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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 $0.33 \pm 0.01\ \mu g/m^3$, and the quantification limit (LOQ) is $0.55 \pm 0.01\ \mu g/m^3$. 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.

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 $75\ \mu g/m^3$ for a short-term exposure of 15 min and a threshold limit value (TLV) of $50\ \mu g/m^3$ (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 Domnick 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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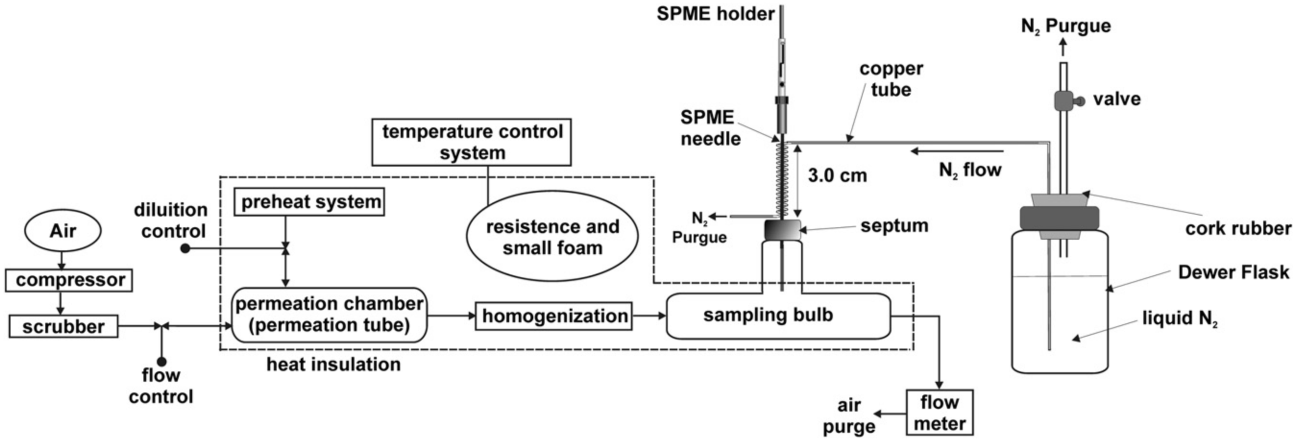

Fig. 1. System for the generation of gaseous standards.

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 ± 0.79 ng/min^1 at 40.0 °C. The tube was maintained at a constant flow with the temperature of 40.0 ± 0.1 °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 ± 1 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:

$$C = 10^3 \times Q/F \tag{1}$$

where C (μg/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 μm 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 m × 0.25 mm × 0.25 μm) 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 °C, was held for 1 min, ramped at 15 °C/min to 200 °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 °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 °C, and the GC/MS interface temperature was 280 °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 ± 2 °C, in Belo Horizonte, a city located in southeastern Brazil (19° 55′ S, 46° 56′ 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.

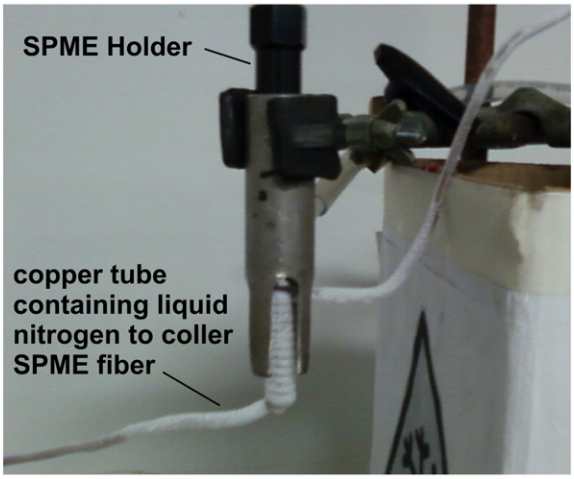

Fig. 2. Cold fiber SPME device.

For each sample collection, the cold fiber was exposed for 15 min in the respiration zone (1.70 ± 0.20 m above ground level). After the collection, the fiber was withdrawn and wrapped in aluminum foil at −15 ± 5 °C until the time of analysis. The maximum period between collection and analysis did not exceed 2 h, so no volatilization of the cold analyte occurred. The analytical protocol for the determination of naphthalene in air samples is schematically depicted in Fig. 3.

2.5. Statistics

Because of the heteroscedasticity of the instrumental responses, the linear model for the calibration curve was constructed by the least squares method weighted by the experimental variance. Basic descriptive analysis was performed using the Origin 8.0 software (OriginLab Corp); p-values below 0.05 were considered significant.

3. Results and discussion

3.1. Analytical characteristics and method validation

A comparative study was performed with the CF-SPME device to evaluate the effect on the extraction yield of cooling the fiber. The experiments were conducted with three extraction replicates for 15 min in the gaseous standard generation system with the permeation tube of naphthalene. The areas obtained for naphthalene at three concentration levels are shown in Fig. 4. In all the evaluated levels, the results showed that the CF-SPME extraction is more efficient than the extraction performed without cooling the fiber. The sorption process that occurred between the analytes and the fiber is exothermic, so the CF-SPME device removes the excess of thermal energy, thereby favoring the mass transfer to the fiber, as was demonstrated by Ghiasvanda and Pawliszyn [24]. To increase the sensitivity, the extractions were performed in CF-SPME mode. The calibration curve was constructed with seven concentration levels, with three steps for each level. The curve obtained ($y = 5261.47x + 10.82$) showed good linearity in the range of 0.55 ± 0.01 to 148.51 ± 0.02 μg/m^3 ($R^2 = 0.998$; p-value < 0.0001). The limits of detection (LOD) and quantification (LOQ) were calculated according to the recommendations of the Eurachem Guide [25] using ten consecutive measurements of the blank. The LOD was 0.33 ± 0.01 μg/m^3, and the LOQ was 0.55 ± 0.01 μg/m^3. In assessing the intra-assay precision (repeatability), ten replicates at the concentration levels of 14.31, 77.42 and 120.97 μg/m^3 were analyzed on the same day. The coefficient of variation (RSD) showed a range of 1.04 to 8.11%, with a mean of 4.75%. These values were lower than the results obtained in other studies for the assessment of naphthalene in ambient air [26,27]. Five replicates at three concentration levels were analyzed on three consecutive days to assess the intermediate precision. The values of RSD obtained in this study varied from 1.04 to 10.03%, with a mean of 5.60%.

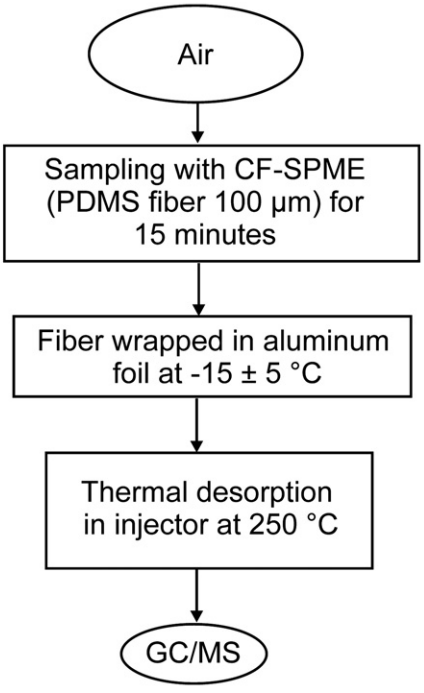

Fig. 3. Analytical protocol for the determination of naphthalene in air samples using CF-SPME-GC/MS.

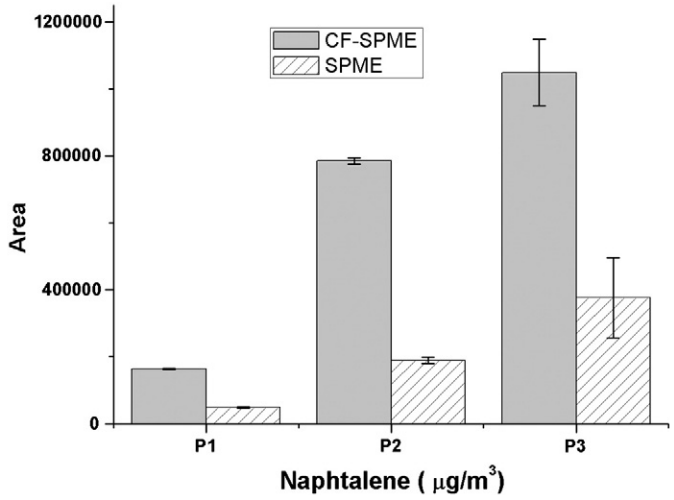

Fig. 4. Naphthalene peak areas at three concentration levels (P1 = 14.30; P2 = 78.50; P3 = 120.90 μg/m^3) to extraction (n = 3) in the system for the generation of gaseous standards with cold fiber-SPME (gray) and SPME (lines).

3.2. Analysis of real samples

The validated method for the determination of naphthalene in the ambient air has been applied to real samples collected in indoor and outdoor environments. Fig. 5 shows the distribution of the results. The average concentrations of naphthalene in indoor and outdoor environments were, respectively, 10.17 ± 14.39 μg/m^3 and 5.47 ± 4.94 μg/m^3. The different types of environments selected for sample collection and the wide variety of emission sources were the probable causes of the large variability observed for naphthalene concentrations in outdoor and indoor ambient air. The median concentration for the indoor air samples in this study was 5.27 μg/m^3. Median concentrations in indoor air reported in the different studies vary considerably, from approximately 0.17 to 4.59 μg/m^3 [28–30]. Indoor concentrations of naphthalene arise from tobacco smoking, use of moth repellents, presence and use of an attached garage, building characteristics, ventilation conditions and emissions from furniture [31–33]. The median concentration determined in outdoor ambient air was 3.81 μg/m^3. Other studies performed in ambient air at urban sites showed a concentration range of 0.01 to 4.15 μg/m^3 [34–36]. In urban areas, concentrations of naphthalene show diurnal and seasonal variations, reflecting variability in emission sources and meteorological influences [37,38].

All samples showed concentrations above the limit of quantification, except for samples 2 and 3 of the outdoor air. Samples 1 to 3 were collected at ecological park sites and are thus close to the background concentrations of naphthalene for urban and suburban centers, which can vary from 0.001 to 1 μg/m^3 [11,29]. The highest concentrations recorded for the outdoor air samples (samples 4 and 5) correspond to

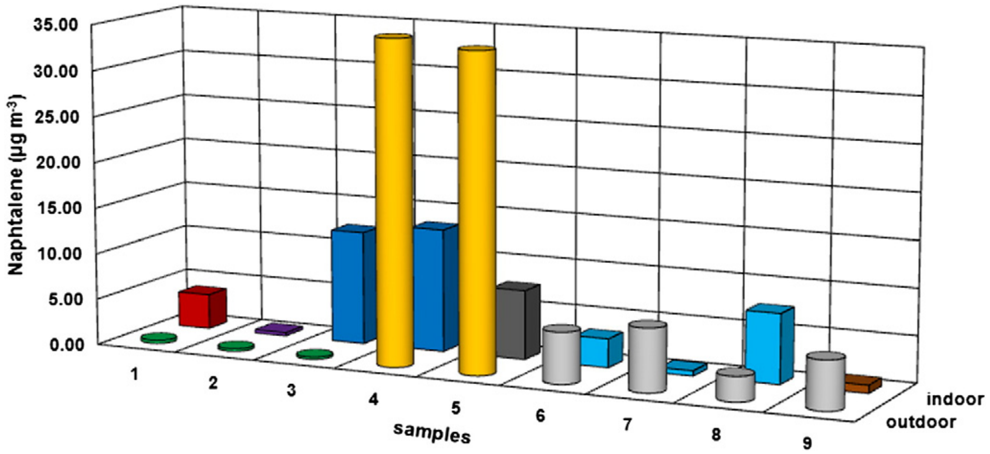

Fig. 5. Concentrations (μg/m^3) of naphthalene in outdoor (cylinders) and indoor (columns) air.

samples taken at fuel resale stations. These values were relatively high because of emissions and fuel evaporation during filling [10]. Samples 6 to 9 were taken on the avenues with heavy traffic, with an average of 12,000 vehicles per day. In indoor environments, the highest concentrations of naphthalene were found in garages at shopping centers (samples 3 and 4) because of the absence of adequate ventilation in these places, resulting in the accumulation of vehicle emissions. Samples 6 to 8 were collected inside parked vehicles. These micro-environments may have elevated levels of naphthalene due to the contribution of the exhaust from other vehicles. The high concentration of naphthalene in sample 8 can be explained by the burning of cigarettes in the vehicle prior to sampling. This residue from smoking is common in environments frequented by smokers and contributes significantly to an increase in the exposure to naphthalene after the act of smoking itself [39]. Residual tobacco smoke pollutants that remain on surfaces after tobacco has been smoked are re-emitted back into the gas phase [40]. Sample 9 represents a sample taken in a public restroom. Occupational environments are represented by samples 1, 2 and 5, which were collected in a research laboratory, in a room with a Xerox copier, and in a garage repair shop, respectively. The presence of naphthalene in indoor and occupational environments constitutes the main contribution to the general population's exposure to this pollutant.

4. Conclusion

This study showed the development of an alternative method for the analysis of naphthalene in ambient air by passive sampling with cooled fiber solid phase microextraction (CF-SPME). The method is simple, fast, and inexpensive. SPME dispensing pumps ensure portability for sampling and pre-concentration. The use of a pattern generation system for gas permeation produced the most appropriate conditions for reproducibility in the atmosphere. This procedure was validated and showed good precision, linearity and sensitivity for the range of environmental interest. The results obtained from the analysis of air samples collected in external and internal environments have demonstrated the ability of the method to measure trace levels of naphthalene in the air in different environments.

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