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Solid phase microextraction sampling for a rapid and simple on-site evaluation of volatile organic compounds emitted from building materials

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ABSTRACT

A new sampling method was developed for a simple and fast evaluation of volatile organic compounds (VOCs) emitted at trace levels from building materials. The device involves an emission cell coupled with solid phase microextraction (SPME) for diffusive sampling. Owing to possible competitive adsorption of VOCs onto the PDMS–Carboxen fiber used, the co-adsorption conditions were determined through kinetics study of isolated and in mixture compounds. Hence, the linear concentration ranges which ensure reliable quantification were determined from 4.8 to 10 mg m^{-3} min according to the VOC studied. Thus, the analyst can select the extraction time that fits for his best analytical objectives. For example, sub μg m^{-3} limits of detection can be achieved for GC–MS analysis for 20 min extraction. On the other hand, 5 min sampling is sufficient for a rapid screening of the major emitted VOCs, since the average limit of quantification reaches 20 μg m^{-3} for GC-FID analysis.

1. Introduction

VOCs group together different chemical families (alcohols, aldehydes, alkanes, ketones, terpenes, etc.) which are considered as indoor air evaluation parameters. These compounds could put people health at risk, because of a sporadic or prolonged exposure. Nowadays, priority to reduce VOCs levels in indoor air consists in controlling sources, especially building materials [1,2]. New products in few European countries, such as floor covering, are currently evaluated through a time-consuming procedure involving a 28 days emission test in an environmental chamber or in a test cell emission [3,4]. Usually, the test cell emission is used in dynamic mode, to transfer the VOCs emitted from building products or furnishing samples to adsorbent tubes [5]. Thus, the extraction phase of this procedure needs clean air supply, air flow meters, adsorbent cartridge and a long sampling time (60 min) to concentrate the low quantity of VOCs emitted by floor coverings. Then, a specific equipment on-line with the gas chromatograph is needed to achieve the thermal desorption of the adsorbent tubes. Hence, this procedure seems not really adapted for a rapid and cheap control required for regular audits to the manufacturer.

With this aim, a new simple and fast on-site sampling method was studied. As VOCs could be emitted at trace levels (μg m^{-3}), SPME was considered for pre-concentration, thanks to its easiness of use and its little equipment requirement [6–8]. The sampling device developed here, consists in coupling a standard emission cell with SPME. Extractions were made in static mode to avoid the use of a pumping system, which is unwieldy to be used on site. Hence, sampling is only due to the diffusion of the molecules from the gas phase to the SPME fiber. In previous work, it has been shown that adsorptive Polydimethylsiloxane–Carboxen (PDMS–Carboxen) fiber was the most effective for VOCs extraction [9–11]. However, competitive adsorptions, leading to inaccurate quantification, were observed, as the volume of the fiber coating is small [10,12]. To overcome this drawback, the operating conditions allowing VOCs co-adsorption should be determined. Therefore, different sampling methods, consisting in "equilibrium" [11–13] or "non-equilibrium" static extraction were developed in our laboratory [12–15]. In the first case, the extraction time is fixed by equilibrium conditions, so co-adsorption is achieved by lowering the sample volume. For indoor air analysis, the best compromise between extraction time and sensitivity was obtained for 250 mL sample volume and 3 h extraction [14]. Under these conditions, concentrations up to 9 μmol m^{-3} can be accurately determined and the average limit of detection is 0.2 μg m^{-3} for GC–MS analysis. Despite the good performance of this method, it would not be convenient for our purpose. Indeed, the total air volume enclosed in the emission

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chamber is 80 mL, so the time required to reach adsorption equilibrium would be over 1 h [6]. Hence, to reduce the sampling time, the "non-equilibrium" extraction approach was considered. Limits of detection in the $\mu g\, m^{-3}$ order can be obtained for only few minutes extraction [12], allowing rapid screening of VOCs with sufficient sensitivity. For this method, the co-adsorption domain for which a reliable quantification would be possible is determined by using the first-order Ficks' diffusion law [11]. The following equation can be written (Eq. (1)):

$$n = \frac{2\pi \times D_g \times L}{\ln(b + \delta/b)} \times \int (C_a - C_{sorb}) dt \qquad (1)$$

where n is the amount of adsorbed analyte, D_g the diffusion coefficient of the chemical of interest, C_a the ambient concentration of the gas, C_{sorb} the concentration of the gas at the adsorbent surface and t the sampling time.

Because the SPME fiber is cylindrical, Eq. (1) takes into account mass transfer by diffusion of compound to a cylinder [16]. L is the length of the fiber, b the radius of the fiber and δ the thickness of the diffusion zone.

At the beginning of the sampling process, C_{sorb} is small and it is assumed that the adsorbent acts as a perfect sink ($C_{sorb} = 0$). There are enough active sites available for the adsorption of the target compounds to overcome competition with other chemicals [6,11,15]. Uptake is linear and can be written as Eq. (2):

$$n = \frac{2\pi \times D_g \times L}{\ln(b + \delta/b)} \times C_a t \qquad (2)$$

Considering,

$$K = \frac{2\pi \times D_g \times L}{\ln(b + \delta/b)}$$

Eq. (2) can be simplified to Eq. (3):

$$n = K C_a t \qquad (3)$$

Considering proportionality between the FID response (peak area (A)) and the analyte quantity (n) introduced in the chromatograph (the thermal desorption of the fiber is quantitative), it is possible to plot (A) as a function of ($C_a t$). The linear part of that curve will therefore enable the determination of the co-adsorption conditions. An advantage of this analytical procedure is that the analyst can select the extraction time according to the concentration range to be studied. Therefore, the objective of the work was to develop and to evaluate this method with regard to its suitability for quantification of VOCs emitted from building materials. In this study, we focused on three different floor coverings: carpet, PVC and wooden floors. The methodology was developed using standard gas generated in laboratory. Hence, 9 model VOCs were selected from a list of 30 compounds established by the CSTB (French Scientific and Technical Center for Buildings) and the AFSSET (French Agency for Sanitary Security) for the evaluation of the sanitary risk due to VOCs emitted by building materials [2,3]. These compounds were selected for their representativeness of building products emission, their toxicity and to study most of VOCs families. To evaluate the effect of competitive adsorption, two compounds, acetic acid and methyl vinyl ketone, which have low affinity with the Carboxen coating, were studied alone and in mixture with the other model VOCs. The same procedure was applied to n-decane, to highlight the different adsorption behavior between compounds having high or low affinity with the adsorbent. Once the ranges of co-adsorption determined from the uptake curves $A = f(C_a t)$, the performances of the method in terms of sensitivity and reproducibility were determined for GC–MS and GC-FID analysis for different sampling times. Finally, the methodology developed was applied to analyze synthetic atmospheres representative of the floor covering studied in order to check the reliability of the method with mixtures including high and low concentrations of VOCs.

2. Experimental

2.1. Reagents and materials

The studied VOCs were methyl vinyl ketone, supplied by Sigma–Aldrich (Steinheim, Germany), benzaldehyde, hexanal purchased from Fluka (Brucks, Switzerland), methyl methacrylate, styrene, n-decane, α-pinene, 2-ethyl-1-hexanol and acetic acid supplied by Acros Organics (New Jersey, USA). All these reagents were at least 99% purity, except hexanal (97%) and α-pinene (98%). Equimassic or equimolar liquid mixtures of pure substances were prepared with studied compounds to generate the different standard gas.

2.2. Standard gas generating device

The detailed principle of gas generation is described in previous papers [8,12,17,18]. The device used here was designed and supplied by Calibrage (Saint Chamas, France). Briefly, single or in mixture compound atmospheres were generated by continuously injecting known amounts of solvents (single, in equimassic or equimolar mixtures) with a syringe pump (Harvard Apparatus, Les Ulis, France), into a measured and controlled airflow. Successive dry air (relative humidity less than 4% and temperature of 23 °C) dilutions of concentrated gas were then applied to reach the desired concentrations. The system is able to generate from $1\, ng\, m^{-3}$ to $1\, g\, m^{-3}$. The reproducibility of the gas generation was evaluated for five measurements of an equimassic mixture of the model compounds at $40\, mg\, m^{-3}$ individual concentrations. The relative standard deviation (RSD) ranges from 4% for styrene to 24% for acetic acid.

2.3. Emission cell

Measurements were performed using the Field and Laboratory Cell: FL-0001 (FLEC®) (Fondis Electronic, Guyancourt, France). The FLEC is a chamber made of acid proof stainless steel, its internal surface is small and especially hand polished to minimize sink effects. For our application, this emission cell was especially equipped with a Viton® fluoroelastomer O-ring covered with Teflon® (Dimatrap, Pau, France) to avoid VOCs adsorption on the O-ring. Then, a septum in polytetrafluoroethylene–silicone was screwed on the FLEC for SPME fiber introduction. Finally, stainless steel tubes and quarter-turn valves were added to sweep clean air or standard gas through the device (Fig. 1). The total sampling chamber volume from the first quarter-turn valves to the second one was evaluated at 80 mL.

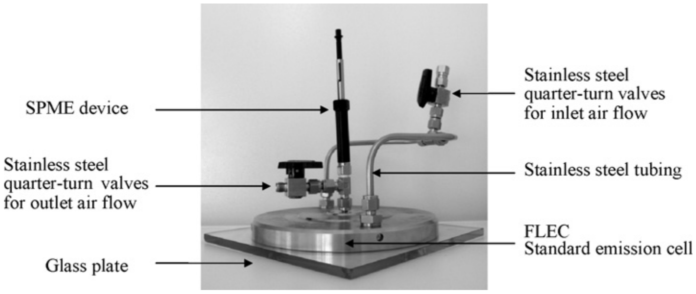

Fig. 1. FLEC–SPME coupling system.