



Recent developments of passive samplers for measuring material emission rates: Toward simple tools to help improving indoor air quality



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ABSTRACT

Passive samplers have recently been proposed as simple and inexpensive tools to measure emissions of Volatile Organic Compounds (VOCs) from building and furnishing materials. These samplers can be used to pinpoint strong emitters of targeted pollutants, including hydrocarbons and oxygenated VOCs, which is of great interest to design efficient strategies aimed at improving indoor air quality. A passive sampler consists of a small cell that is exposed on a flat surface to trap material emissions. Three Passive Flux Samplers (PFS) have been developed at Mines Douai, an engineering school from Northern France, to carry out source apportionment studies of formaldehyde, acetaldehyde, and aromatic hydrocarbons, including benzene, toluene, xylenes, and higher molecular weight compounds. Over a 6-h exposure duration, these PFS exhibit linear responses and detection limits of a few $\mu\text{g m}^{-2} \text{h}^{-1}$ that are low enough for monitoring material emissions and to perform extensive source apportionment studies. A few other samplers, designed using different geometries, have also been proposed in the literature. This publication summarizes findings on the development and the use of passive samplers with the objective to highlight the potential of these new tools for indoor air quality studies.

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1. Introduction

While monitoring pollutant concentrations has become a common task to evaluate Indoor Air Quality (IAQ), detailed investigations of pollution sources are still difficult to carry out. This issue is mainly due to a lack of analytical tools to identify main emitters of gaseous pollutants such as Volatile Organic Compounds (VOCs) in indoor environments.

High levels of VOCs observed indoors are a consequence of multiple emission sources confined in a small volume. On one side, VOCs are emitted by discontinuous sources due to human activities, such as heating [1,2], cooking [3,4], the use of household products [5,6], and smoking [7–9]. On the other side, VOCs are continuously emitted by building and furnishing materials such as wood panels,

flooring, and wall coating products. These two types of sources emit a large range of VOCs, including alkanes, alkenes, aromatics, and carbonyls. Formaldehyde, benzene, and other VOCs are ubiquitous in indoor environments and are considered as worrisome pollutants, with the two former classified as carcinogenic pollutants by the International Agency for Research on Cancer [10]. In order to develop strategies of emissions control, it is important to understand the contribution of each type of emission sources to the budget of indoor pollutants, especially emissions from building and furnishing materials.

Several normalized methods are currently used to measure VOC emissions from building materials, including emission test chambers (ISO 16000-9), micro-chambers (ISO 16000-25), and the Field and Laboratory Emission Cell (FLEC, ISO 16000-10). However, the two former can only be used in the laboratory and require a sample of the material. These chambers are coupled to active sampling techniques using cartridges filled with an adsorbent (Tenax[®], Carbograph[™], Carbopack[™], ...) or beads coated with a chemical reagent (DNPH: 2,4-dinitrophenylhydrazine). These cartridges are

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then analyzed by gas or liquid chromatography techniques. Emission test chambers are operated under normalized conditions frequently observed in indoor environments to derive emission rates that are on the same order of magnitude than real indoor emissions. These chambers are also used to investigate the consequence of varying some operating conditions (temperature, relative humidity, air exchange rate, ...) on pollutant emission rates [11]. It is interesting to note that the use of normalized conditions in emission chambers allows a direct comparison between all tested materials to rank them depending on their emission rates [12].

A FLEC takes advantage of a portable cell to perform in-situ measurements of emission rates [13], but also requires cumbersome equipment such as cylinders of zero air, pumps, and mass flow controllers since this device is coupled to active sampling techniques similar to that used for emission test chambers. A FLEC can only be used to measure emission rates of pollutants on one material at a time while indoor environments usually contain several dozen of different materials. This device is therefore not suitable to carry out rapid and exhaustive investigations of emission sources.

There is a need for inexpensive and easy-to-use devices that could be used in-situ to identify emitting materials and to quantify their emissions. In this context, passive sampling has been proposed as a promising method for in-situ measurements of material emissions [14]. This approach is based on exposing a sampler on a solid material to trap emitted pollutants by adsorption onto—or reaction with — a substrate. A chemical or optical analysis of the substrate allows a quantification of an emission rate for targeted pollutants by measuring a collected mass or a variation of an optical property of the substrate. Passive samplers meet the requirements of inexpensive and easy-to-use tools, and multiple samplers can be deployed together to conduct exhaustive investigations of emission sources in indoor environments.

Maré et al. [14] recently reviewed passive sampling methods proposed in the literature. Most of these devices have been developed to monitor emissions of carbonyl compounds, especially

formaldehyde and acetaldehyde. These tools are reported in Table 1 together with three samplers described in this publication. For example, the ECSMS (Emission Cell for Simultaneous Multi-Sampling) [15] and the ADSEC (Advanced Diffusive Sampling Emission Cell) [16] consist of a stainless steel cell containing a cartridge made of coated silica (DNPH) allowing to sample formaldehyde emissions. The cartridge is set parallel or orthogonal to the material surface for the ECSMS and ADSEC samplers, respectively. The ADESC system was also extended to the measurement of hydrocarbon emissions using a cartridge made of Carboxen-B and Carboxen-564.

The term 'Passive Flux Samplers (PFS)' has been used to describe a particular type of passive samplers made of a cylindrical cell with a trapping substrate placed at the bottom end of the cell, parallel to the material surface. Two PFS have been developed by Shinohara et al. [21,23] for monitoring formaldehyde emissions. These PFS consist of a petri dish containing a quartz filter coated with DNPH [21] and a PET (polyethylene terephthalate) enclosure containing an enzyme test sheet [23], which turns red in the presence of formaldehyde. The latter was called PECS (Passive Emission Colorimetric Sensor). This type of PFS was also used for measuring emissions of hydrocarbons [22] and semivolatile organic compounds (SVOCs) such as phthalates [25] and flame retardants [26]. Detection limits for VOCs are lower than $10 \mu\text{g m}^{-2} \text{h}^{-1}$ but were not reported for SVOCs.

The ECSMS has been used in a school and a house [24], the ADSEC in one apartment [16], and the PFS in a studio [22]. To the best of our knowledge, the PECS has not been deployed in indoor environments. In these studies, only a few materials (up to 9) were sampled while dozens of materials are usually present in indoor environments. There is therefore a lack of studies to test the robustness of this sampling method, to compare different designs of samplers, and to assess the potential of these tools for source apportionment of VOCs in indoor environments.

Three PFS have been developed and characterized in this study with the objective of proposing new tools capable of measuring

Table 1
Passive samplers reported in the literature and in this study. Detection Limits (DL) and precisions ($\mu\text{g m}^{-2} \text{h}^{-1}$).

Sampler	Targeted species	Trapping substrate	Linearity studied?	DL (3σ) 6-h exposure (unless stated otherwise)	Precision (1σ)	Reference
PFS#1	Formaldehyde	DNPH	Yes	1.2	8% at $100 \mu\text{g m}^{-2} \text{h}^{-1}$	[17–19] This work
PFS#2	Acetaldehyde Formaldehyde	Fluoral-P	Yes	4.6 1.4	NA 3% at $100 \mu\text{g m}^{-2} \text{h}^{-1}$	This work [20] This work
PFS formaldehyde	Formaldehyde	DNPH	No	3.7 (2-h exposure) 0.9 (8-h exposure)	8.3% (emission rate not indicated)	[21,22]
PECS	Formaldehyde	Enzyme	Yes	3.1 (0.5-h exposure)	<10% (emission rate not indicated)	[23]
ECSMS	Formaldehyde	DNPH	No	NA	NA	[15,24]
PFS#3	Benzene Tolene Styrene EthylBenzene o-xylene m,p-xylene TMB	Carbograph 4 TM	Yes	7.9 2.1 1.6 2.0 0.6 1.6 3.0	NA NA NA NA NA NA NA	This work
PFS hydrocarbons	Tolene EthylBenzene o-xylene m,p-xylene 1,2,4-TMB	Carbotrap B TM	No	NA	6% (emission rate not indicated)	[22]
ADSEC	Formaldehyde Toluene Ethylbenzene m,p-xylene o-xylene Styrene	DNPH Tenax TA [®]	No	NA		[16]

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