



New method to determination of naphthalene in ambient air using cold fiber-solid phase microextraction and gas chromatography–mass spectrometry

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ABSTRACT

Naphthalene, a highly volatile polycyclic aromatic hydrocarbon (PAH), is classified as possibly carcinogenic to humans and can be found in various environments. This paper describes a cold fiber (CF) solid phase microextraction (SPME) sampling method coupled with gas chromatography/mass spectrometry (GC/MS) for determining naphthalene in ambient air. The method uses a 100 μm polydimethylsiloxane (PDMS) fiber to generate gaseous standards using a permeation tube. The method shows good results for many validation parameters. The intra-assay precision shows a relative standard deviation (RSD) ranging from 1.04 to 8.11%; the limit of detection (LOD) is $0.33 \pm 0.01 \mu\text{g}/\text{m}^3$, and the quantification limit (LOQ) is $0.55 \pm 0.01 \mu\text{g}/\text{m}^3$. The method was applied to the determination of naphthalene from real samples collected from indoor and outdoor air. The results have shown the ability of the method to measure trace levels of naphthalene in the air in different environments.

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1. Introduction

Naphthalene, the simplest polycyclic aromatic hydrocarbon (PAH), is one of the more volatile of the class of pollutants classified as semivolatile organic compounds (SVOC) by the U.S. Environmental Protection Agency [1]. The International Agency for Research on Cancer (IARC) has classified naphthalene as possibly carcinogenic to humans [2]. This probable human carcinogenicity is based on an increased risk of rare nasal tumors in male rats [3]. The World Health Organization (WHO) is considering the development of an indoor air guideline for naphthalene [4]. Naphthalene can be found in various environments. Because of its volatility, the atmosphere is the main repository [5]. In the air, naphthalene is distributed between the gaseous and particulate phases, depending on the temperature, precipitation and environmental factors [6]. The half-life of naphthalene in the atmosphere is 8 h because of photodegradation by hydroxyl radicals [7]. The largest exposures to this compound occur near sources emitting naphthalene [8]. Chemical industries, burning of biomass, insect repellents, gasoline and oil burning are the main anthropogenic sources of naphthalene [9]. In urban areas, vehicle emissions represent the most important source [10,11]. Occupational exposure occurs from creosote impregnation, the manufacture of mothballs, oil refineries, the manufacture of phthalic anhydride, cooking plants, foundries, and the production of surfactants and pesticides [12,13]. Burning cigarettes contribute significantly to the

increase of exposure to naphthalene in micro-environments [14]. Occupational exposure guidelines formulated for naphthalene include a reference exposure limit (REL) of $75 \mu\text{g}/\text{m}^3$ for a short-term exposure of 15 min and a threshold limit value (TLV) of $50 \mu\text{g}/\text{m}^3$ (a time-weighted average (TWA) measured over an 8 h period) [15]. Several techniques can be applied to sample volatile and semivolatile organic compounds in the air, including the use of metal containers, bags, and sorbent enrichment [16–18]. These techniques are efficient, but they have many steps. One technique that has proven to be very efficient for sampling volatile compounds in air is solid phase microextraction (SPME). SPME combines sampling and preconcentration in a single step, with subsequent desorption directly into the analytical instrument [19,20]. The present study used a system constructed [21] to generate naphthalene standards by permeation, with a new alternative device for cold fiber (CF) SPME sampling in ambient air. After direct desorption into the injector of the GC, determinations by gas chromatography coupled to mass spectrometry (GC/MS) were performed. The optimized method is simple and sufficiently sensitive for the analysis of naphthalene in environmental air samples.

2. Materials and methods

2.1. Generator of naphthalene standard

The system for the generation of gaseous standards, developed in a previous study [22], is presented in Fig. 1. The air was conducted to a UHP-10ZA Brand Dornick Hunter scrubber after compression to 345 kPa and then passed through a spiral copper pipe for preheating. After the dilution control valve, the air entered the permeation chamber and passed through a permeation tube of polymer material containing

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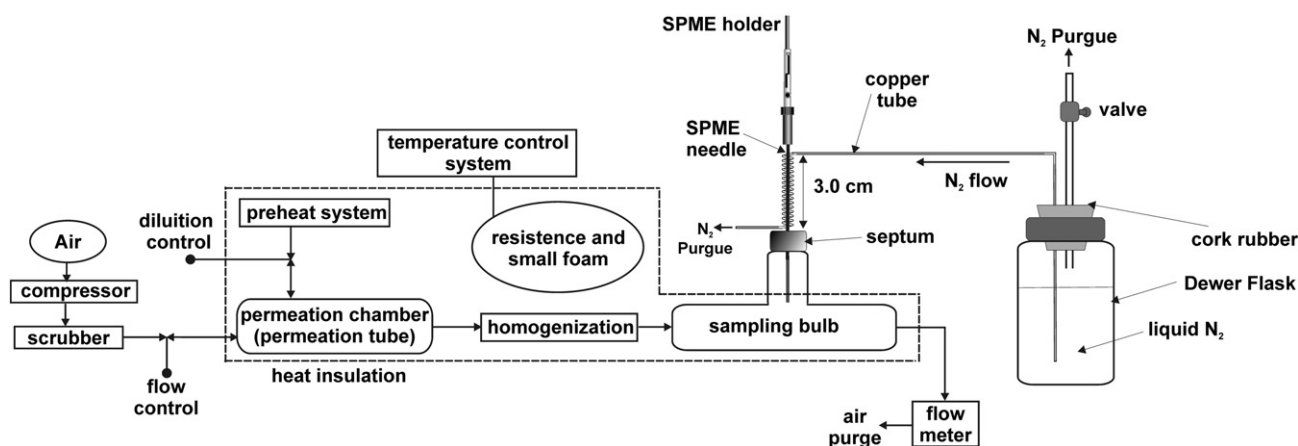


Fig. 1. System for the generation of gaseous standards.

naphthalene. The tube, manufactured by VICI Metronics, Inc., and certified for traceability by NIST (National Institute of Standards and Technology) was 3.5 cm in length, and the rate of permeation was $16.62 \pm 0.79 \text{ ng/min}^1$ at $40.0 \text{ }^\circ\text{C}$. The tube was maintained at a constant flow with the temperature of $40.0 \pm 0.1 \text{ }^\circ\text{C}$ controlled by a thermostat. The temperature control system was connected to a resistor and a small fan for even distribution of heat throughout all the components inserted into the space bounded by heat insulation (dotted rectangle of Fig. 1). The mixture of air with naphthalene was homogenized in a spiral glass tube before reaching the sampling bulb where the CF-SPME fiber was then exposed. The flow was measured with a Supelco Optiflow 650 digital flowmeter. The system pressure was maintained at $99 \pm 1 \text{ kPa}$ by a flow control valve in all the experiments. The dilutions required for the construction of the naphthalene calibration curve in ambient air were obtained through the control of the air flow in the permeation chamber. The concentrations of naphthalene were calculated from the expression:

$$C = 10^3 \times Q/F \quad (1)$$

where C ($\mu\text{g/m}^3$) is the concentration of naphthalene at 101.3 kPa and 298 K, Q (ng/min) is the permeation rate, and F is the corrected flow (mL/min) at 101.3 kPa and 298 K. For each concentration level of the analytical curves, the flow was altered, and after the 150 min equilibrium time, the flow was measured in replicate ($n=7$). The readings of the blank were obtained after withdrawing the permeation tube and allowing diluent air to flow for 24 h before performing the extraction.

2.2. Cold fiber-SPME device

The device for the extraction using the CF-SPME fiber [23] is connected to the sampling bulb through a silicone septum, as shown in Fig. 1. A copper tube was used to transfer liquid nitrogen from a Dewar flask to the SPME device. One end of the tube was inserted into the Dewar flask through a rubber stopper, and the other end, composed of a 3 cm spiral, held the needle of a manual SPME holder containing a $100 \mu\text{m}$ polydimethylsiloxane (PDMS) fiber. The SPME device and fiber were obtained from Supelco (Bellefonte, PA, USA). By closing the valve, the liquid nitrogen evaporated slowly and passed through the spiral at a constant rate, absorbing heat from the manual SPME holder and the fiber (Fig. 2). For the extraction, the cooled fiber was immersed in the sample bulb. The air sampling extraction time was 15 min.

2.3. GC/MS analysis

The analysis was performed with an Finnigan Trace DSQ GC/MS equipped with an ion trap mass spectrometer from Thermo Scientific

(West Palm Beach, FL, USA), and a capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) containing 5% diphenyl and 95% dimethylpolysiloxane HP-5MS from Agilent Technology, Inc. (Santa Clara, CA, USA) was used. The oven temperature program began at $35 \text{ }^\circ\text{C}$, was held for 1 min, ramped at $15 \text{ }^\circ\text{C/min}$ to $200 \text{ }^\circ\text{C}$, and held for 2 min. The carrier gas was helium at a flow rate of 4.0 mL/min . The injector was operated at $250 \text{ }^\circ\text{C}$ in splitless mode for 1 min, followed by a 1:20 split ratio (RD). The mass spectrometer was operated in electron ionization mode (EI) with an energy of 70 eV. The ion source temperature was $200 \text{ }^\circ\text{C}$, and the GC/MS interface temperature was $280 \text{ }^\circ\text{C}$. The analysis was performed in full scan mode (mass range: 50–300 m/z), with a scan time of 3 scans/s. The quantification was achieved by selected ion monitoring (SIM) using the ion fragment m/z 128. The collection of raw data was performed using an X-Calibur 1.4 software system from Thermo Scientific (West Palm Beach, FL, USA).

2.4. Sample collection

The urban air samples were obtained during the period from February to March, 2011, with an average temperature of $24 \pm 2 \text{ }^\circ\text{C}$, in Belo Horizonte, a city located in southeastern Brazil ($19^\circ 55' \text{ S}$, $46^\circ 56' \text{ W}$). Belo Horizonte has 2.4 million inhabitants and 1.1 million vehicles in circulation. Eighteen sampling points distributed outdoors (such as avenues and parks) and indoors (such as laboratories, fuel resale stations, parking garages, bathrooms, and car interiors) were selected. A high traffic density ($> 10,000$ vehicles per day) was considered in the selection of the avenues. All the parks selected were within the urban perimeter of the city.

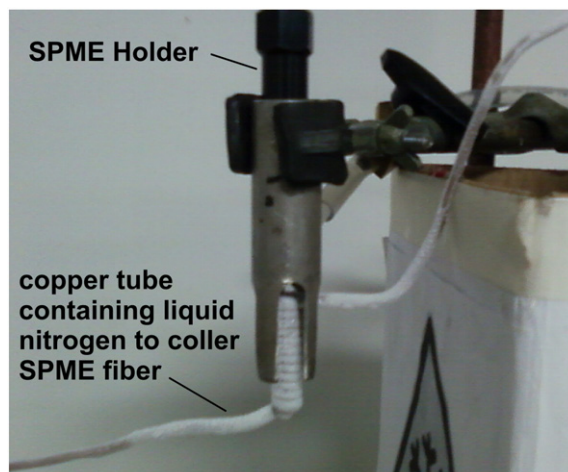


Fig. 2. Cold fiber SPME device.

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