

A simple and rapid analysis for gas-phase polycyclic aromatic hydrocarbons using an organic-solvent-based method



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HIGHLIGHTS

- A simple and fast sampling method for gas phase compounds was developed.
- The performance is comparable to that of XAD-2 resin-based method.
- This is suitable for sampling of volatile and semivolatile organic pollutants.
- Field test showed good sampling efficiency and reproducibility for PAHs.

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ABSTRACT

Monitoring of atmospheric organic pollutants is usually conducted by means of active or passive air samplers. In this study, we developed a simple, conventional, economic and fast sampling method for volatile and semivolatile compounds that is based on a liquid-phase organic solvent. Laboratory tests showed the feasibility of the method, and the major parameters of the method, such as temperature, organic solvent, carrier gas and air flow rate, were preliminarily optimized. For 16 kinds of polycyclic aromatic hydrocarbons (PAHs), the recovery, relative standard deviation and detection limit were ranged from 87.0 to 104.4%, 2.6 to 15.6% and 0.08 to 0.45 ng mL⁻¹, respectively. Field application of the new method also showed good sampling efficiency for PAHs in real air samples, comparable to the results with an XAD-2 resin-based method. The similarity was closed to 1, suggesting that the new method is suitable for sampling of volatile and semivolatile organic pollutants in air and has great potential for air-pollution monitoring.

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1. Introduction

During the past several decades, increased public awareness of environment pollutants and the health risks they pose has stimulated global interest in environmental research and monitoring, resulting in a requirement for determination of toxic contaminants in different environmental matrices (Pawliszyn, 2003), such as air (Esteve-Turrillas et al., 2009; Li et al., 2006; Purg Infante et al., 1993), water (Marty et al., 1997; Rezaee et al., 2006), soils (Klánová et al., 2008; McLachlan et al., 1996), and biota (Bordajandi et al., 2003; Zohair et al., 2006). Active air samplers have been widely used for monitoring of volatile and semivolatile organic pollutants in air. The particle phase is trapped on a quartz or glass-

fiber filter and the gas phase is collected by a solid absorbent such as polyurethane foam (PUF) (Meijer et al., 2008), Tenax (U.S. EPA, 1988) or amberlite XAD resin (Andersson et al., 1981; Ligon, 1978; Wei et al., 2007). However, deployment of active samplers is not always convenient or feasible because of power requirements and facility constraints. Moreover, long-term large-area monitoring using an active sampler is labor/time-consuming, and the required equipment and consumables are costly.

Therefore, recently, passive air samplers (PASs) have been developed and used for monitoring of atmospheric organic pollutants (Chen and Pawliszyn, 2003; Kucklick and Helm, 2006; Larroque et al., 2006; Tao et al., 2009; Xiao et al., 2006). The use of various types of PAS in the monitoring of semivolatile organic compounds (SVOCs) has dramatically increased since the late 1990s (Choi et al., 2007). PASs seek to overcome some of the limitations of active air samplers which require continuous field maintenance and electricity (Bartkow et al., 2004). A PAS is based on the free flow

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of analyte molecules from the sample matrix to the receiving solid phase absorbent by diffusion and/or penetration, and it is relatively inexpensive and easy to use for deployment, retrieval and analysis (Bartkow et al., 2005; Ouyang and Pawliszyn, 2007). So far, the most widely used PASs are semi-permeable membrane devices (SPMDs) (Lohmann et al., 2001; Ockenden et al., 1998), polyurethane foam disks (Gouin et al., 2005; Jaward et al., 2005), resin-based PASs (Wania et al., 2003), solid-phase microextraction (SPME) devices (Chen and Pawliszyn, 2003), etc. Although PASs are suitable for long-term collection of gas phase volatile and semi-volatile chemicals and have some advantages over active air samplers, most of their sampling materials are based on solid-phase absorbents except SPMDs. The solid-phase absorbents require pre-cleaning and extraction before and after air sampling using relatively large amounts of organic solvent. These processes are time-consuming and tedious, and they also increase the risk of secondary environmental pollution.

In this study, we developed an air sampling method for gas-phase atmospheric organic micropollutants using a liquid phase and optimized various operational conditions to maximize extraction efficiency, such as temperature, organic solvent, flow rate etc. We also evaluated its sampling efficiency through laboratory testing and field application.

2. Experimental section

2.1. Materials and chemicals

Eighteen polycyclic aromatic hydrocarbons (PAHs), syringe recovery standard ($^2\text{H}_{10}$ -labeled phenanthrene), and surrogate standard ($^2\text{H}_{10}$ -labeled acenaphthene and perylene) were obtained from Chem Service (USA). The purity of standards was higher than 99%. All organic solvents including acetone, dichloromethane (DCM), trichloromethane (TCM), hexane and methanol were pesticide grade and were purchased from Caledon (Canada). Stock standard solutions of PAHs (20 mg L^{-1}) were prepared in methanol and hexane, respectively. Amberlite XAD-2 resin (surface area: $300 \text{ m}^2 \text{ g}^{-1}$, porosity: 1–56 Å, diameter: $680 \mu\text{m}$) was bought from Shanghai Quandao Technical Company (China). Before each test, the XAD-2 resin was extracted 8 h in DCM by Soxhlet. Mixed

cellulose ester ($0.8 \mu\text{m} \times 47 \text{ mm}$) was bought from Advantec MFS Inc., USA. The purity of nitrogen (N_2) was higher than 99.999% and was bought from Changchun Oxygen (Jilin province, China).

2.2. Laboratory tests

For the laboratory model experiment, six kinds of PAHs (2.0 mg L^{-1}) were prepared in hexane as standard working solutions, and artificial air was continually manufactured by mixing nitrogen gas and gas-phase PAHs. The gas-phase PAHs were prepared by heating the standard working solutions to form the gas phase. A detailed drawing of the liquid–phase organic-solvent-based method for the laboratory experiment is shown in Fig. 1(A). The apparatus consisted of three parts: the gas-sample introduction part (part I), the gas absorber part (part II) and the gas condensing part (part III). Each part was connected using copper tubing, and the gas flow was controlled by a gas flow meter and control valves. In the gas sample introduction part, nitrogen gas was used as the auxiliary gas and the standard working solutions of target compounds were added to the gas generator, which is consisted of a ceramic heater, a digital thermometer monitor, 1/16-inch stainless steel tubes and a glass T tube. One line of the T tube was used to introduce nitrogen gas into the gas generator, another to draw off the standard working gas and the third was used as the standard sample solution inlet. The ceramic heater generates heat when an electric current is applied and can raise its temperature to $350 \text{ }^\circ\text{C}$ within tens of seconds. A digital temperature sensor (DS18B20) was used to measure the gas generator temperature. As shown in Fig. 1, the gas absorber part was simply fabricated by slight modification of a Soxhlet extractor. The distillation tube of the Soxhlet extractor was removed, the downside hole was blocked and the upside tube was fitted with a control valve for use as the organic solvent inlet. The siphon tube was connected with part I for introduction of the gas-phase chemicals generated by the ceramic heater into the extraction solvent. The condensing part consisted simply of a condenser and ice-water.

At the start of each experiment, 2.0 mL PAH standard working solution (2.0 mg L^{-1} , 6 PAHs) and 30 mL organic solvent were added to the gas generator and gas absorber, respectively, and surrogate internal standards were added to the gas generator. In order to

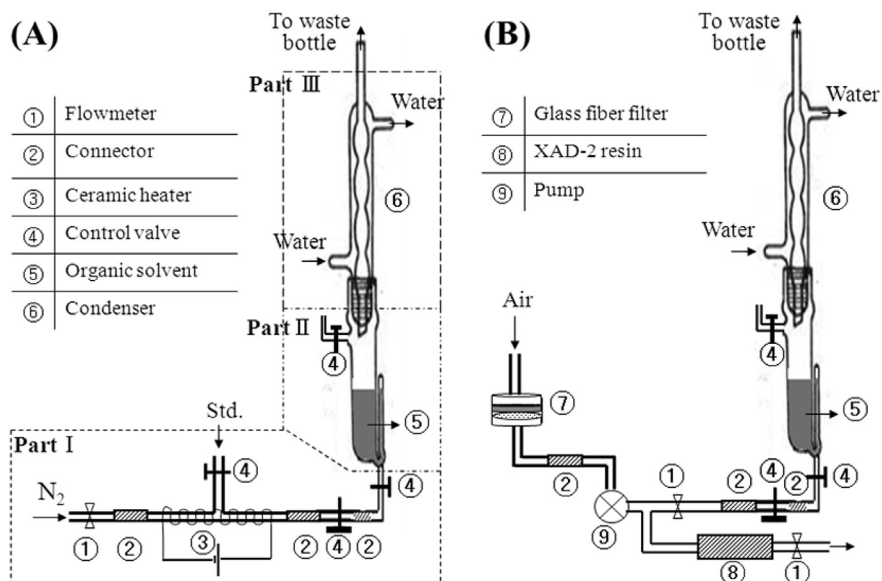


Fig. 1. Schematic of the liquid-phase organic-solvent-based air sampling method for laboratory tests (A) and field tests (B).

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