Journal of Chromatography A, 1216 (2009) 3031–3037

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

# Flexibility of solid-phase microextraction for passive sampling of atmospheric pesticides

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ARTICLE INFO

*Article history:*
Received 26 November 2008
Received in revised form 2 February 2009
Accepted 2 February 2009
Available online 10 February 2009

*Keywords:*
Atmospheric pesticides
Solid-phase microextraction
Sampling rates
SPME configurations

ABSTRACT

For low volatile pesticides, the applications of solid-phase microextraction (SPME) as an air sampler were reported with sampling time chosen in the linear stage of the sorption kinetics because of long equilibrium time. In these pre-equilibrium conditions, sampling rates (*SRs*) expressed as the volume of air sampled by the SPME sampler per unit of time, were used to estimate analytes concentrations in air. In the present study, to achieve good extraction performance and accurate calibration, the sorption kinetics of several pesticides with SPME were investigated in detail, with a focus on parameters influencing *SRs*. Linear air velocity was found to be the main parameter affecting *SRs*. For exposed fibers, with air velocities below 20–25 cm $s^{-1}$, *SRs* increased with increasing air velocity. When linear air velocity was equal to or greater than 25–30 cm $s^{-1}$, it had little effect on *SRs*. To improve the flexibility of SPME, different configurations of SPME were compared, i.e. different lengths of fibers exposed, retracted fibers, exposed fibers with grids. *SRs* were linearly proportional to exposed lengths of fibers. Using grids, lower *SRs* and wider calibration time range were achieved. *SRs* for retracted fibers were the lowest among the different experimented configurations. The accuracy of calibration was improved and more flexibility of SPME was provided.
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## 1. Introduction

Solid-phase microextraction (SPME) presents many advantages over traditional analytical methods by combining sampling, preconcentration, and the transfer of the analytes to gas or liquid chromatograph. To date, SPME has been widely used in numerous fields such as environmental, food, flavor, fragrance, pheromone, pharmaceutical, clinical, and forensic [1]. More recently, SPME has been developed as a new passive air sampler. Because of minimal sample preparation and simplicity of operation, the applications have spread from volatile organic compounds, formaldehyde, and volatile organic sulfur compounds [2–4], etc. to less volatile compounds like phosphate esters [5], hydrocarbons [6], and pesticides [7,8]. SPME sampling can last from a few minutes (even seconds) to obtain "instantaneous" concentrations, to several hours or days, providing time-weighted average (TWA) concentrations of gaseous analytes.

The SPME uptake kinetics follows the typical curve for passive samplers, which has three parts: linear uptake stage and curvilinear stage, which are described as non-equilibrium conditions, and equilibrium stage [9]. To carry out a quantitative analysis, there must be a proportional relationship between the amount of analytes sorbed by the SPME fiber coating and the concentration of the analyte in the sample matrix [10]. At equilibrium and for absorptive coatings like polydimethylsiloxane (PDMS), the concentration of analytes in the fiber is proportional to the concentration in the air, through the partition or distribution coefficient [11,12]. These coefficients depend on the particular analyte, fiber type, and temperature [13]. Some of them have been published, and it is also possible to calculate them from readily available physical parameters using regression equations. Calibration at equilibrium has been widely used for SPME [14–16].

For many less volatile compounds, with equilibrium time ranging from several hours to several days, calibration is usually performed in non-equilibrium conditions, specifically in the linear uptake stage. The extracted amount of the analyte in the fiber is proportional to the bulk air concentration $C$ and the sampling time $t$ [17].

Sampling rates, *SRs*, expressed as the volume of air sampled by the SPME sampler per unit of time, are used with the amount of target analytes accumulated ($n_{SPME}$) in SPME fiber coating to estimate air concentrations:

$$C = \frac{n_{SPME}}{SR \times t} \quad (1)$$

For SPME, several models have been developed to describe the mass transfer processes. The most traditional one is based on Fick's

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doi:10.1016/j.chroma.2009.02.011

law of diffusion [18,19]. In Fick's diffusive model, assuming that mass transfer is limited by diffusion in the air boundary layer, the following equation could be obtained:

$$SR = \frac{D_g A}{Z} \quad (2)$$

where $D_g$ is the gas-phase molecular diffusion coefficient, $A$ is the diffusion surface and $Z$ is the thickness of the diffusion layer.

This law can describe analyte uptake with SPME fibers, whatever the sampling configuration is (exposed or retracted, "in needle" fiber) [20]. In retracted SPME, the thickness $Z$ of the diffusion layer is the diffusion path length, also referred as the gap between the needle opening and the fiber in the needle. It has been shown elsewhere that *SRs*, in this configuration, were air velocity-independent [19,21].

In exposed SPME, the effective thickness of the boundary layer can be estimated with different equations [10,22]. In our previous work [23], Eq. (2) was developed and the following relationship was given to clearly describe which environmental parameters could influence the *SRs* in the exposed mode:

$$SR = \frac{K \times T^{1.085} \times A \times (2u)^{0.62}}{9.52 \times b^{0.38} \times \nu^{0.24}} \quad (3)$$

where $K = \{0.001\sqrt{1/M_{air} + 1/M_O}/p[{V_{air}}^{1/3} + {V_O}^{1/3}]^2\}^{0.62}$, $M_{air}$ and $M_O$ are molecular weights for air and organic gases of interest, $p$ is the absolute pressure (atm, 1 atm = 101,325 Pa), $V_{air}$ and $V_O$ are the atomic diffusion volumes of air and the organic gases of interest ($cm^3\ mol^{-1}$) [24]. $T$ is the absolute temperature, $b$ is the coated fiber radius, $u$ is the linear air velocity ($cm\ s^{-1}$), and $\nu$ is the kinematic viscosity for air ($cm^2\ s^{-1}$). Clearly, temperature and air velocity around the fiber were the influencing parameters.

To date, most of the work published on passive air sampling for pesticides and other persistent organic pollutants (POPs) implied the determination of "field" *SRs* [8,25]. Rearranging and adapting Eq. (1):

$$SR = \frac{n}{C_{known} \times t} \quad (4)$$

where $C_{known}$ was determined using high/low volume air sampling techniques. Precise calibration and estimation of *SR* for passive samplers is essential for quantifying the various contaminants in air [26]. This requires knowledge of the uptake kinetics of target compounds. Impact of environmental conditions on the samplers' performance should be examined. The interpretation of results obtained with the use of passive samplers requires conducting studies in strictly defined (modelled) conditions.

In this paper, retracted and exposed SPME sampling modes (defined as "extreme" modes) were assessed for atmospheric pesticides. The other objective was to implement some intermediate uses of SPME. In order to succeed, a standard gas-generating device was developed. Concentrations could vary, as well as air velocity, and temperature could be kept constant. Sorption kinetics were studied, under different sampling configurations, i.e. fully exposed fiber, partially exposed fiber, exposed fiber with grids, and retracted fiber. *SRs* could be determined and the effects of air velocity were better understood. Also repeatability and reproducibility were evaluated. Finally the applicability of SPME for sampling atmospheric pesticides was better defined.

## 2. Experimental

### 2.1. Chemicals and materials

Seven pesticides were selected as the target compounds. Chlorothalonil, kresoxym methyl, vinclozolin, pyrimethanil and cyprodinil (all Pestanal grade) were purchased from Sigma–Aldrich (Seelze, Germany). Trifluralin and dichlorvos (both Pestanal grade) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Pesticides standards were dissolved in hexane or a mixture of hexane/acetone. Standard solutions were prepared with hexane to appropriate levels in a 2-mL auto sampler vial for the GC/MS and GC/MS/MS. Diethyl ether was also used with hexane for Soxhlet extractions. All the solvents were Pestanal/analytical grade and have been purchased from Sigma–Aldrich. Internal calibration was used and according to the recommendation of EPA TO-10 method, and [$^2H_8$]naphthalene (naphthalene-$d_8$) (ISOTEC, Miamisburg, OH, USA) was chosen as the internal standard considering the property of the compound. PTFE tube for containing the pesticides was from Lyon Vannes et Raccords (Bron, France). Two kinds of protective grid for the SPME fiber, made from stainless steel wire with ca. 1-mm or 0.5-mm-meshes (quadrate shape) were designed by the mechanical workshop of University of Bordeaux I, France. The protective grids were set into a cylinder with a diameter of 0.8 cm and 4 cm in length.

### 2.2. GC/MS method

GC/MS/MS and GC/MS were performed on a Varian CP3800 GC-Saturn 2200 ion trap mass spectrometer (Varian, Walnut Creek, CA, USA) equipped with a waveboard and MS/MS software. The GC was equipped with a VF-5MS (30 m × 0.25 mm, 0.25 μm film thickness) column (Varian). The GC oven temperature was programmed from 50 °C (hold for 1 min) to 190 °C at a ramp of 10 °C $min^{-1}$ and then increased to 225 °C at 3 °C $min^{-1}$ followed by a ramp of 10 °C $min^{-1}$ to 280 °C and held for 10 min. The injector was set at 250 °C and the helium (high purity) was used as carrier gas at a constant flow rate of 0.8 mL $min^{-1}$. SPME fibers were desorbed in the injector equipped with a 0.8 mm inner diameters (I.D.) liner for 4 min in splitless mode. The injection volume was 1 μL for liquid injections in splitless mode for 2 min with a 2 mm I.D. liner. The CTC CombiPAL auto sampler (Zwingen, Switzerland) was used for the injection of liquid samples. The instrument was checked daily for calibration using a liquid calibration standard. In addition, quality of peak shapes, resolution, and retention times were carefully monitored to ensure all chromatography was within specification.

The mass spectrometer was operated in the electron impact ionization mode (70 eV). Both MS and MS/MS were run with filament emission current at 10 μA and manifold temperature at 40 °C. The automatic gain control (AGC) prescan ionization time for MS/MS was 1500 μs and the AGC target was set depending on the parent ion mass. For MS, the AGC prescan ionization time was 100 μs and the AGC target counts was 20,000. The MS/MS conditions (isolation windows, excitation amplitude, excitation mode, etc.) for each pesticide optimized in preliminary work [23] were used here.

### 2.3. Standard gas-generating device

A laboratory device was used to generate gaseous pesticides. A first module (Model PUL200S, Calibrage, Saint Chamas, France) was equipped with two thermostated ovens which contained permeation and/or diffusion tubes filled with neat pesticides. Dry air was used as transfer gas. The flow rate of standard gas mixture from the first module was 112.2 ± 0.9 mL $min^{-1}$. Then, diluting air at different flow rate was added in a second module (Model DGM100, Calibrage, Saint Chamas, France). glass-sampling bulbs with different I.D. (workshop of the Institute for Molecular Sciences (ISM), University of Bordeaux, France) were connected at the exit of the device for SPME sampling and active sampling with polyurethane foam (PUF) cartridges. The temperature in the room during experiments was within 18–23 °C. In this system, the concentration and air velocities could be controlled and modified through changing the dilution gas flow rate and the glass-sampling bulb. In our experiments, the

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