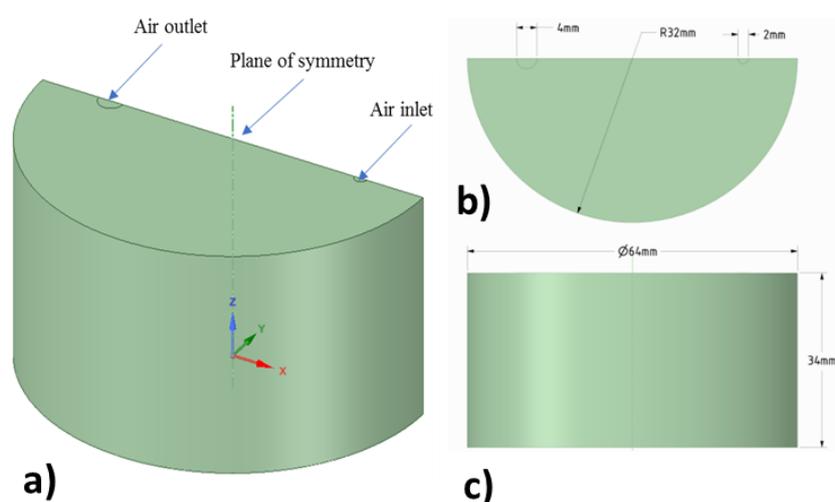


Figure 10: a) A schematic representation of the geometry of the cell of the μ -CTE (half-cell) used for simulating air velocity at the surface of the material, b) top view of the cell, c) front view

To validate the developed model, simulations were performed first for the μ -CTE120 model taking the same dimensions of the cell, air change rate, and air density used by Liang et al. [44]. The obtained average velocity value across the internal surfaces of the closed cell of the μ -CTE120 (bottom, top, and walls) is 0.075 m/ s. This obtained value is smaller than 0.1 m/ s as obtained by the numerical stimulations of Schripp et al. [43]; moreover, the % error between it and the experimentally determined velocity by Liang et al. (0.09 m/ s) is 18% [44]. Therefore, the developed model is considered as double validated.

After validation of the model using the μ -CTE120, simulations of air velocity at the surface of the material in the μ -CTE250 was performed (Figure 11). The used parameters are listed in Table 9.

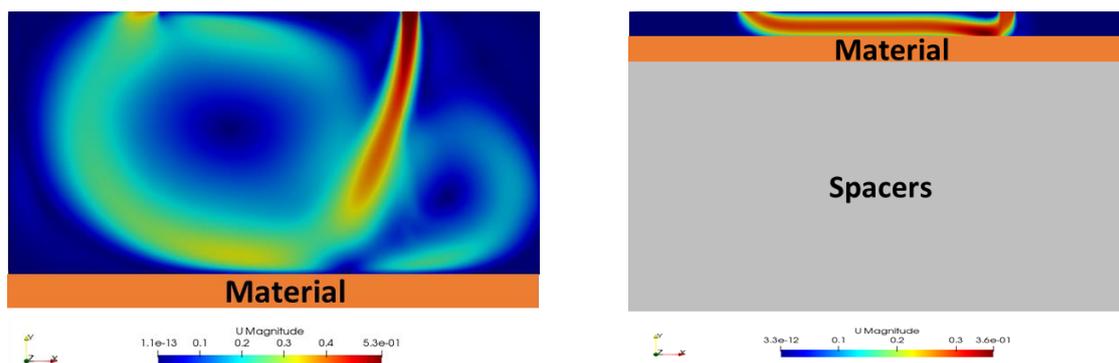


Figure 11: Computational fluid dynamics (CFD) calculations of the air velocity at the surface of the material in the μ -CTE250: placed at the bottom of the cell to the left and lifted on spacers to the right with air inlet on the top right and air outlet on the top left

Table 9: The different used parameters for the development of the computational fluid dynamics code (CFD) to calculate the air velocity on the surface of the material in the four-cells μ -CTE250.

Parameter	Value
Cell volume (mL)	114
μ -CTE outlet diameter (mm) ^a	4
μ -CTE cell diameter (mm) ^b	64
μ -CTE inlet diameter (mm) ^a	2
μ -CTE cell depth (mm)	36
Air density (ρ_{air} , kg/m ³) ^c	1
Air pressure at outlet	Atmospheric pressure

^aMeasured in this study,

^btaken from the specification sheet of the four-cells μ -CTE, ^ctaken from literature [44]

Air velocity at the surface of the material in the μ -CTE250 is calculated at the two air flow rates used in this study: 55 and 120 mL/ min and at two heights over the surface of the material: 34 mm (when the material is placed at the bottom of the cell) and 3 mm (when the material is lifted on aluminum collar spacers). The obtained results are shown in Table 10. Flow of air on the surface of the material is considered laminar since Reynolds number (Re) is less than 2000. Based on the performed simulations, air velocity values are higher at the material surface placed at the bottom of the cell than that lifted on spacers. This is supported by the fact that passages of air exist between the piece of material and spacers and between spacers and the walls of the cell (i.e. not 100% airtight).

By changing the air density, simulations occurred at 25 and 80 °C and at 0 and 50% RH to check the effects of temperature and relative humidity on the change in air velocity at the surface of the material.

The obtained results showed that the change of temperature has no effect on air velocity at the surface of the material while RH caused a slight increase of 18%.

Table 10: The obtained computational fluid dynamics (CFD) simulation air velocity values at the surface of a 3-mm thick material in the four-cells μ -CTE250 at two different air flow rates and material positions.

Air flow rate (mL/ min)	Air exchange rate (ACH, h ⁻¹)	Inlet air velocity value (m/ s)	Average air velocity on the surface of the material according to material position (m/ s)	
			3-mm depth	33-mm depth
55	28.9	0.29	0.0034	0.0064
120	63.2	0.64	0.0088	0.039

After calculating D and determining the air velocity of the surface of the material, h_m was calculated for DnOP and DiNP at different temperatures and flow rates. The h_m calculated values for these two compounds are shown in Table 11.

Table 11: The calculated values of $h_m \times 10^{-4}$ (m/ s) for DnOP and DiNP at the different used temperatures and flow rates

Flow rate (mL/ min)	55						120					
	25	40	50	60	70	80	25	40	50	60	70	80
DnOP	3.36	3.54	3.65	3.77	3.89	4.01	8.26	8.69	8.98	9.27	9.56	9.85
DiNP	3.28	3.45	3.57	3.68	3.8	3.91	8.07	8.49	8.77	9.05	9.34	9.62

4. CONCLUSION

The first two parts of this chapter present the development and validation of a thermal desorption connected to gas chromatography and mass spectrometry (TD-GC-MS) method. This method showed a good sensitivity for the characterization of eight phthalates and six organophosphate flame retardants (OPFRs).

Several parameters such as tube and trap desorption temperature and time, outlet split, and GC temperature programming were critical in the thermal desorption of these compounds. The developed TD-GC-MS was validated in terms of linearity, repeatability, and by calculating the limits of detection (LOD) and quantification (LOQ). It is well repeatable with an average RSD less than 15% for both

families. Moreover, this method has about 6- and 8- to 38-lower LOD for phthalates and OPFRs, respectively than some reported in literature.

This method is efficient for quantifying collected samples of phthalates and OPFRs emitted from vinyl floorings and polyurethane foams (PUF), respectively at room temperature in the μ -CTE. We were able for the first time to quantify both families of compounds using the same method.

In addition, the description of the used test chamber and the followed experimental protocols to develop the measurement methods for determining γ_0 (discussed in chapters 3 and 4) are also presented in the last part of this chapter.

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Chapter 3.

Development of a new method
for determining the gas-phase
concentration of phthalates
in equilibrium with the material
surface

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Emission of SVOCs from indoor materials is considered one of the main sources of indoor air pollution [1]. Therefore, in order to understand the behavior of phthalates in indoor environments and evaluate the risk of human exposures to these compounds, emission from materials should be characterized. The gas-phase concentration in equilibrium with the material surface (y_0) is considered the key parameter in estimating the indoor emissions of phthalates from building and consumer materials and calculating the associated risk of human exposure to these compounds [2]–[8]. Therefore, y_0 is an important parameter that should be determined. One way to determine y_0 of emitted phthalates is by determining their steady-state gas-phase concentration (y_{ss}) and applying it in equation 12 (chapter 1, part 3.1.4) [2], [3].

A group of measurement methods has been developed to determine this parameter as documented in chapter 1; however, due to their physico-chemical properties, sorption of phthalates on the inner surfaces of the test chambers (sink effect) has been always a limitation and challenging point when characterizing their emission. This resulted in inaccurate measurements and long experimentation time until the emission of these compounds reached steady state [9]. For this reason, there is always a need to develop new and fast methods for estimating y_0 of emitted phthalates at room temperature.

The increase in temperature is known to increase the emission of phthalates from the material and reduce their sink effect [10], [11]. Therefore, the thermal extractor/ μ -CTE is used in this study for its integrated heating system.

This chapter presents the development of a rapid method for determining y_0 of phthalates emitted from polymeric materials at ambient temperature using the μ -CTE. This is done in two ways.

The first way is inspired from the work done by Zhu et al. [12]:

- Determining the steady-state gas phase concentration of emitted phthalates (y_{ss}) from the material to the air of the μ -CTE at 6 different temperatures ranging from 25 to 80 °C.
- Calculating y_0 at each temperature based on equation 12 (chapter 1, part 3.1.4) provided by Liang and Xu [3].
- Determining y_0 of emitted phthalates at 25 °C by extrapolation from higher temperatures according to the obtained linear relationship between $\ln(y_0)$ and the reciprocal of temperature [13], [12] and compare it to the experimentally obtained value.

This method allows us to also validate the effect of temperature on the emission of phthalates.

While the second way consists of reducing the volume of the test chamber through lifting the material on spacers. The possibility of assimilating the steady-state concentration of emitted phthalates (y_{ss}) to y_0 will be studied.

Moreover, the built-in heating system of the μ -CTE enabled easy recovery of the sorbed amount of phthalates on its surfaces which allowed us to calculate their surface/ air partitioning coefficient (K_s).

Clausen et al. showed no considerable effect of relative humidity on emission of phthalates at ambient temperature [14]. However, its effect was not studied at elevated temperature at which temperatures in vehicles can reach to up to 89 °C [15]. Therefore, it is interesting to verify if the effect of humidity on the emission of phthalates remains negligible at moderate to high temperatures. For this reason, the effect of humidity on their emission from vinyl floorings is studied in this chapter at 40 and 80 °C.

In addition to the effects of temperature and humidity, the effect of flow rate on the emission of phthalates from vinyl floorings was also studied in this chapter.

1. PRELIMINARY WORK

A collaborative study between the Health and Comfort Division at CSTB and Dr. Jiping Zhu from the Exposure and Biomonitoring Division of Health Canada was made in 2017 during the first two months of this thesis. Similar to the objective of this thesis, this collaborative study aimed to develop a rapid method for determining y_0 of DEHP emitted from pure liquid standard and vinyl floorings at ambient temperature.

In this study, samples were placed at the bottom of the cell of the μ -CTE120 ($V = 44$ mL). The gas-phase concentration (y) of emitted phthalates at different elevated temperatures ranging from 45 to 75 °C for DEHP standard and from 55 to 85 °C when using vinyl floorings was determined. Air flow rate was set at 44 mL/ min and sampling occurred using multi-bed adsorbent tubes packed with 250 mg of glass beads, 200 mg of Carbopack C (60/ 80 mesh), and 100 mg of Carbopack B (60/ 80 mesh), as previously mentioned in chapter 2. The experimentation time was equal to one day per temperature where four measurements were taken before raising the temperature to the next level. y was calculated as the average of these four measurements, and then applied in equation 12 (chapter 1, part 3.1.4) to calculate y_0 . In this study, adsorbent tubes were analyzed by a TD-GC-MS developed by Dr. Zhu and not by the developed method presented in chapter 2.

$\ln y_0$ versus $1/T$ was plotted trying to determine y_0 of DEHP by extrapolation according to Clausius-Clapeyron equation [10] (Figure 1).

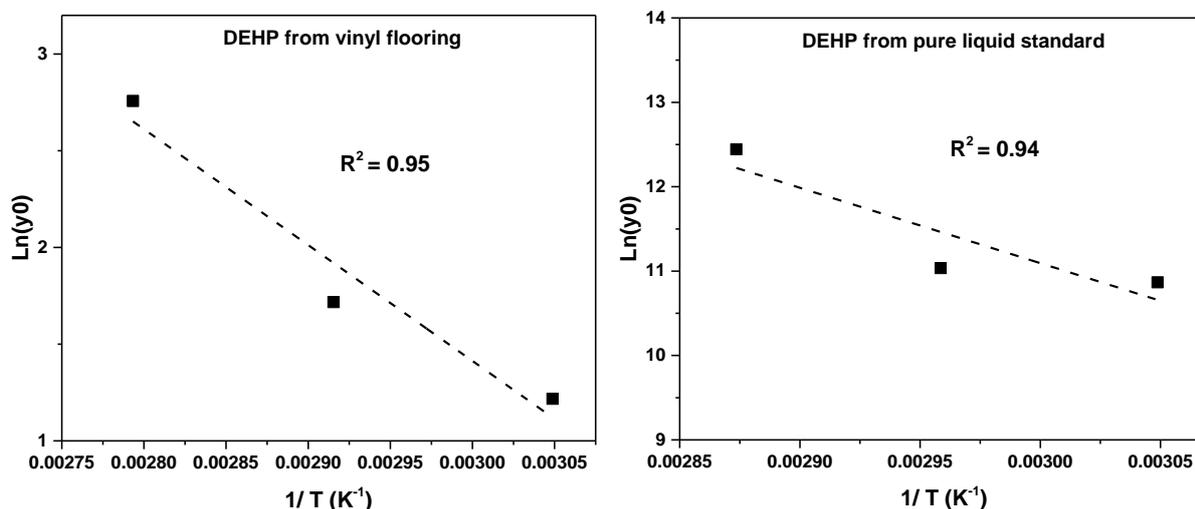


Figure 1: Plots of $\ln y_0$ versus $1/T$ for DEHP emitted from vinyl floorings and pure DEHP standard solution

A linear relationship between $\ln y_0$ and $1/T$ was obtained with a correlation coefficient of 0.95 and 0.94 for DEHP emitted from vinyl floorings and pure DEHP standard, respectively. These results showed a promising preliminary method for determining y_0 of DEHP at room temperature by extrapolation.

However, attaining steady state was not certain in this study due to the limited number of measurement points at each studied temperature. This might lead to inaccurate calculation of y_0 upon using equation 12. In addition, this method was not validated i.e. y_0 of DEHP was not determined experimentally at 25 °C to compare it to the obtained extrapolated y_0 .

Therefore, the concept of the extrapolation method was further developed throughout this thesis for accurate measurements of steady-state gas phase concentrations and thus y_0 .

Based on these preliminary results, it was important to have an idea on the time needed for emissions of phthalates to reach steady state in the μ -CTE120. For this reason, primary characterization of the emissions of DEHP from pure liquid standards occurred at 80 °C and 55 mL/min air flow rate. Samples were collected using Tenax TA tubes and analyzed using the TD-GC-MS developed in chapter 2.

As shown in Figure 2, steady state is reached very fast (within a couple of hours) at elevated temperature and in small-volume chambers, like the μ -CTE.

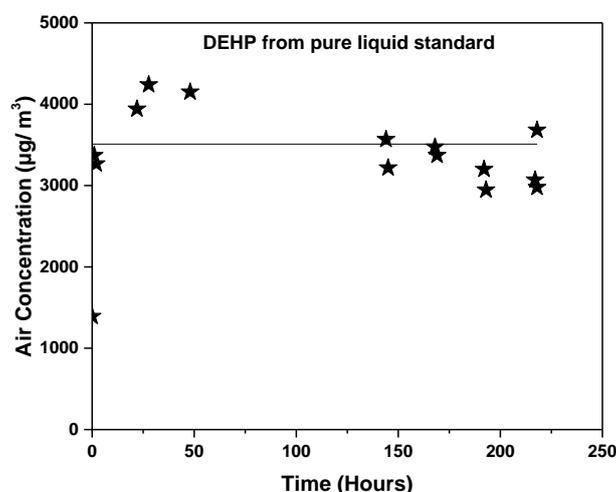


Figure 2: Air concentration of emitted DEHP from pure liquid standard at 80 °C in the μ -CTE120

This preliminary work evidenced the adaptability of using μ -CTE for rapid evaluation of the emissions of phthalates. Therefore, characterizing the emission of phthalates at different elevated temperatures was the next step. However, the μ -CTE250 ($V = 114$ mL) was used instead of μ -CTE120 for its larger emission to sorption surface, which is supposed to further reduce experimentation time at other temperatures. The presence of volatile compounds others than DEHP in materials might influence SVOC emissions. Therefore, for a realistic application, the development and optimization of the method were realized on real samples.

2. EMISSION EXPERIMENTS WITH VF PLACED AT THE BOTTOM OF THE CELL

After the characterizing the emission of DEHP from pure standard, the emission of other phthalates from vinyl floorings was characterized by determining their y_0 at different elevated temperature to develop the extrapolation method, characterizing their adsorption on inner surfaces, and studying the effects of several parameters on their emission.

2.1. Effect of temperature

The increase in temperature greatly affected the emission of DnOP and DiNP from VFs. y_{SS} increased significantly with increasing temperature Figure 3. The specific emission rate (SER), is calculated according to the following equation [16]:

$$\text{SER} = \frac{y \cdot Q}{A} \quad (1)$$

Where y is the gas concentration of phthalates in the chamber air ($\mu\text{g}/\text{m}^3$), Q is the air flow rate into the μ -CTE (m^3/h), and A is the surface area of the test material (m^2).

SER increased by about 75 folds from 0.25 to 18.9 $\mu\text{g}/\text{m}^2 \cdot \text{h}$ for DnOP and 100 folds from 1.7 to 171.9 $\mu\text{g}/\text{m}^2 \cdot \text{h}$ for DiNP, respectively when increasing the temperature from 40 to 80 °C. These results are consistent with those found in literature. Liang and Xu have noted an average 300-fold increase in SER with a 30 °C increase temperature when studying the emission of DBP and DEHP from VF using their developed sandwich method [17]. Moreover, Clausen et al. has observed a 211-fold increase in y_{SS} with a 38 °C increase in temperature while Wu et al. has reported a 5-fold increase with a 10 °C increase when studying the emission of DEHP from vinyl floorings using the FLEC and a modified sandwich-like chamber, respectively [10], [18].

Since no covalent bonds exist between phthalates and the polymer of the material, higher temperatures enhance their emission from the resin chains [19]. Moreover, the increase in temperature leads to a slight increase in h_m due to the changes in the air diffusivity and viscosity. This all leads to an increase in the emission rate and y_{SS} of phthalates [10], [17].

The change in temperature has also changed the time for emission of DnOP and DiNP to reach steady state. It decreased from 21 and 13 days for DnOP and DiNP, respectively at 25 °C to a couple of hours for both compounds at 80 °C. Therefore, the increase in temperature in addition to the small volume of the cells of the thermal extractor (i.e. small sorption surface) [7] reduces partitioning between its different surfaces and air [17], and thus steady state is reached more quickly. However, even if

emission of more volatile compound, i.e. DnOP, should arrive at steady state faster, the initial content of SVOCs in the material plays an important role as well; higher initial concentrations leads to higher emissions [20].

Therefore, the higher content of DiNP (9.1%) in vinyl floorings than the content of DnOP (3.3%) explains why DiNP reached steady state faster than DnOP.

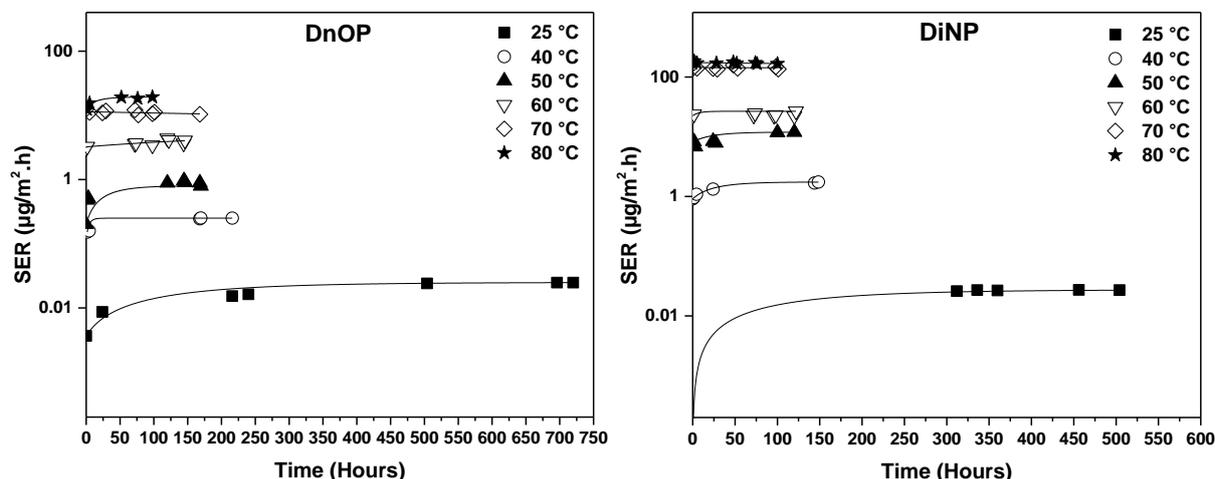


Figure 3: The effect of the increase in temperature on the specific emission rate (SER) of DnOP and DiNP emitted from vinyl flooring placed at the bottom of the cells of the μ -CTE and on the time for their emission to reach steady state

2.2. Accuracy of the emission

The accuracy of the emission of DnOP and DiNP in the μ -CTE was studied by repeating the experiment twice ($n = 2$) at each temperature: 40 and 80 °C with 55 mL/ min of dry air when material is placed at the bottom of the cell. The % difference at 40 °C was 16 and 13% for DnOP and DiNP, respectively; however, the method was less accurate at 80 °C with % difference of 28 and 23% for DnOP and DiNP, respectively (Table 1).

Table 1: The % difference of the emissions of DnOP and DiNP from vinyl flooring placed at the bottom of the cell between two measurements at 40 and 80 °C

Compound	y_{ss} ($\mu\text{g}/\text{m}^3$) at 40 °C			y_{ss} ($\mu\text{g}/\text{m}^3$) at 80 °C		
	Sample 1	Sample 2	% Difference	Sample 1	Sample 2	% Difference
DnOP	0.25	0.21	16	18.9	26.1	28
DiNP	1.6	1.4	13	164.9	213.1	23

2.3. Determination of y_0 by extrapolation

y_0 was calculated at the different studied temperatures according to equation 12 (chapter 1, part 3.1.4). The obtained values are reported in (Table 2).

Table 2: The calculated values of y_0 of emitted DnOP and DiNP from vinyl flooring placed at the bottom of the cell of the μ -CTE at different temperatures

Sample	Phthalate	y_0 ($\mu\text{g}/\text{m}^3$)					
		25 °C	40 °C	50 °C	60 °C	70 °C	80 °C
1	DnOP	0.04	0.4	1.5	7.1	18.3	37.8
2	DiNP	0.4	2.8	20.6	40.7	238.3	326.2

Upon characterizing the emission of phthalates from materials at different temperatures, Liang and Xu showed an exponential relationship between C_0/y_0 and the reciprocal of temperature ($1/T$) [17]. Recently, Yang et al. established a linear relation between $\ln(y_0)$ and $1/T$ for a group of SVOCs, including some phthalates, emitted from materials used in cars [13]. Interestingly a linear relationship between $\ln(y_0)$ and $1/T$ was also obtained in this study with a correlation coefficient (R^2) of 0.99 and 0.96 for DnOP and DiNP, respectively (Figure 4).

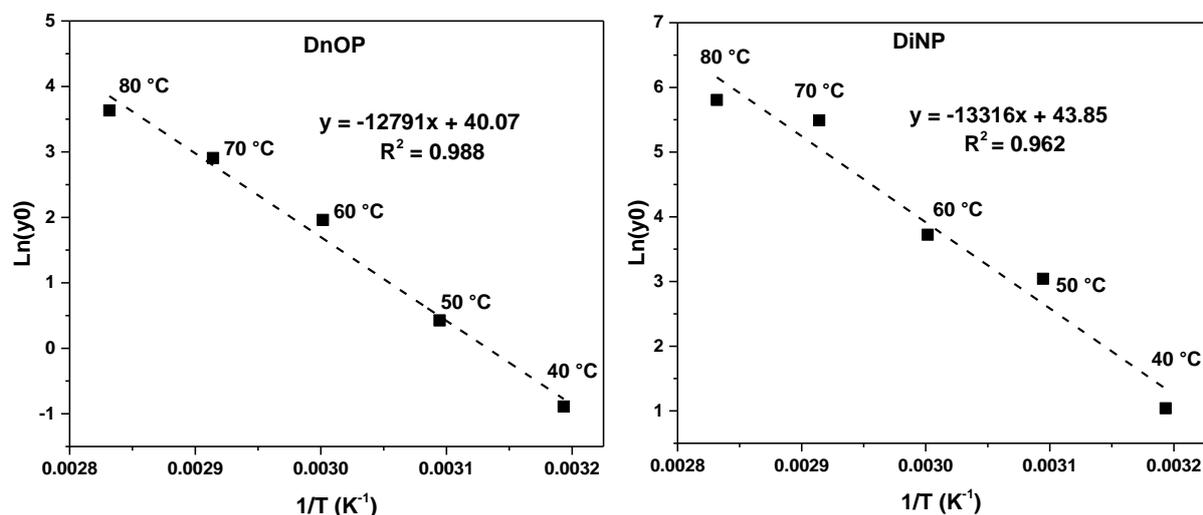


Figure 4: $\ln(y_0)$ of DnOP and DiNP emitted from vinyl flooring as a function of the reciprocal of temperature (40, 50, 60, 70, and 80 °C)

Characterizing the emission of phthalates from materials at room temperature is challenging due to the long experimentation time and sink effect. In the aim of reducing experimentation time and sink

effect, Zhu et al. determined the gaseous bulk concentration (y) of DBP and DEHP at room temperature by extrapolation from elevated temperatures according to Clausius-Clapeyron equation, and then used its obtained value to calculate y_0 [12]. In this study, this approach is further developed to directly determine y_0 of emitted DnOP and DiNP at room temperature by extrapolation according to the obtained linear relationship. The extrapolated y_0 at 25 °C was equal to 0.06 and 0.44 $\mu\text{g}/\text{m}^3$ for DnOP and DiNP, respectively. The % error between the extrapolated and experimental y_0 (Table 2) is about 42% for DnOP and 10% for DiNP. Therefore, the extrapolation method with the 5 temperature points is well validated for DiNP.

To improve the % error for DnOP, the point at 80 °C was removed. Thus, the % error between the experimental and the extrapolated value for DnOP decreased to 7% for the same R^2 value (0.99). This can be explained by the fact that DnOP has a higher vapor pressure than DiNP, and is thus more volatile. Therefore, high temperatures starting from 80 °C make its emission less stable than at lower temperatures. This assumption is supported by the precedent % error value of 28% for DnOP when studying the accuracy of its emission at 80 °C (Table 1).

Since the main objective of this study is to develop a rapid and robust method for estimating y_0 of emitted phthalates at room temperature, it was also important to find the extent to which the relation between $\ln(y_0)$ and $1/T$ remains linear with a good correlation coefficient (R^2), acceptable % error (< 20%) between the two y_0 values, and mostly the fastest time of experimentation. For this reason, different temperature sets (Table 1 and Table 2 in annex) with the % error between the extrapolated and experimental value, linearity correlation coefficient (R^2), and experimentation time.

Even if for certain temperatures sets, R^2 is in the acceptable linearity range (0.95 to 0.99), the % error between the extrapolated and experimentally determined y_0 is very high. This allows us to deduce that linearity or high R^2 value alone is not a good indicator of the ability to determine y_0 at room temperature by extrapolation. Moreover, the % error of sets with only high temperatures (50-80 °C) are very high. However, when adding the point of 40 °C, it was decreased in almost all cases. Thus, we can conclude that high or low temperatures alone are not sufficient for determining y_0 of emitted phthalates at room temperature by extrapolation. For a reliable value of y_0 , a minimum of three temperatures should be used with at least one low (e.g. 40 °C) and one high temperatures (e.g. 70 or 80 °C) depending on the volatility of the compound.

The developed extrapolation method is a promising method to estimate y_0 of emitted phthalates at room temperature by extrapolation from higher temperatures within 5 to 6 days of experimentation.

2.4. Determination of the enthalpy of vaporization (ΔH_{vap})

The obtained linear relation between $\ln(y_0)$ and $1/T$ is in accordance with van't Hoff's and Clausius-Clapeyron equations [4].

However, van't Hoff's equation is applied when a chemical reaction takes place [21] which is not the case of the emission of phthalates since no chemical bonds exist between these compounds and the material polymer resin [22]–[24]. Clausius-Clapeyron equation, on the other hand, is applied when there is a phase change, from solid to gaseous phase in the case of phthalates emissions [4]. In order for this equation to be applied, y_0 should be related or close to the vapor pressure (V_p) of pure phthalates. Clausen et al. found that y_0 of DEHP is close to its V_p [10]. Later on, Liang and Xu showed that y_0 is influenced by both C_0 and V_p [17]. According to their study, when the sample contains relatively high levels of phthalates, y_0 is relatively close to V_p . This hypothesis was applicable to DEHP and other alternative plasticizers, such as di(2-ethylhexyl) adipate (DEHA), of 4 to 23% content in the material, but was not applicable to other phthalates such as DBP, BBP, and DiNP. While for low DEHP content (0.1%), y_0 was shown to be lower than V_p and linearly related to C_0 . However, this assumption was not well validated due to the lack of accurate measured values of V_p . Therefore, Clausius-Clapeyron equation was applied in our case to determine ΔH_{vap} , especially because the content of DnOP and DiNP in the material is 3.3 and 9.1%, respectively (much higher than 0.1%).

ΔH_{vap} of DnOP and DiNP was determined from the slope of the linear plots. The average obtained values of ΔH_{vap} are 116 ± 7 and 112 ± 5 KJ/ mol for DnOP and DiNP, respectively. These values are very close to the enthalpy of vaporization ΔH_{vap} , 122.6 and 93.8 KJ/ mol [17], [25], respectively. The difference might be since ΔH_{vap} is also affected by C_0 [17], [26]. This allows us to conclude that the emission of DnOP and DiNP from the bulk of the material into its surface occurs by evaporation. Once at the surface of the material, diffusion of these compounds into air (including the boundary layer) takes place.

2.5. Effect of air flow rate

Several studies were conducted to study the effect of air flow rate on VOCs emission from building products, but information on its effect on the emission of SVOCs is scarce [27], [28]. Moreover, the effect of air flow rate on the emission of SVOCs varies within studies. Clausen et al. showed that SER of DEHP emitted from vinyl floorings is six times higher when increasing air change rate (ACH) from 450 to 3000 mL/ min in the FLEC, but y_{SS} of DEHP remains almost constant [29]. Xu and Zhang and Liu et al. developed models to predict the effect of ACH on the emission of SVOCs from materials in indoor

environments. They showed that y_{ss} of SVOCs is supposed to decrease upon increasing air flow rate due to air dilution. However, this decrease is offset by the increase in emission rate [1], [30].

Their results were validated by the experimentation done by Liang and Xu in the sandwich-like chamber. y_{ss} of DEHP emitted from vinyl floorings decreases by about 50% when increasing the flow rate from 300 to 3000 mL/min on one hand while SER is about eight times higher [5]. However, Xu et al. found that y_{ss} of phthalates increases with increasing ACH in real indoor environments [31].

To study the effect of flow rate on the emission of DnOP and DiNP in the μ -CTE at 80 °C, we have chosen to work with air flow rates of 55 and 120 mL/min which correspond to surface air velocity of 0.0064 and 0.039 m/s, respectively as obtained by the CFD simulations.

The change in flow rate has a great effect on the emission of phthalates from vinyl floorings placed at the bottom of the cell of the μ -CTE. y_{ss} of DnOP decreased by about 35% from 38.7 to 12.4 $\mu\text{g}/\text{m}^3$ while that of DiNP decreased by about 65% from 160.6 to 106.6 $\mu\text{g}/\text{m}^3$ as the air flow rate decreased from 120 to 55 mL/min, respectively. However, the time to reach steady state was not affected by the change in flow rate at 80 °C i.e. steady state was reached in less than 24 hours regardless of the change of flow rate (Figure 5).

The decrease in air flow rate leads to a decrease in the air velocity at the surface of the material resulting in a lower mass transfer coefficient in the boundary layer adjacent to the material surface [5], [31]. As a result, the emission rate of phthalates from the material into indoor air decreases leading to lower y_{ss} .

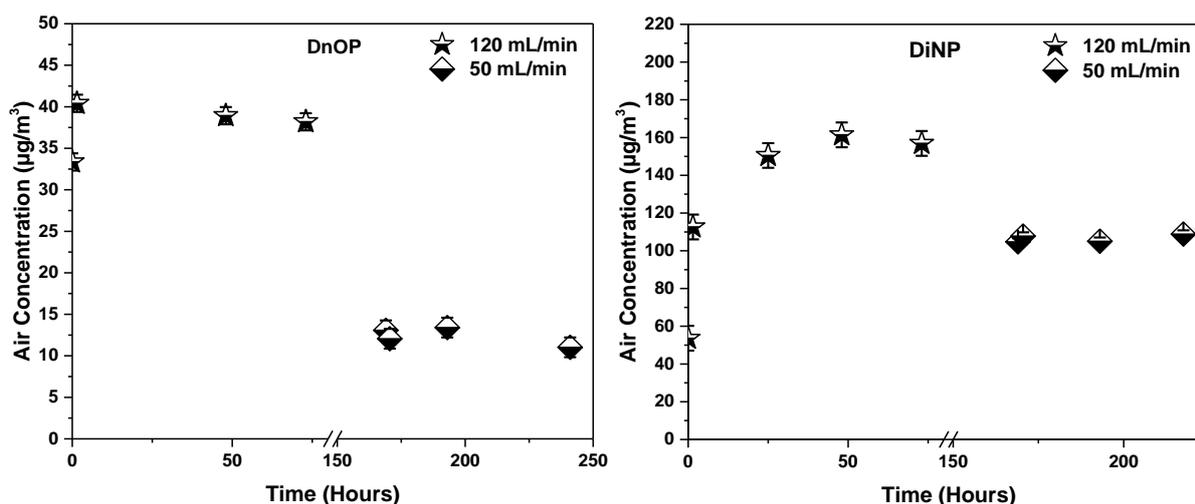


Figure 5: The effect of changing air flow rate in the μ -CTE on the time to reach steady state and air concentration of DnOP and DiNP emitted from vinyl flooring placed at the bottom of the cell at 80 °C

2.6. Effect of relative humidity (RH)

The emission of phthalates from the hosting material is subjected to external control, i.e. it depends on h_m , the material/ air partitioning coefficient (K), and their adsorption into interior surfaces [32]. Clausen et al. showed that none of these three parameters or phenomena is significantly impacted by RH at ambient temperature [14]; however, it is interesting to check the effect of RH on the emission of phthalates at moderately high (40 °C) to extremely high temperature indoor environments (more than 80 °C), such as in cars [13], [15].

First of all, steady state was maintained when humid air replaced dry air at both temperatures (40 and 80 °C, **Figure 6**).

At 40 °C, the steady-state gas phase concentration (y_{ss}) was approximately the same 1.4 and 1.5 $\mu\text{g}/\text{m}^3$ for DiNP at 0 and 50% RH, respectively and 0.2 $\mu\text{g}/\text{m}^3$ for DnOP for both RH values. This is explained by the fact that phthalates are hydrophobic molecules and are more strongly bound to material surface sites than water molecules and thus it is hard for these latter to displace them [14].

At 80 °C; however, the effect of RH on the emission of DnOP and DiNP from VF was more significant. y_{ss} of DnOP decreased by about 20% from 25.3 to 21.1 $\mu\text{g}/\text{m}^3$ while that of DiNP increased by about 30% from 213.1 to 312.2 $\mu\text{g}/\text{m}^3$. Knowing that the octanol/ water partitioning coefficient (K_{ow}) of DiNP is greater than that of DnOP [33], one expects that if there is an effect of RH on the emission of phthalates, the air concentration of DnOP should increase and that of DiNP must decrease. However, since the inverse is obtained, the difference in concentration is not necessarily only due to emissions of these compounds from materials, but also to analytical factors due to the increase of the water content of humid air with increasing temperature. Guillot et al. showed that even if Tenax TA is a hydrophobic adsorbent, water traces exist in Tenax TA tubes at high humidity levels [34]. This affects the texture of the adsorbent, adsorption on the tubes, and chromatographic analysis. Therefore, further experiments should be done at 80 °C and 50% RH on pure liquid phthalates to validate if the reason behind the change of phthalates concentration at these conditions is analytical or due to emission from material.

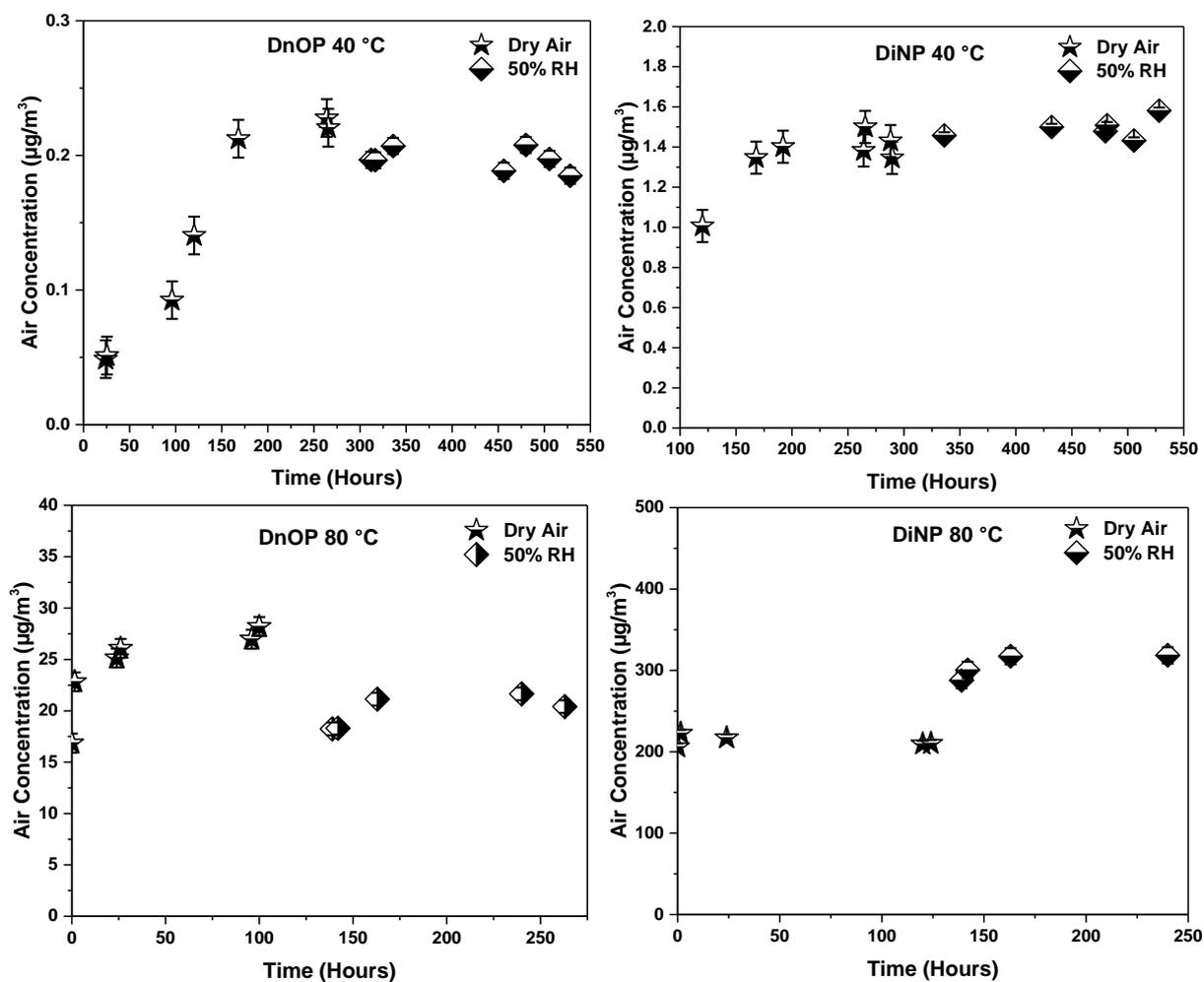


Figure 6: The effect of relative humidity on the air concentration of DiNP and DnOP emitted from vinyl floorings placed at the bottom of the μ -CTE at 40 and 80 °C and a constant air flow rate of 55 mL/min

3. EMISSION EXPERIMENTS WITH VF LIFTED ON SPACERS

The vinyl flooring was lifted on aluminum collar spacers to characterize the effect of reducing the cell volume on the emission of DiNP, and consequently on γ_0 . Moreover, the effects of the change in temperature, air flow rate, and relative humidity on its emission were also studied in this case.

3.1. Effect of temperature

Lifting the VF on aluminum collar spacers had a great effect on the time to reach steady state and the emission of DiNP compared to that placed at the bottom of the cell. In this case, the space between the material and the lid of the μ -CTE is almost negligible (3 mm); therefore, the material becomes closer to the air inlet and sampling ports with better air mixing on its surface, and thus the design of the cell of the μ -CTE when using spacers resembles that of the emission cell FLEC.

The concentration of emitted DiNP was measured at 3 temperatures: 25, 40, and 80 °C at a constant flow rate of about 55 mL/ min. SER of DiNP increased by about 200 folds, from 1.9 to 381 $\mu\text{g}/\text{m}^2 \cdot \text{h}$, upon increasing the temperature from 40 to 80 °C. Since the used mass transfer model to calculate γ_0 neglects the resistance to the mass transfer near the surface and since A_s of the μ -CTE is small, sorption onto inner surfaces does not affect the accumulation of DiNP in the gaseous phase and the time to reach steady state [2]. However, since the steady-state air concentration increased upon lifting the material on spacers, accumulation of DiNP molecules in the gaseous phase is higher. So, the time to reach steady state is decreased from 13 to 9 days at 25 °C and from 7 days to couple of hours at 40 °C while it was reached in less than one hour at 80 °C (Figure 7).

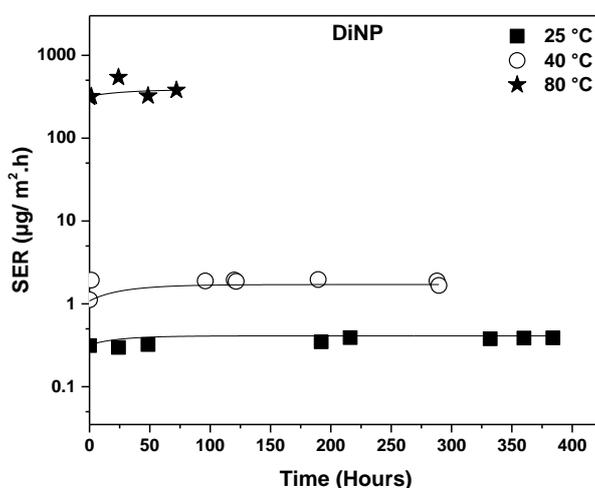


Figure 7: The effect of the increase in temperature on the specific emission rate (SER) of DiNP emitted from vinyl flooring when lifted on aluminum collar spacers in the μ -CTE and on the time for their emission to reach steady state

3.2. Direct measurement of y_0

Clausen et al. showed that when the air flow rate inside the FLEC is up to 450 mL/ min, y_{ss} is approximately equal to y_0 [10], [29]. This is confirmed by the CFD simulations done in this study. It was observed that at a flow rate of 55 mL/ min, the air velocity on the surface of the material decreases greatly when lifted on spacers which means that air flow on the top of the material becomes very low or even negligible. Thus the measured y_{ss} when using spacers is also almost equal to y_0 in the case of emissions of DiNP in the μ -CTE. Therefore, y_{ss} of DiNP measured at the 3 temperatures when material is lifted on spacers is considered equal to y_0 .

To validate this assumption, a comparison of the calculated y_0 when the material is placed at the bottom of the cell to the measured y_{ss} when the material is lifted on spacers is shown in Table 3. The two values are comparable with a % error up to 25%. The difference can be due to analytical measurement errors, lower stability of emissions at high temperatures compared to lower ones, and uncertainties in calculating h_m . This shows that y_0 could be directly measured when reducing the volume of the chamber.

Therefore, another new method is developed in this study for a faster and direct measurement y_0 of phthalates by changing the configuration of the test chamber.

Table 3: Comparison of the time to reach steady state (t_{ss}), y_{ss} ($\mu\text{g}/\text{m}^3$), and y_0 ($\mu\text{g}/\text{m}^3$) of DiNP emitted from the vinyl flooring placed at the bottom of the cell of the μ -CTE to that lifted on spacers, standard deviations are calculated from three measurements at steady state

DiNP	25 °C			40 °C			80 °C		
	t_{ss}	y_{ss}	y_0	t_{ss}	y_{ss}	y_0	t_{ss}	y_{ss}	y_0
Bottom of the cell	312	$0.21 \pm 8.8 \times 10^{-4}$	0.39 ± 0.001	168	1.5 ± 0.08	2.8 ± 0.1	< 1	189 ± 11.8	326.2 ± 20.4
Lifted on spacers	216	0.39 ± 0.005		1.5	2.1 ± 0.3		< 1	381 ± 4.6	

3.3. Effect of air flow rate

The effect of flow rate is confirmed in this experiment also. y_{ss} of DiNP decreased by about two folds, from 745 to 381 $\mu\text{g}/\text{m}^3$, upon decreasing the air flow rate from 120 to 55 mL/ min (Figure 8).

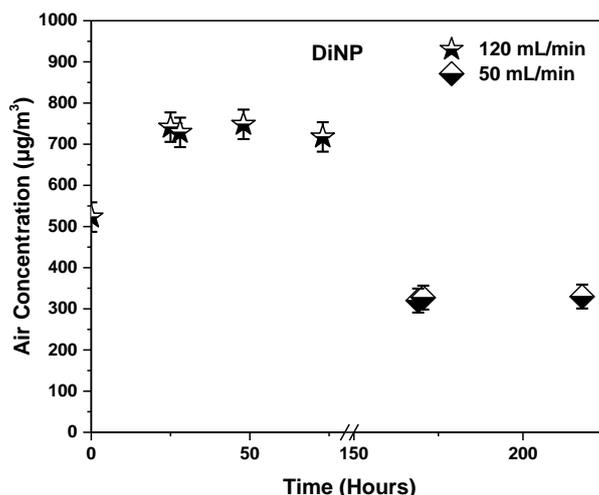


Figure 8: The effect of air flow rate on the emission of DiNP from vinyl flooring lifted on collar aluminum spacers at 80 °C

3.4. Effect of RH

Similar to the previous results, the change in relative humidity did not have a great effect on the emission of DiNP from VF when lifted on spacers (Figure 9) y_{ss} of DiNP remained constant about 2.1 $\mu\text{g}/\text{m}^3$ at 40 °C. However, the effect of RH was more considerable at 80 °C than at 40 °C at which the concentration of DiNP increased in this case also by about 30%, from about to 533 to 746 $\mu\text{g}/\text{m}^3$.

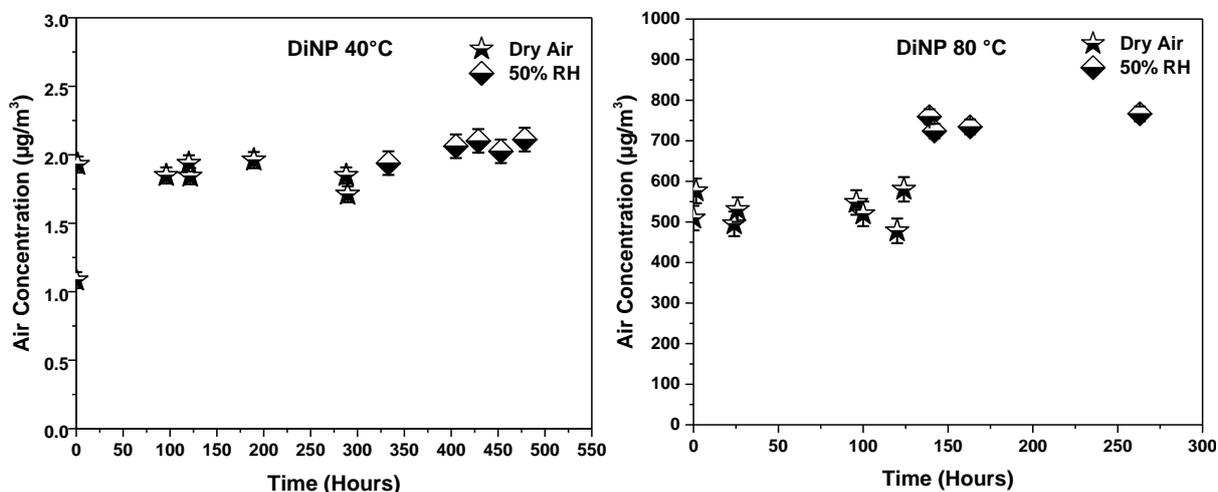


Figure 9: The effect of relative humidity on the emission of DiNP from vinyl flooring lifted on collar aluminum spacers at 40 and 80 °C and at a constant flow rate of 55 mL/ min

4. SORPTION EXPERIMENT

Due to the physico-chemical properties of phthalates as mentioned previously, DnOP and DiNP were adsorbed on the different surfaces of the μ -CTE [6], [35]. Knowing the area of the cells of the μ -CTE and the used spacers, q was calculated. K_s is considered to be constant since Liang and Xu have assumed that sorption of phthalates on the inner surface of the chamber follows a linear isotherm [2]. Therefore, K_s was calculated based on equations 9 (chapter 1, part 3.1.4) upon dividing q by the steady-state gas phase concentration (y_{ss}) in case the material placed at the bottom of the cell and by y_0 once lifted on spacers. The calculated values of q and K_s are shown in Table 4.

Table 4: Determined values of the q and K_s at 25°C and comparison with K_s values from the literature

	Position	q ($\mu\text{g}/\text{m}^2$)	$K_s \times 10^3$ (m)				
			This study	Liang and Xu [2]	Wu et al. [6]	Clausen et al. 2004 [9]	Clausen et al. 2012 [10]
DiNP	At the bottom of the cell	361.3	1.69				
	Lifted on spacers	697	1.73				
DnOP	At the bottom of the cell	33.5	1.34				
DEHP				0.9 - 2.2	1.7	6.8	1

However, when lifting the material on spacers, air continued to pass to the bottom of the cell since there were small spaces between the cut material and the walls of the cell and between the walls of the cell and the spacers as well (not 100 % tight). So the surface sorption area in this case was counted as the sum of the inner surface area of the cell of the μ -CTE in addition to that of the used spacers. This, in addition to the higher gas-phase concentration, explains the 3 times higher q of DiNP when the material was lifted on spacers than that when placed at the bottom of the cell.

The obtained K_s values are comparable with those found in literature (Table 4). For DiNP, the K_s value determined by Liang and Xu was 2.1×10^3 m in the sandwich-like chamber [2] while no K_s values for DnOP are found in literature. However, since DEHP and DnOP are isomers, a similar behavior could be expected and thus their K_s values should be close. K_s of DEHP ranged from 0.9 to 2.2×10^3 m in the sandwich-like chamber and when using the adsorbent tube method [13], [16], equal to 1 or 6.8×10^3 m in the FLEC [10], [9], and ranged between 10^2 and 10^4 m according to the developed model by Xiong et al. [36]. These values are of the same order of magnitude as K_s of DnOP calculated in this study (1.34

$\times 10^3$ m). The slight difference is possibly due to normal measurement errors of y_{ss} and q , especially when changing the tubes during the desorption experiment. The obtained results validate that as the volatility of the compound increases, K_s decreases [2]. Moreover, we can also deduce from the results that partitioning of DnOP and DiNP on aluminum collar spacers is similar to their partitioning on stainless steel surfaces.

5. CONCLUSION

In this chapter, we succeeded to develop two new and relatively fast approaches for determining the gas-phase concentration in equilibrium with the material surface (y_0) of DnOP and DiNP emitted from vinyl floorings using a micro-chamber-type thermal extractor (μ -CTE).

A linear relationship was obtained between the logarithm of y_0 and the reciprocal of temperature based on experimental data obtained in this study. This enabled us to develop the first method for estimating y_0 at room temperature. Using the built-in heat system of the μ -CTE, y_0 of the emitted DnOP and DiNP was determined first at high temperatures (up to 80 °C) since the increase in temperature increases the emission of phthalates and decreases sink effect. Then y_0 at ambient temperature was estimated by extrapolation based on the obtained linear relationship between $\ln(y_0)$ and the reciprocal of temperature. Experimentation time ranged between 5 to 6 days for both phthalates in this case. The developed extrapolation method was validated by comparing the obtained y_0 values to the measured y_0 at room temperature. The % difference between the two values was down to 7 and 10% for DnOP and DiNP, respectively. The obtained linear relation is in accordance with Clausius-Clapeyron equation. Thus, the enthalpies of vaporization of DnOP and DiNP were determined from its slope emphasizing that these compounds are emitted from the material by evaporation.

In the second approach, y_0 of DiNP was directly measured at a flow rate of 55 mL/ min by decreasing the volume of the test chamber through lifting the sample on spacers. In this case, y_0 is equal to the steady-state gas phase concentration (y_{ss}) which is reached 4 days faster than when the material is placed at the bottom of the cell of the μ -CTE. This allowed us to have more accurate values of y_0 since the uncertainties in estimating the convective mass transfer (h_m) are eliminated. Therefore, this configuration is better to use when characterizing the emission of SVOCs from materials.

Sorption of DnOP and DiNP on the internal surfaces of the chamber was also studied. Due to the built-in heating system of the μ -CTE, desorption of the sorbed amount of these two compounds was easily determined to calculate their surface/ air sorption coefficient (K_s). The obtained values are coherent with values reported in literature.

Moreover, we have confirmed the effect of temperature increase and demonstrated the effects of the change in air flow rate and relative humidity on the emissions of these two phthalates. The increase of temperature and air flow rate increased greatly the emission of DnOP and DiNP from vinyl floorings in the μ -CTE. However, the effect of relative humidity on their emission is negligible at low temperatures and more considerable at high temperatures. More research should be done to study the effect of relative humidity on the emission of phthalates at extreme high temperatures which are representable of conditions in other indoor environments such as vehicles.

This study is a primary work on the development of new methods for characterizing the emission of SVOCs from building and consumer materials; therefore, more experiments should be performed to validate its performance on SVOCs other than DnOP and DiNP and other types of phthalate-containing materials than vinyl floorings.

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Chapter 4.

Application of the developed method for OPFRs emission

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After developing the extrapolation method using the μ -CTE for phthalates in chapter 3, it was challenging to test its efficiency for other families. For this reason, organophosphate flame retardants (OPFRs) were chosen as the target compounds due to their abundance in indoor environments and the potential human health effects they cause as thoroughly discussed in chapter 1. In addition, few chamber studies that characterize their emissions are available.

Based on the results obtained in chapter 3, y_0 of OPFRs emitted from polyurethane foams (PUF) was determined at different temperatures ranging from 25 to 80 °C. This allows studying the effect of temperature on emissions of different OPFRs and establishing the relationship between $\ln(y_0)$ and the reciprocal of temperature for testing the efficiency of the developed extrapolation method on OPFRs as well for determining their y_0 at room temperature.

Moreover, sorption of these compounds on inner chamber surfaces is rarely characterized. A recent study characterized their sorption on glass [107]. However, up to now, characterization of the adsorption of these compounds on stainless steel has not been studied. Therefore, it was necessary to characterize the sorption of OPFRs on the inner surfaces of the μ -CTE, calculate the surface/ air partitioning coefficient, and compare their partitioning between surfaces of different natures for a better understanding of their behavior in closed chambers.

As discussed in chapter 3, y_0 of SVOCs can be directly measured in the μ -CTE by lifting the material on aluminum collar spacers up to a depth of 3 mm above its surface. This configuration not only allowed direct measurement of y_0 of phthalates, but also reduced experimentation time. Therefore, in this chapter, the same configuration has been chosen for rapid and direct measurement of y_0 .

Thus the tested PUF was lifted on five collar aluminum spacers of 5 mm thickness each leading to a total surface sorption area (A_s) of 0.018 m².

The emission of OPFRs was studied at six temperatures of 25, 40, 50, 60, 70, and 80 °C and a flow rate of 55 mL/ min following the same procedure as previously explained for phthalates.

Since the initial % by weight of OPFRs in the PUF is high, sampling times were adjusted to range from 24 hours at 25 °C to 15 minutes at 80 °C and an air flow rate of 55 mL/ min. Backup tubes were connected to check for breakthrough, especially at high temperatures. No breakthrough was observed during this experiment.

1. EMISSION EXPERIMENTS WITH PUF LIFTED ON SPACERS

As for phthalates, the main objective of the experiment is to develop a rapid method that allows estimating y_0 of OPFRs emitted from building and consumer materials at room temperature. This method is based on extrapolation from higher temperatures.

However, the PUF containing 7.6% of the six OPFRs was damaged at 80 °C at which its color has changed from yellow to brown. Moreover, the emissions at 40 and 60 °C for this PUF and at 40 °C for the 10% TCPP could not be recovered due to analytical problem caused by a rapid drop in the area of the internal standard affecting calculations. Therefore, emissions from the 7.6% PUF were only characterized at 25, 50, and 70 °C.

1.1. Effect of temperature

The emission of all OPFRs was greatly affected by the change in temperature. OPFRs were added to the PUF upon their manufacturing. Thus, no covalent bonds exist between these compounds and the polymer matrix [1], [2]; therefore, OPFRs are susceptible to be released when increasing temperature. In addition, the increase in their vapor pressure with increasing temperature [3], leads to higher diffusion in air of these compounds from the surface of the material to the bulk air of the chamber, which also increases y_0 of almost all OPFRs (Figure 1 and Figure 2).

The volatility of the compound greatly affects y_0 and the time to reach steady state [4]. Among all OPFRs, TEP, the highest volatile, behaved differently. Its y_0 increased during the first couple of hours of emission and then decreased over time during the rest of the experiment at all 3 temperatures. Liang et al. explained this observation based on the increase of vapor pressures of OPFRs with temperature making less volatile compounds more volatile, and leading to a change from SVOC- to VOC-type behavior [3]. However, as the temperature increased from 25 to 50 °C, y_0 of TEP increased from about 33.7 to 132.7 $\mu\text{g}/\text{m}^3$ whereas it decreased tremendously to 7.3 $\mu\text{g}/\text{m}^3$ when the temperature increased from 50 to 70 °C. This can be explained by the fact that the highest volatile OPFRs are quickly depleted from the foam material with increasing temperature (within about three weeks). This hypothesis seems a more realistic explanation of the decrease in y_0 of OPFRs than a behavioral change from SVOC to VOC.

On the other hand, TDCPP, which is the least volatile OPFR, was not quantified at temperatures lower than 60 °C. Even at 70 °C, its y_0 was so small (62.6 $\mu\text{g}/\text{m}^3$) compared to other OPFRs with the same initial concentration. For TPP, which is the second lowest volatile OPFR after TDCPP, y_0 at 25 °C was 0.4

$\mu\text{g}/\text{m}^3$ compared to 114 and 310 $\mu\text{g}/\text{m}^3$ for TCPP and TBP, respectively. This validates that the risk of having high indoor air concentrations of the least volatile OPFRs is low.

Moreover, for the same initial concentration of OPFRs in the PUF, y_0 measured at 25 °C increased as the volatility of the OPFR increased (Table 1). The concentration of TBP at 25 °C, for example, was 3, 9, and 777 times higher than that of TCEP, TCPP, and TPP, respectively.

At 25 °C, the steady state concentration of TBP was reached directly within the first 24 hours while that of all other OPFRs is reached after 9 days. However, at temperatures ranging from 50 to 80 °C, steady state was attained in less than 24 hours for all OPFRs regardless of the initial concentrations.

y_0 of OPFRs not only depends on the volatility of the compound, but also on its initial concentration in the material (C_0). Liang et al. obtained a linear relationship between y_0 and the mass fraction (proportional to C_0) of SVOCs [5]. This relationship was applied to phthalates and OPFRs with a mass fraction up to 15% in the material. For this reason, the gaseous concentration at different temperatures was higher for TCPP, TPP, and TDCPP at 10% by weight than at 7.6% (Table 1).

Table 1: Measured y_0 values ($\mu\text{g}/\text{m}^3$) of OPFRs at different temperatures and different % by weight in the foam (ND = not detected), standard deviations are calculated from three measurements at steady state

T (°C)	PUF + 7.6% OPFRs			PUF + 10% OPFRs		
	25	50	70	25	50	70
TBP	310.8 ± 11.9	3879.1 ± 61.6	5941.7 ± 102.4			
TCEP	33.2 ± 0.6	544.3 ± 17.9	1406.1 ± 37.1			
TCPP	114.3 ± 4.8	848.7 ± 25.8	2459.1 ± 21.2	301.7 ± 51.4	1175.1 ± 33.4	2548.4 ± 33.3
TPP	0.4 ± 0.003	7.6 ± 1.2	284.1 ± 10.8	0.4 ± 0.02	8.4 ± 0.2	329.8 ± 12
TDCPP	ND	ND	62.6 ± 1	ND	ND	197.1 ± 9.6

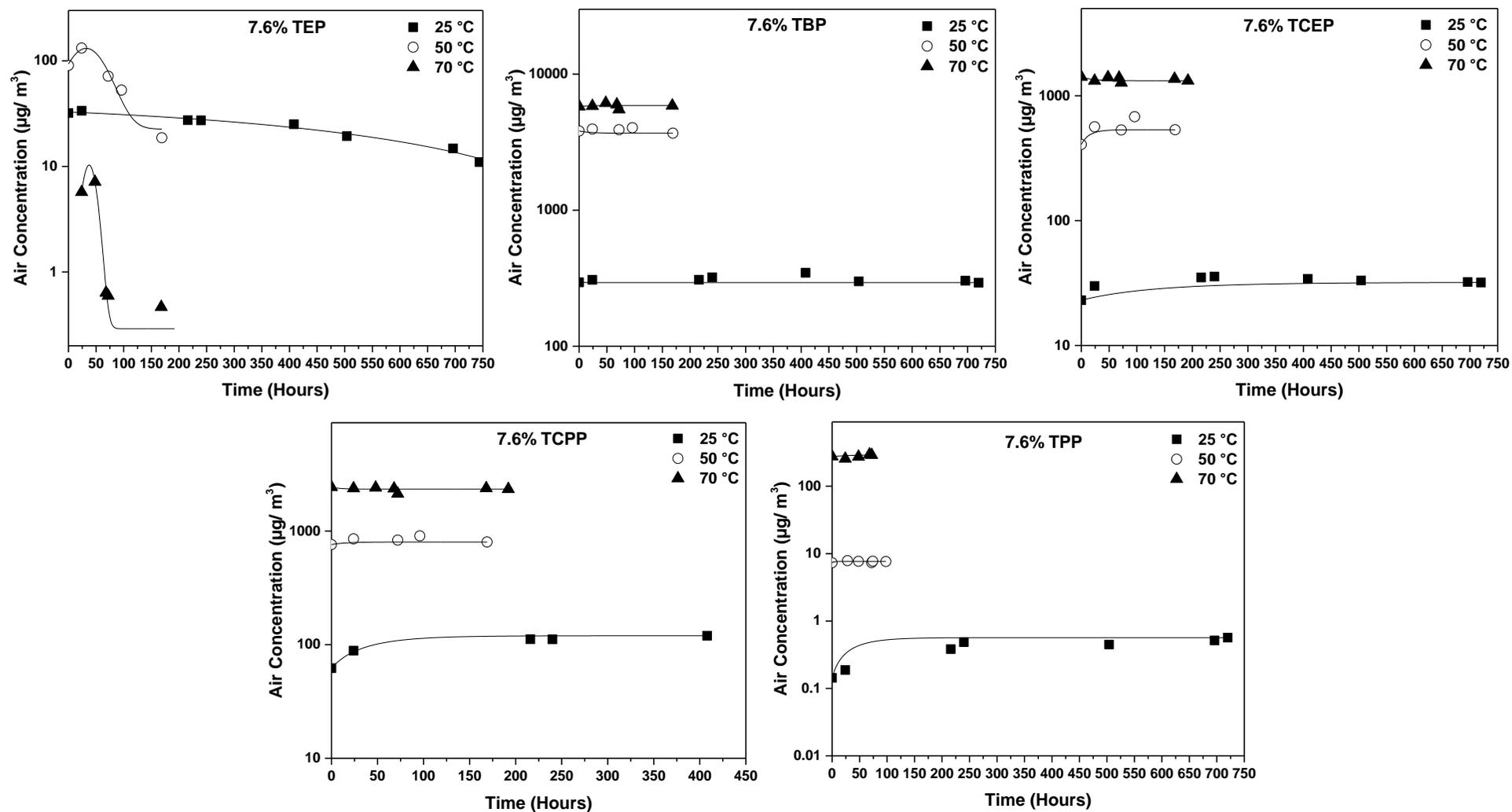


Figure 1: The change in the gas-phase concentration of OPFRs with the change in temperature at 7.6 % by weight in the PUF

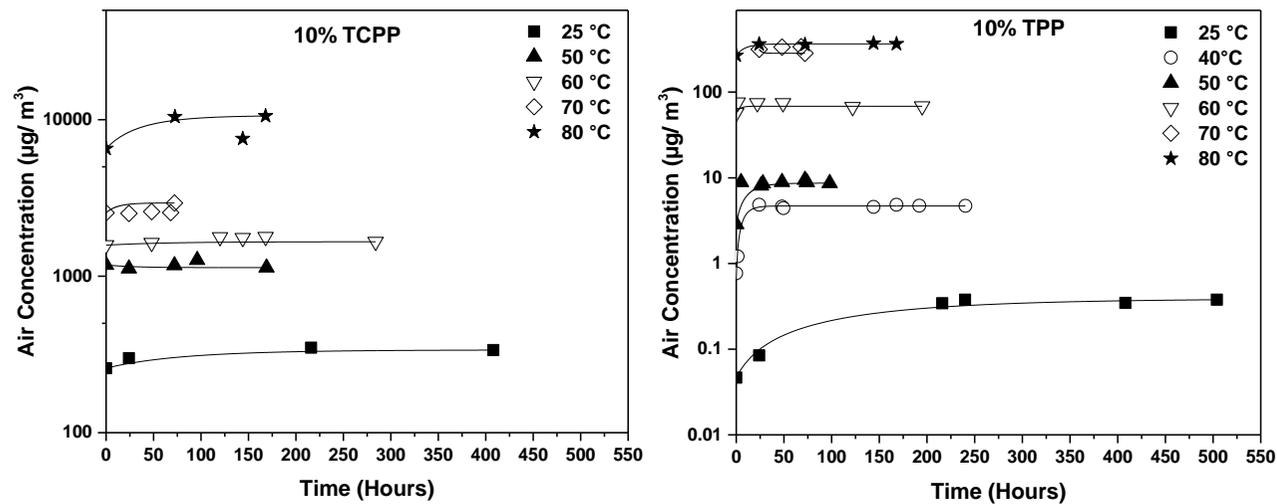


Figure 2: The change in the gas-phase concentration of OPFRs with the change in temperature at 10% by weight in the PUF

1.2. Determination of y_0 by extrapolation

The relationship between y_0 and the reciprocal of temperature has been studied in literature for phthalates, but not for OPFRs [6], [7]. After succeeding in determining y_0 of DnOP and DiNP at room temperature by extrapolation from higher temperatures, it was challenging to test if this method can be also applied for OPFRs.

After determining y_0 of TCPP and TPP at the different temperatures, $\ln(y_0)$ as function of the reciprocal of temperature ($1/T$) is plotted (Figure 3). A linear relationship was also obtained between these two parameters with a correlation coefficient (R^2) equal to 0.88 and 0.96 for TCPP and TPP, respectively.

The extrapolated y_0 of TCPP at 25 °C is 116.8 $\mu\text{g}/\text{m}^3$. The % error between this estimated value and the experimental y_0 is 61.2%. This discrepancy can be explained by the low regression accuracy attested by an R^2 less than 0.9. Therefore, to improve linearity and the extrapolation of y_0 , different temperature sets were tested as done for phthalates in chapter 3 (Table 3 in annex).

It is observed that when removing the experimental point obtained at 80 °C, R^2 becomes higher than 0.99 and the error between the extrapolated and experimental y_0 decreases to about 18%. This allows us to conclude that the emission of TCPP is not very stable at temperatures higher than 70 °C. Moreover, in some temperature sets including the 80 °C experimental point, R^2 values are higher than 0.95. However, the error between estimated and experimental values is very high indicating that relatively high regression accuracy is not always a good indicator of the method and confirming the hypothesis made in chapter 3.

For TPP, the extrapolated y_0 is 0.43 $\mu\text{g}/\text{m}^3$ with 18.7% error between the extrapolated and experimental values including the point at 80 °C. Similar to the results obtained for DnOP and DiNP, TPP is more stable at 80 °C because it is less volatile than TCPP. However, unlike phthalates, a three-point temperature set is not sufficient to determine y_0 of TCPP; y_0 of TCPP should be determined at least at four temperatures for the extrapolation method to be accurate.

Since the aim behind this method is to develop a rapid method for determining y_0 of OPFRs, several temperatures sets were also tested for TPP. This was done to check the extent of linearity of the method with acceptable % error between the extrapolated and experimental y_0 (< 20%) and experimentation time (Table 4 in annex). The obtained results are variable. In some cases, the error is less than 10% with $R^2 > 0.95$ while in others error was very high even if R^2 is equal to 0.99. Therefore, it is hard to determine for OPFRs what temperatures are sufficient for extrapolating, but in general

similar to phthalates, a minimum of three points is required with one low temperature (40 to 50 °C) and one high (70 or 80 °C) depending on the volatility of the compound.

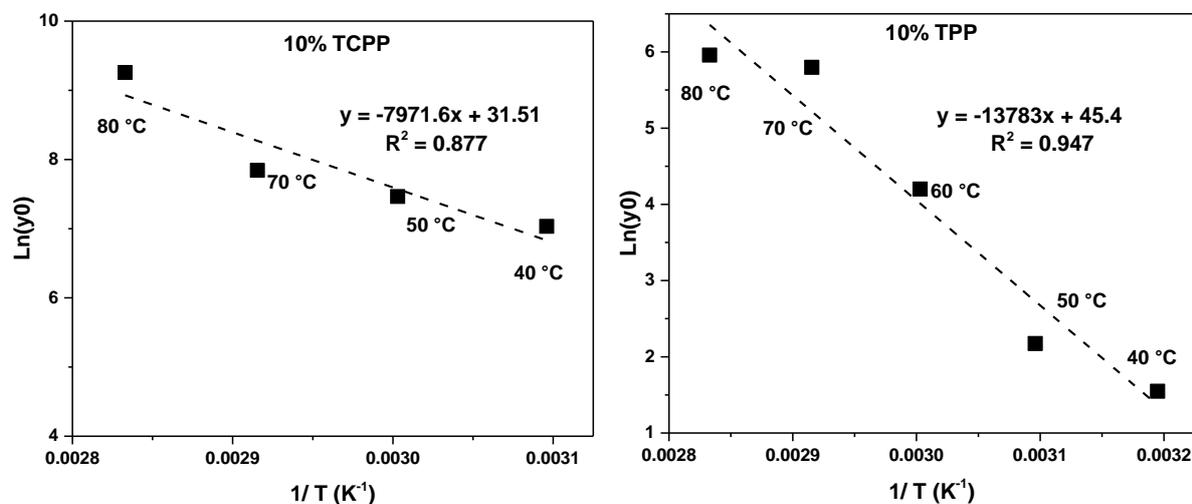


Figure 3: $\ln(y_0)$ of TCPP and TPP emitted from PUF as function of $1/T$: 50, 60, 70, and 80 °C for TCPP and 40, 50, 60, 70, and 80 °C for TPP

1.3. Determination of the enthalpy of vaporization (ΔH_{vap})

In chapter 3, we have shown that the obtained linear relationship between $\ln(y_0)$ and reciprocal of T is in accordance with Clausius-Clapeyron equation, and that ΔH_{vap} can be deduced from the slope [8], [7]. This allowed us to conclude that phthalates are emitted from the core of the material to its surface by vaporization. Therefore, it was important to verify this assumption also for OPFRs.

The average ΔH_{vap} for TCPP and TPP was determined from the assemblies with $R^2 > 0.9$. The estimated average ΔH_{vap} is equal to 54.9 ± 25 kJ/mol and 117.2 ± 19 kJ/mol for TCPP and TPP, respectively. The reported values of ΔH_{vap} for TCPP and TPP are 85.2 and 92.8 kJ/mol [9], respectively which results in a difference of 27.3 and 33.4% between the two values, respectively. Therefore, we can conclude that OPFRs, similarly to phthalates, are vaporized from the core of the material to its surface where they diffuse into the chamber air.

1.4. Is y_0 of OPFRs constant?

In almost all chamber studies on emission of SVOCs from materials, C_0 and y_0 are considered constant particularly for phthalates. Recently, Liang et al. showed that the ratio of the Biot number to the material/air partitioning coefficient ($B_{i,m}/K$) values of TCEP, TCPP, and TDCPP are greater than 1 when their % by weight in the PUF is less than 10% [5].

This indicates that internal diffusion within the material is not negligible and consequently C_0 and y_0 of OPFRs cannot be considered constant. Moreover, Pei et al. showed that y_0 of TCPP emitted from PUF decreased by 36% within 60 days of emission [10]. To verify this observation, a comparison between y_0 obtained in this study for TBP and TCPP emitted from the PUF with 7.6% OPFRs and y_0 obtained by Ghislain et al. using the emission cell-SPME method has been done [4].

It is shown in Table 2 that y_0 of TBP and TCPP decreased by 95 and 82%, respectively within about 3 years. However, one might think that some of this difference can be due to the different analytical methods including the used analytical technique, sampling method, test chamber, etc. For this reason, y_0 of TCPP obtained by Ghislain et al. was compared to a recently determined value with the emission cell-SPME and the same analytical method. The recently obtained y_0 200 $\mu\text{g}/\text{m}^3$ indicating a 68% depletion of TCPP within 3 years. This experimentally observed depletion can presumably be explained by an aging process of the PUF, increasing the pore size and the diffusion of OPFRs within the material and subsequently decreasing C_0 as suggested by Pei et al. [10].

Therefore, assuming that internal diffusion of OPFRs is negligible due to a constant C_0 in the material is not always true. This was shown by the decrease of C_0 and y_0 values of TCPP in this study. Moreover, the feasibility of this assumption differs even between compounds belonging to the same SVOC family depending on their volatility. Pei et al. have shown that C_0 of DEHP decreases more slowly than that of DBP [10] which can be explained by the slower emission rate of DEHP due it is lower volatility.

Table 2: Values of y_0 ($\mu\text{g}/\text{m}^3$) obtained in this study and other studies using the same PUF + 7.6% OPFRs

Compound	This study	Ghislain et al.	Recently determined in the emission cell-SPME
TBP	310.8 \pm 11.9	5700 \pm 300	
TCPP	114.3 \pm 4.8	630 \pm 30	200 \pm 6

2. SORPTION EXPERIMENT

OPFRs are also sorbed on the inner surfaces of the test chambers [4], [11].

After determining the sorbed amount of OPFRs on the inner surfaces of the μ -CTE, the sorbed concentration of OPFRs (q) was calculated by dividing the determined sorbed mass by the total area of the μ -CTE cells and spacers (A_s) (Table 3).

Sorption of OPFRs on inner surfaces of the μ -CTE also depends on the compound volatility. TBP, TCEP, and TCPP were detected in both gaseous and adsorbed phases with TBP being the most abundant

OPFR in both phases [12]. The adsorbed amount of the lowest volatile OPFR, TEP, was very low compared to the other OPFRs. It represented 2% of the adsorbed amount of TBP. Moreover, even if TDCPP was not detected and TPP was slightly detected in the gaseous phase at 25 °C, they were adsorbed on inner surfaces.

Table 3: Determined values of q of the studied OPFRs from the PUF + 7.6% OPFRs

Compound	TEP	TBP	TCEP	TCP	TDCPP	TPP
Sorbed amount (μg)	0.6	33.9	15	56.3	11.3	5.2
q ($\mu\text{g}/\text{m}^2$)	32.1	1885.5	831.6	3126.1	626.2	286.4

For further characterization of the sorbed amount of OPFRs on inner surfaces of the μ -CTE, it is important to determine the surface/ air partitioning coefficient (K_s) of OPFRs. Ghislain et al. were the first to calculate the glass surface/ air partitioning coefficient (K_{glass}) of OPFRs [4]. However, to our knowledge, there is no study so far in the literature reporting their partitioning coefficient on stainless steel (K_{SS}). Therefore, similarly to DnOP and DiNP, assuming that sorption of SVOCs on inner surfaces follows a linear isotherm [13], [14], K_{SS} is considered constant and was calculated in this study according to equation 9 (chapter 1, part 3.1.4).

Moreover, K_{SS} was estimated from the linear relationship, obtained by Ghislain et al., between K_{glass} and K_{SS} [4]:

$$\mathbf{LogK_{SS} = 1.13logK_{glass} + 3.78} \quad (1)$$

The calculated and estimated values of K_s are shown in Table 4. These values are very close.

From the obtained values of K_s , it is shown that partitioning of OPFRs on internal surfaces, regardless of its nature, is inversely related to the volatility of the compound i.e. as the volatility increases, K_{SS} decreases [13], [14]. Therefore, it is interesting to examine the relationship between the partitioning of OPFRs on the surfaces and their vapor pressure similar to the study done by Liang et al. for phthalates (equation 2) [13] and by Ghislain et al. for OPFRs (equation 3) [4]:

$$\mathbf{LogK_{SS} = -0.53logV_p + 0.63} \quad (2)$$

$$\mathbf{LogK_{glass} = -0.51logV_p - 2.88} \quad (3)$$

A linear relationship between $\log(K_{\text{SS}})$ and $\log(V_p)$ has also been obtained in this study (Figure 4). Using this relationship, we estimated K_{SS} of TEP and TDCPP which could not be determined due to the lack of γ_0 value at 25 °C (Table 4). Interestingly, the plot of $\log K_{\text{SS}}$ versus $\log V_p$ have approximately the same

slope that the plot of $\log K_{\text{glass}}$ as function of $\log V_p$. This means that OPFRs behave similarly on glass and stainless steel and even on aluminum (collar spacers). Therefore, partitioning of OPFRs on inner surfaces seems to be mainly affected by their physico-chemical properties and not by the nature of the adsorbing surface.

K_{SS} values were also estimated according to equation 3 obtained for phthalates [13]. The calculated values are also comparable indicating that partitioning coefficients of both phthalates and OPFRs can be estimated from the linear relationship between $\log K_{\text{SS}}$ and $\log V_p$. Therefore, K_{SS} of DnOP and DiNP were estimated based on the obtained linear relationship in this study. The estimated K_{SS} was equal to 1.1×10^3 and 8.5×10^3 m for DnOP and DiNP, respectively. These values are of the same order of magnitude of the K_{SS} values obtained in chapter 3 for DnOP and DiNP: 1.3×10^3 and 1.73×10^3 m, respectively.

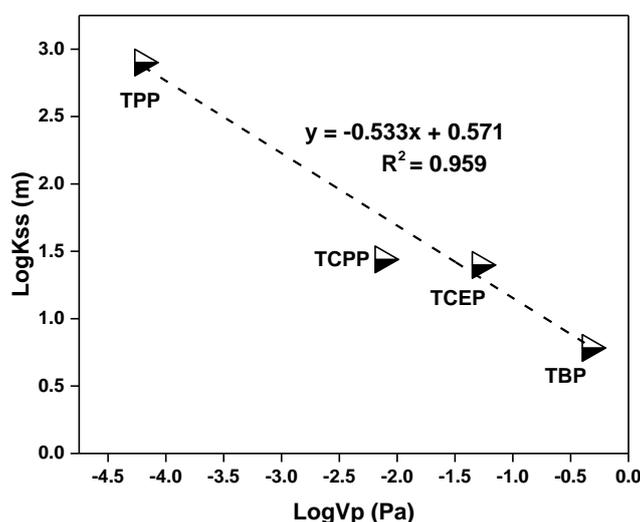


Figure 4: The obtained relationship between K_{SS} and V_p of OPFRs

Table 4: Values of stainless steel/ air partitioning coefficients (K_{SS}) of OPFRs obtained in this study and from two literature studies

Compound		TEP	TBP	TCEP	TCPP	TPP	TDCPP	
K_{SS} (m)	This study	Measured	ND	6.1	25	27.35	791.7	ND
		Estimated	0.7					843.9
	Estimated using equation 1 by Ghislain et al. [4]		0.2	6.1	11.8	37.6	596	800.9
	Estimated using equation 2 by Liang et al. [13]		0.5	11.6	20.1	56.5	719	928

3. CONCLUSION

In this study the gas-phase concentration in equilibrium with the material surface (y_0) of OPFRs emitted from polyurethane foams (PUF) was directly measured at different temperatures and by reducing the volume of the cell of the μ -CTE.

The developed extrapolation method for phthalates presented in chapter 3 has been also used for OPFRs. y_0 of OPFRs was determined at room temperature by extrapolation from higher temperatures according to the obtained linear relationship between $\ln(y_0)$ and $1/T$. This method was validated by comparing the experimentally obtained y_0 with the estimated value obtained by extrapolation. The observed relation is in accordance with the Clausius-Clapeyron equation, allowing the determination of the enthalpy of vaporization of OPFRs and indicating that these compounds are emitted from the material into indoor air by evaporation.

In addition, it was shown that C_0 and y_0 of OPFRs cannot always be considered constant during the emission phase, and thus internal diffusion of these compounds in the materials should be taken into consideration according to their mass fraction.

Moreover, sorption of OPFRs on stainless steel surfaces was experimentally characterized for the first time in this study. The partitioning of these compounds greatly depends on their volatility or vapor pressure. The stainless-steel surface/ air partitioning coefficient (K_{SS}) of OPFRs was calculated, and a linear relationship between $\log K_{SS}$ and $\log V_p$ has been obtained. This relationship allowed us to deduce that the partitioning OPFRs is similar on different surfaces regardless their nature (glass, stainless steel, aluminum).

Finally, after applying the extrapolation method to phthalates and OPFRs, it will be interesting to test it for other families of SVOCs.

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General Conclusion and Perspectives

Studies on semi-volatile organic compounds (SVOCs) have recently increased due to the occurrence of these compounds in indoor environments and the severe health effects they may cause. Indoor sources of SVOCs are multiple; however, emission from building and consumer materials is considered as the major source. Among SVOCs, phthalates and organophosphate flame retardants (OPFRs) are considered two of the most abundant and toxic indoor pollutants. These compounds can be released from the materials into the different indoor compartments increasing the risk of human exposure. In order to evaluate the risk of human exposure to phthalates and OPFRs indoors, it is important to characterize their emissions from materials. Since diffusion of SVOCs within the material is assumed negligible, the gas-phase concentration in equilibrium with the material surface (y_0) is considered the key parameter for characterizing the emissions of these compounds. The risk of human exposure to SVOCs can be predicted by applying the value of y_0 in the different exposure equations. However, the determination of this value is an experimental challenge.

To determine y_0 of phthalates and OPFRs emitted from materials, the thermal extractor (μ -CTE) was used in this work. This type of chambers is recommended for studying SVOCs emissions due to its limited volume and inner surfaces and to the integrated heating system allowing desorption of SVOCs from surfaces. Materials can be either placed at the bottom of the cell of the μ -CTE or lifted on spacers at a constant temperature and air flow rate. Sampling occurs continuously until reaching steady state using Tenax TA adsorbent tubes placed at the outlet of the cell. Collected air samples are subsequently analyzed by thermal desorption connected to gas chromatography -mass spectrometry (TD-GC-MS).

Therefore, the main objectives of this thesis were to:

- develop and validate a sensitive TD-GC-MS method for quantifying both phthalates and OPFRs emitted from materials.
- develop a new rapid method for determining their y_0 at room temperature using the μ -CTE.

Research questions addressed in this study are presented hereafter with the obtained results. Some perspectives are also proposed for future characterization of the emissions of SVOCs from materials.

i) Can phthalates and OPFRs emitted from materials be quantified using the same analytical method?

Since adsorbent tubes are one of the most used sampling techniques for phthalates and OPFRs emitted from building and consumer materials, a sensitive TD-GC-MS method was developed and validated to characterize 8 phthalates and 6 OPFRs.

This method was optimized by studying the influence of different parameters, such as tube desorption time and temperature, outlet splits, and GC temperature programming, on the elution of phthalates. Then it was validated for both families of compounds in terms of linearity, repeatability, and limits of detection (LOD) and quantification (LOQ) were calculated.

Results showed that the developed method is repeatable with an average relative standard deviation (RSD) value less than 15% for both compounds. Moreover, LOD of this method was 2 and 5 times lower than the LOD of other reported methods in literature for phthalates and OPFRs, respectively.

This method was further validated by quantifying phthalates and OPFRs emissions from real samples such as vinyl floorings and polyurethane foams (PUF) with an average LOD of 0.01 and 0.04 $\mu\text{g}/\text{m}^3$ for emitted phthalates and OPFRs, respectively for a sampling volume of about 80 L in the thermal extractor (μ -CTE).

Therefore, this TD-GC-MS method appears to be the first method for the characterization of emissions of both phthalates and OPFRs from materials.

ii) How can we rapidly determine y_0 of emitted phthalates and OPFRs at ambient temperature?

This study proposes two robust measurement methods for estimating y_0 of phthalates and OPFRs emitted from building and consumer materials at room temperature. These methods rely on a micro-chamber type thermal extractor (μ -CTE250) used in two different configurations.

First approach. Since high temperatures increase emissions of SVOCs and decrease sink effect, the steady-state gas-phase concentration of emitted phthalates were determined at different temperatures ranging from 40 to 80 °C and their y_0 were calculated. A linear relationship between $\ln y_0$ and the reciprocal of temperature was obtained assuming that these compounds are emitted from the material by vaporization. Then, y_0 was estimated at room temperature by extrapolation from higher temperatures. This approach was validated by comparing the experimentally determined y_0 of phthalates at 25 °C with the extrapolated value. Obtained results showed that determining y_0 by extrapolation is a promising method since the average % error between both values was less than 10%.

After successfully determining y_0 of phthalates at room temperature, it was interesting to test the efficiency of the extrapolation method for OPFRs. The average % error between the experimental and extrapolated values of y_0 for OPFRs was 18% indicating that this method is robust and can be applicable simultaneously to different families of SVOCs such as phthalates and OPFRs.

Moreover, based on the hypothesis of emission of SVOCs from the material by vaporization, the obtained relation is in accordance with the Clausius-Clapeyron equation and the enthalpy of vaporization of phthalates and OPFRs has been deduced from the slope of the experimental plot. The obtained value was in the same order level than the values reported in the literature confirming the emission mechanism.

Second approach. An innovative approach was proposed in this study for a fast and accurate determination of y_0 of SVOCs at room temperature. We assumed y_0 can be directly measured at steady state in the μ -CTE using spacers to limit the volume at its minimum. This approach was already applied and verified for emission measurements in static mode (with no air flow rate in the chamber). However, its application to dynamic emission testing has been rarely addressed. In this work, the depth of the μ -CTE cell above the material's surface was decreased from 36 to 3 mm by lifting the test materials on collar spacers. In this configuration, the steady-state gas phase concentration of phthalates and OPFRs was shown to be equal to y_0 measured in the conventional configuration of the μ -CTE. The time to reach steady state was decreased from days to few hours at temperatures starting from 40 °C.

iii) Do phthalates and OPFRs adsorb on the walls of the μ -CTE?

Due to their physical and chemical properties, SVOCs do adsorb on several surfaces, but using the heating system of the μ -CTE, the sorbed amount of phthalates and OPFRs on inner surfaces were determined. The stainless-steel/ air partitioning coefficients (K_{SS}) of these compounds were calculated as well. Obtained K_{SS} values for phthalates are in accordance with values reported in literature.

For OPFRs, surface/ air partitioning coefficients were previously determined on glass by Ghislain et al. [1]; however, values of this coefficient for stainless steel surfaces have not been reported. Therefore, the obtained K_{SS} values in this study are the first experimentally determined data. Moreover, a linear relationship between K_{SS} and the vapor pressure of OPFRs was determined. This relationship, similar to that obtained for glass, indicates that adsorption of SVOCs seems to be independent of the nature of the adsorbing surface.

iv) Can we consider y_0 of phthalates and OPFRs constant?

In most studies focusing on phthalates, y_0 is assumed to be constant due to the constant initial concentration of these compounds in materials. As a consequence, internal diffusion of these compounds within the material is considered negligible. However, our measurements showed that y_0 of OPFRs decreased by about 70% within three years [1]. This can be explained due to the aging process of the PUF resulting in increasing the size of pores and thus increasing the diffusion of OPFRs within the material and decreasing C_0 [2]. This observation has been confirmed by a similar trend observed on the same material using another analytical technique. Therefore, neglecting internal diffusion cannot be generalized for all families of SVOCs.

v) Are there any effects of temperature, humidity, and air flow rate on the emission of phthalates and OPFRs from materials?

The effects in temperature, air flow rate, and relative humidity were studied on the emission of phthalates and the effect of temperature was studied on the emission of OPFRs.

The increase of temperature was associated with an increase of phthalates and low volatile OPFRs emissions. However, for the lowest volatile OPFR, triethyl phosphate (TEP), the increase in temperature leads to its rapid depletion from the material.

Similar to temperature, the increase of air flow rate increased the emission of phthalates from the materials. However, the change in relative humidity showed no effect on emissions at 40 °C, but this change was more significant at high temperatures (80 °C).

vi) What else should be done for further characterization of the emissions of SVOCs from materials?

The perspectives of this work are numerous. They can be divided into short- and long-term perspectives.

Short-term perspectives:

- The evaluation of the performance of the developed TD-GC-MS for other families of SVOCs is interesting.
- The effects of air flow rate and relative humidity on the emissions of OPFRs should be characterized since these compounds showed different emission behavior compared to phthalates.

- The method of direct measurement of y_0 was only tested at 55 mL/ min. Thus, the application of this method using higher flow rates should be evaluated. Moreover, it is necessary to determine the air flow rate range where the developed method for direct measurement of y_0 remains applicable.
- The developed extrapolation method was tested to some SVOCs and materials. Evaluating the efficiency of this method on: i) phthalates and OPFRs emitted from indoor materials other than vinyl floorings and polyurethane foams and ii) other families of SVOCs such as parabens and biocides is necessary.
- The main limitations encountered in this study was the determination of the convective mass transfer coefficient (h_m) of phthalates and OPFRs. It is interesting and innovative to develop a method for accurately determining the value of this coefficient at different experimental conditions in order to create a database on this parameter in addition to the diffusion and material/ air partitioning coefficients and vapor pressures of SVOCs emitted from materials.

Long-term perspectives:

- It will be interesting to use the developed micro-chamber method to:
 - estimate the risk of humans' exposure to SVOCs in indoor environments and thus determine the consequential health effects.
 - set up regulations to classify materials based on their SVOCs' content before placing them on the market.

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Annex

Table 1: Different temperature sets for determining y_0 of emitted DnOP from vinyl floorings at room temperature by extrapolation with the obtained correlation coefficients (R^2), % error between the extrapolated and experimental values, duration of experimentation, and enthalpy of evaporation (ΔH_{vap}).

No. of points	5-points	4-points					3-points									
T (°C)	40-80	40-70	50-80	40, 50, 60, 80	40, 50, 70, 80	40, 60, 70, 80	40-60	50-70	60-80	40, 50, 80	40, 50, 70	40, 60, 70	40, 60, 80	40, 70, 80	50, 60, 80	50, 70, 80
R^2	0.99	0.99	0.98	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.99
Extrapolated y_0 ($\mu\text{g}/\text{m}^3$)	0.06	0.045	0.08	0.061	0.055	0.062	0.036	0.047	0.23	0.06	0.046	0.047	0.063	0.055	0.083	0.064
% Error	41.6	7	90.9	46.1	33	48.9	13.4	11.94	445	38.8	9.5	12.9	51.5	32.2	98.1	53.9
Total time of experiment (days)	12.1	12.1	4.2	12.1	12.1	7.2	12.1	5.1	0.2	12.1	12.1	7.1	7.1	7.1	5.1	5.1
ΔH_{vap} (KJ/ mol)	106.3	115.6	100.6	104.8	106.2	105.6	123.4	114.6	81.9	103.4	113.2	114.7	104.3	106.2	99	103.5

Table 2: Different temperature sets for determining y_0 of emitted DiNP from vinyl floorings at room temperature by extrapolation with the obtained correlation coefficients (R^2), % error between the extrapolated and experimental values, duration of experimentation, and enthalpy of evaporation (ΔH_{vap}).

No. of points	5-points	4-points					3-points									
T (°C)	40-80	40-70	50-80	40, 50, 60, 80	40, 50, 70, 80	40, 60, 70, 80	40-60	50-70	60-80	40, 50, 80	40, 50, 70	40, 60, 70	40, 60, 80	40, 70, 80	50, 60, 80	50, 70, 80
R^2	0.96	0.97	0.93	0.97	0.96	0.97	0.93	0.93	0.87	0.97	0.99	0.99	0.99	0.97	0.99	0.96
Extrapolated y_0 ($\mu\text{g}/\text{m}^3$)	0.44	0.28	0.98	0.5	0.46	0.32	0.35	0.51	0.67	0.5	0.27	0.21	0.35	0.33	1.13	1.3
% Error	10	29.9	142.9	24.2	14.2	19.6	11.8	27.6	64.7	25	33.1	47.9	12.8	17.3	180.3	229.1
Total time of experiment (days)	11.1	11.1	4.2	11.1	11.1	6.2	11.1	5.1	0.2	10.1	10.1	6.1	6.1	6.1	4.1	4.1
ΔH_{vap} (KJ/ mol)	110.7	125.5	95.6	104.8	110.8	115.6	117	112.3	102.5	105	130.2	129.9	109.7	115.4	89.2	91.5

Table 3: Different temperature assembles for determining y_0 of emitted TCP from PUF at room temperature by extrapolation with the obtained correlation coefficients (R^2), % error between the extrapolated and experimental values, duration of experimentation, and enthalpy of phase change (ΔH_{vap}).

No. of points	4-points	3-points			
	50-80	50-70	60-80	50, 60, 80	50, 70, 80
T (°C)	50-80	50-70	60-80	50, 60, 80	50, 70, 80
R^2	0.88	0.99	0.89	0.97	0.87
Extrapolated y_0 ($\mu\text{g}/\text{m}^3$)	116.8	355.4	36.2	101.7	129.4
% Error	61.2	18.1	87.9	66.2	57
Total time of experiment (days)	1	1	1	1	1
ΔH_{vap} (KJ/ mol)	66.3	37.3	87.2	72.5	65

Table 4: Different temperature assemblies for determining y_0 of emitted TPP from PUF at room temperature by extrapolation with the obtained correlation coefficients (R^2), % error between the extrapolated and experimental values, duration of experimentation, and enthalpy of phase change (ΔH_{vap}).

No. of points	5-points	4-points					3-points									
	40-80	40-70	50-80	40, 50, 60, 80	40, 50, 70, 80	40, 60, 70, 80	40-60	50-70	60-80	40, 50, 80	40, 50, 70	40, 60, 70	40, 60, 80	40, 70, 80	50, 60, 80	50, 70, 80
T (°C)	40-80	40-70	50-80	40, 50, 60, 80	40, 50, 70, 80	40, 60, 70, 80	40-60	50-70	60-80	40, 50, 80	40, 50, 70	40, 60, 70	40, 60, 80	40, 70, 80	50, 60, 80	50, 70, 80
R^2	0.95	0.96	0.92	0.87	0.88	0.97	0.9	0.99	0.83	0.87	0.91	0.99	0.99	0.97	0.96	0.93
Extrapolated y_0 ($\mu\text{g}/\text{m}^3$)	0.43	0.26	0.26	1.5	1.4	0.7	0.41	0.05	2.1	1.5	0.75	0.4	0.73	0.66	0.32	0.2
% Error	18.7	28.8	25.5	319.5	294.9	85.9	12.7	86.1	490.5	325.8	107.3	11.2	102	82.8	11.5	43.7
Total time of experiment (days)	2	1	1	2	2	2	2	1	1	2	2	2	2	2	1	1
ΔH_{vap} (KJ/ mol)	114.7	131.4	123.9	91.5	96.8	107.7	114.4	167.2	86.6	91.9	120.1	124.7	101.7	107.8	115.5	127.4

